

THERMODYNAMICS OF INDIVIDUAL IONS IN VARIOUS SOLVENT SYSTEMS FROM ELECTROMOTIVE FORCE MEASUREMENTS

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ABSTRACT

Standard e.m.f. values for the cells

$\text{Pt, H}_2(\text{g}, 1 \text{ atm}) | \text{HX}(m), \text{solvent} | \text{AgX}, \text{Ag}$

and

$\text{M}(\text{Hg}) | \text{MX}_2(m), \text{solvent} | \text{AgX}, \text{Ag}$

in water and in mixtures of water with methanol, 2-propanol, acetone or dioxane were used to determine standard absolute electrode potentials of the hydrogen, Ag, AgX ($X = \text{Cl, Br and I}$) and $\text{M}(\text{Hg}) | \text{M}^{2+}$ ($\text{M} = \text{Zn and Cd}$) electrodes in these solvents. The data at different temperatures were utilized to compute the standard thermodynamic quantities both for the electrode reaction and for the transfer of individual ions from water into water + cosolvent mixtures. Cation solvation in various solvents as well as the influence of the solvent on the thermodynamic properties of individual ions are discussed. The results provide further evidence of the adequacy of the new method (M.M. Elsemongy, *Thermochim. Acta*, 80 (1984) 239; 103 (1986) 387; 108 (1986) 133) of determination of the thermodynamics of individual ions and of its general applicability to different cells containing different 1:1 or 2:1 electrolytes in various solvent systems.

INTRODUCTION

The problem of determining absolute electrode potentials and the thermodynamics of individual ions, by both experimental and theoretical means, has long been a subject of interest [1–10]. A new, simple method described recently [4] was successfully applied to the e.m.f. data of cells joining Ag, AgX electrodes with hydrogen, glass or alkali metal amalgam electrodes, all containing 1:1 electrolytes in aqueous and non-aqueous, protic and aprotic solvents [4–6]. However, all the results recognized that the oxidation potential scale only should be used for all treatments of e.m.f. data and that plots of standard transfer free energy or entropy against the reciprocal of the anionic or cationic radius related to the reduction potential scale cannot be used to obtain the thermodynamics of single ions [4–6]. In the present

investigation, further evidence of the adequacy of the new method of determination of the thermodynamics of individual ions and of its general applicability to different cells containing different 2:1 electrolytes is presented.

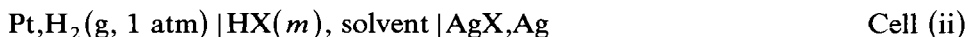
The standard electromotive forces of the cell



where $M = \text{Zn}$ or Cd and $X = \text{Cl}, \text{Br}$ or I , in an aqueous medium at $0\text{--}40^\circ\text{C}$ were tabulated by Robinson and Stokes [11]. Recently, the standard e.m.f. values of cell (i) for $M = \text{Zn}$ and $X = \text{Cl}$ were determined in water [12,13] and in mixtures of water with methanol at $25\text{--}40^\circ\text{C}$, with acetone, dioxane or acetic acid at 25°C [12] or with 2-propanol at $20\text{--}40^\circ\text{C}$ [13]. In this paper the new method [4] is theoretically developed to apply to cells with 2:1 electrolytes. It is then applied to the e.m.f. data of cell (i) in various solvent systems, not only to verify its use for such cells but also to obtain standard absolute electrode potentials at different temperatures. These were utilized to compute the standard thermodynamic quantities for the electrode reaction and for the transfer of individual ions from water into water + cosolvent mixtures.

THEORY

The new method [4] for the determination of absolute electrode potentials and the thermodynamics of individual ions in solution depends on the fact that there generally are two possibilities for the variation of the electrode potential (and thus the free energy change associated with the electrode reaction) with the radius r of the solvated ion on whose activity the potential depends: (I) the oxidation potential varies directly with r (case I) or (II) the reduction potential varies inversely with r (case II). Therefore, the standard e.m.f. E_m^\ominus of a cell, e.g.



(which is the difference between two standard oxidation or reduction potentials) is given as either

$$E_m^\ominus = {}^{\text{ox}}_L E_m^\ominus - {}^{\text{ox}}_R E_m^\ominus = a_1^\ominus r_+ - a_1^\ominus r_- \quad (1\text{--}I)$$

or

$$E_m^\ominus = {}^{\text{red}}_R E_m^\ominus - {}^{\text{red}}_L E_m^\ominus = a_2^\ominus / r_- - a_2^\ominus / r_+ \quad (1\text{--}II)$$

where r_+ and r_- are the radii of solvated H^+ and X^- ions respectively and all the symbols have their usual significance [4–6]. Therefore, the cell e.m.f. E_m^\ominus , or the free energy change involved in the cell reaction, is proportional to the radius of the solvated ion which is being varied in a series of electrolytes having a common ion [4–6].

Let us now apply these two possibilities to cell (i) containing 2:1 electrolytes, in any solvent. In this cell the electrode reactions are as follows.

(a) M is oxidized to M^{2+} ions at the left-hand (L) electrode, i.e.



The standard free energy change $^{\text{ox}}[\Delta G_L^\ominus]$ involved in the oxidation reaction at this electrode is

$$^{\text{ox}}[\Delta G_L^\ominus] = -2F_L^{\text{ox}}E_m^\ominus \quad (3\text{-I})$$

and thus [4]

$$^{\text{ox}}[\Delta G_L^\ominus] = -Fa_1^\ominus r_+ \quad (4\text{-I})$$

The corresponding expressions based on the reduction potential scale are

$$^{\text{red}}[\Delta G_L^\ominus] = -2F_L^{\text{red}}E_m^\ominus \quad (3\text{-II})$$

and thus [4]

$$^{\text{red}}[\Delta G_L^\ominus] = -Fa_2^\ominus/r_+ \quad (4\text{-II})$$

where F is the Faraday constant, r_+ is the radius of the solvated M^{2+} ion, $^{\text{ox}}E_m^\ominus = -^{\text{red}}E_m^\ominus$ and $^{\text{ox}}[\Delta G^\ominus] = -^{\text{red}}[\Delta G^\ominus]$. Equations (3) and (4) lead to eqns. (5-I) or (5-II) which reflect the dependence of the left-hand electrode potential on the radius of the solvated cation

$$2L^{\text{ox}}E_m^\ominus = a_1^\ominus r_+ \quad (5\text{-I})$$

or

$$2L^{\text{red}}E_m^\ominus = a_2^\ominus/r_+ \quad (5\text{-II})$$

(b) AgX is reduced to Ag at the right-hand (R) electrode



The standard free energy change $^{\text{red}}[\Delta G_R^\ominus]$ involved in the reduction reaction at this electrode is

$$^{\text{red}}[\Delta G_R^\ominus] = -F_R^{\text{red}}E_m^\ominus \quad (7\text{-II})$$

and thus [4]

$$^{\text{red}}[\Delta G_R^\ominus] = -Fa_2^\ominus/r_- \quad (8\text{-II})$$

The corresponding expressions based on the oxidation potential scale are

$$^{\text{ox}}[\Delta G_R^\ominus] = -F_R^{\text{ox}}E_m^\ominus \quad (7\text{-I})$$

and thus [4]

$$^{\text{ox}}[\Delta G_R^\ominus] = -Fa_1^\ominus r_- \quad (8\text{-I})$$

where r_- is the radius of the solvated anion. Equations (7) and (8) lead to

eqns. (9-I) or (9-II) which reflect the variation of the right-hand electrode potential with the radius of the solvated anion

$${}^{\text{ox}}E_m^{\ominus} = a_1^{\ominus} r_- \quad (9\text{-I})$$

or

$${}^{\text{red}}E_m^{\ominus} = a_2^{\ominus} / r_- \quad (9\text{-II})$$

The complete cell reaction for the passage of 2 Faradays is



and the free energy change accompanying the cell reaction is

$$\Delta G^{\ominus} = -2FE_m^{\ominus} \quad (11)$$

The value of ΔG^{\ominus} for the cell reaction is the difference of ΔG^{\ominus} for each half-cell reaction, both based on the same (oxidation or reduction) potential scale [4-6]. Therefore, ΔG^{\ominus} is given as either

$$\Delta G^{\ominus} = {}^{\text{ox}}[\Delta G_L^{\ominus}] - 2{}^{\text{ox}}[\Delta G_R^{\ominus}] \quad (12\text{-I})$$

or

$$\Delta G^{\ominus} = 2{}^{\text{red}}[\Delta G_R^{\ominus}] - {}^{\text{red}}[\Delta G_L^{\ominus}] \quad (12\text{-II})$$

Thus substitution of ΔG^{\ominus} values from eqns. (3), (7) and (11) into eqns. (12-I) and (12-II) leads to eqns. (13-I) and (13-II) respectively

$$-2FE_m^{\ominus} = -2F_L^{\text{ox}}E_m^{\ominus} - 2(-F_R^{\text{ox}}E_m^{\ominus})$$

i.e.

$$E_m^{\ominus} = {}^{\text{ox}}_L E_m^{\ominus} - {}^{\text{ox}}_R E_m^{\ominus} \quad (13\text{-I})$$

or

$$-2FE_m^{\ominus} = 2(-F_R^{\text{red}}E_m^{\ominus}) - (-2F_L^{\text{red}}E_m^{\ominus})$$

i.e.

$$E_m^{\ominus} = {}^{\text{red}}_R E_m^{\ominus} - {}^{\text{red}}_L E_m^{\ominus} \quad (13\text{-II})$$

As would be expected, these equations show that the cell e.m.f. is an intensive property independent of the number of faradays passed through the cell and is equal to the difference between two oxidation or reduction potentials [4-6]. This proves the validity of the derived relations. However, substitution of ${}_L E_m^{\ominus}$ and ${}_R E_m^{\ominus}$ values from eqns. (5) and (9) respectively into eqns. (13-I) and (13-II) yields

$$E_m^{\ominus} = \frac{1}{2}a_1^{\ominus} r_+ - a_1^{\ominus} r_- \quad (14\text{-I})$$

or

$$E_m^{\ominus} = a_2^{\ominus} / r_- - \frac{1}{2}a_2^{\ominus} / r_+ \quad (14\text{-II})$$

It is evident [4] from these equations that the e.m.f. of cell (ii) is either

directly (case I) or inversely (case II) proportional to the radius of the solvated ion which is being varied in a series of electrolytes having a common ion. Therefore, in any solvent the plot of the standard e.m.f. (E_m^\ominus) values of cell (i), where for example $M = \text{Zn}$ and $X = \text{Cl, Br and I}$, i.e. cells containing ZnCl_2 , ZnBr_2 or ZnI_2 , against r_- (case I) or $1/r_-$ (case II), would yield a straight line of (I) negative slope ($-a_1^\ominus$) and positive intercept ($\frac{1}{2} a_1^\ominus r_+ = {}^{\text{ox}} E_m^\ominus$) or (II) positive slope (a_2^\ominus) and negative intercept ($-\frac{1}{2} a_2^\ominus / r_+ = -{}^{\text{red}} E_m^\ominus$), according to eqns. (14-I) and (14-II) respectively, at any temperature. The standard absolute potentials of the left-hand and right-hand electrodes, and also the radius of the solvated Zn^{2+} cation in the standard state, can thus be obtained for both case I and case II. One would expect that two different sets of values for the standard absolute electrode potential (and thus related thermodynamics of individual ions), based on different (oxidation or reduction) potential scales, would be obtained. However, the results and features seen in the following sections will determine which set of data should be accepted and, at the same time, add further strong support to the previous conclusion [4-6].

For the transfer of 1 mol of MX_2 from the standard state in water (superscript w) into the standard states of respective solvents (superscript s)

$$\text{MX}_2(\text{in water}) = \text{MX}_2(\text{in respective solvents}) \quad (15)$$

the standard Gibbs free energy of transfer ΔG_t^\ominus is given [11] by

$$\Delta G_t^\ominus = 2F({}^w E_m^\ominus - {}^s E_m^\ominus) \quad (16)$$

Substitution of E_m^\ominus values from eqns. (13-I) and (13-II) into eqn. (16) yields

$$\Delta G_t^\ominus = 2F[{}^w({}^{\text{ox}} E_m^\ominus - {}^{\text{ox}} E_m^\ominus) - {}^s({}^{\text{ox}} E_m^\ominus - {}^{\text{ox}} E_m^\ominus)] \quad (17-I)$$

or

$$\Delta G_t^\ominus = 2F[{}^w({}^{\text{red}} E_m^\ominus - {}^{\text{red}} E_m^\ominus) - {}^s({}^{\text{red}} E_m^\ominus - {}^{\text{red}} E_m^\ominus)] \quad (17-II)$$

which on rearrangement gives

$$\Delta G_t^\ominus = 2F[{}^w({}^{\text{ox}} E_m^\ominus) - {}^s({}^{\text{ox}} E_m^\ominus)] - 2F[{}^w({}^{\text{ox}} E_m^\ominus) - {}^s({}^{\text{ox}} E_m^\ominus)] \quad (18-I)$$

or

$$\Delta G_t^\ominus = 2F[{}^w({}^{\text{red}} E_m^\ominus) - {}^s({}^{\text{red}} E_m^\ominus)] - 2F[{}^w({}^{\text{red}} E_m^\ominus) - {}^s({}^{\text{red}} E_m^\ominus)] \quad (18-II)$$

i.e.

$$\Delta G_t^\ominus = {}^{\text{ox}}[\Delta G_t^\ominus(+)] - 2{}^{\text{ox}}[\Delta G_t^\ominus(-)] \quad (19-I)$$

or

$$\Delta G_t^\ominus = 2{}^{\text{red}}[\Delta G_t^\ominus(-)] - {}^{\text{red}}[\Delta G_t^\ominus(+)] \quad (19-II)$$

where $\Delta G_t^\ominus(+)$ and $\Delta G_t^\ominus(-)$ are the standard transfer thermodynamic

quantities, on the molal scale, of positive and negative ions respectively and are given by

$${}^{\text{ox}}[\Delta G_t^\ominus(+)] = 2F[{}^{\text{w}}({}_{\text{L}}^{\text{ox}}E_m^\ominus) - {}^{\text{s}}({}_{\text{L}}^{\text{ox}}E_m^\ominus)] = F[{}^{\text{w}}(a_1^\ominus r_+) - {}^{\text{s}}(a_1^\ominus r_+)] \quad (20\text{-I})$$

or

$${}^{\text{red}}[\Delta G_t^\ominus(+)] = 2F[{}^{\text{w}}({}_{\text{L}}^{\text{red}}E_m^\ominus) - {}^{\text{s}}({}_{\text{L}}^{\text{red}}E_m^\ominus)] = F[{}^{\text{w}}(a_2^\ominus/r_+) - {}^{\text{s}}(a_2^\ominus/r_+)] \quad (20\text{-II})$$

and

$${}^{\text{ox}}[\Delta G_t^\ominus(-)] = F[{}^{\text{w}}({}_{\text{R}}^{\text{ox}}E_m^\ominus) - {}^{\text{s}}({}_{\text{R}}^{\text{ox}}E_m^\ominus)] = F[{}^{\text{w}}(a_1^\ominus r_-) - {}^{\text{s}}(a_1^\ominus r_-)] \quad (21\text{-I})$$

or

$${}^{\text{red}}[\Delta G_t^\ominus(-)] = F[{}^{\text{w}}({}_{\text{R}}^{\text{red}}E_m^\ominus) - {}^{\text{s}}({}_{\text{R}}^{\text{red}}E_m^\ominus)] = F[{}^{\text{w}}(a_2^\ominus/r_-) - {}^{\text{s}}(a_2^\ominus/r_-)] \quad (21\text{-II})$$

RESULTS AND DISCUSSION

It is of interest to examine the results of applying the proposed relations to the e.m.f. data of cell (i) in various solvent systems. Pauling radii [14], supported by recent results of Marcus [15], were also used in the present work for the reasons mentioned previously [4]. In an aqueous medium, plots of E_m^\ominus values [11] of cell (i), where $M = \text{Zn}$ and $X = \text{Cl, Br}$ and I , against r_- values (case I) or $1/r_-$ values (case II) gave almost perfect straight lines at each of the five different temperatures available. The least-squares results are recorded in Table 1. The extent of correlation is reflected by the correlation coefficients (corr) as well as the differences $\Delta(\text{mV})$ between the E_m^\ominus values calculated using eqn. (13) and those obtained experimentally. The standard e.m.f. values of cell (i) where $M = \text{Cd}$ and $X = \text{Cl}$, i.e. cell (i) containing CdCl_2 , are also reported [11]. Therefore, the standard absolute potential of the $\text{Cd}(\text{Hg})|\text{Cd}^{2+}$ electrode can be obtained using eqn. (13) and known values (Table 1) of the right-hand Ag,AgCl electrode potential. Furthermore, the radius of the solvated Cd^{2+} ion can be calculated using eqn. (5). These results are included in Table 1.

A comparison can now be made between results based on the oxidation potential scale (case I) and those on the reduction potential scale (case II). Table 1 reveals that the same important and interesting general features which have already been observed in the previous work [4-6] are apparent again in this work. Furthermore, for useful and helpful comparison, the new method [4] has been applied to two sets of standard e.m.f. values of cell (ii) containing 1:1 electrolytes in an aqueous medium at the same five tempera-

TABLE 1

The least-squares results of applying eqns. (14) to the e.m.f. data of cell (i) in an aqueous medium at 20–40 °C

Temperature (°C)		20	25	30	35	40
Case I						
–Corr (10^{-2})		99.9992	99.9993	99.9994	99.9996	99.9998
Δ (mV)	X = Cl	–0.51	–0.49	–0.43	–0.36	–0.28
	Br	+0.85	+0.81	+0.72	+0.60	+0.46
	I	–0.34	–0.32	–0.29	–0.24	–0.19
a_1^\ominus (10^{10} V m $^{-1}$)		1.0735	1.0691	1.0645	1.0600	1.0555
r_+ (10^{-10} m)	M = Zn	5.4607	5.4615	5.4623	5.4627	5.4628
	Cd	4.6928	4.6936	4.6942	4.6946	4.6949
${}_L E_m^\ominus$ (V)	M = Zn	2.9310	2.9195	2.9074	2.8953	2.8829
	Cd	2.5188	2.5090	2.4985	2.4882	2.4777
${}_R E_m^\ominus$ (V)	X = Cl	1.9430	1.9351	1.9268	1.9186	1.9104
	Br	2.0933	2.0848	2.0758	2.0670	2.0582
	I	2.3187	2.3093	2.2994	2.2896	2.2798
Case II						
Corr (10^{-2})		99.8970	99.8961	99.8944	99.8918	99.8889
Δ (mV)	X = Cl	+5.51	+5.51	+5.53	+5.57	+5.62
	Br	–9.89	–9.89	–9.93	–10.01	–10.10
	I	+4.38	+4.38	+4.40	+4.43	+4.47
a_2^\ominus (10^{-10} V m)		4.2114	4.1942	4.1761	4.1582	4.1404
r_+ (10^{-10} m)	M = Zn	1.5800	1.5805	1.5810	1.5813	1.5814
	Cd	1.2026	1.2029	1.2031	1.2033	1.2035
${}_L E_m^\ominus$ (V)	M = Zn	1.3327	1.3269	1.3207	1.3148	1.3091
	Cd	1.7509	1.7433	1.7355	1.7278	1.7202
${}_R E_m^\ominus$ (V)	X = Cl	2.3267	2.3172	2.3073	2.2974	2.2875
	Br	2.1597	2.1509	2.1416	2.1324	2.1233
	I	1.9497	1.9417	1.9334	1.9251	1.9168
a_2^\ominus/a_1^\ominus (10^{-20} m 2)		3.9231	3.9230	3.9230	3.9229	3.9227

tures. These are the e.m.f. data of our recent studies [16] and those of Robinson and Stokes [11]. The least-squares results are given in Tables 2 and 3 respectively. It is evident from Tables 1–3 that the values of a_1^\ominus and a_2^\ominus and thus the ratio (a_2^\ominus/a_1^\ominus) at each temperature do not vary within experimental error. The constancy of a_1^\ominus and a_2^\ominus values and thus ${}_R E_m^\ominus$ values obtained from different cells with different electrolytes presents further strong evidence to support the fact reported earlier [4–6] that these a_1^\ominus and a_2^\ominus values appear to be universal constants for all electrodes and are dependent only on the medium, at any temperature. The ratio (a_2^\ominus/a_1^\ominus) was found [4–6] to be constant and is the same for all solvent systems and for all solvent compositions, at each temperature.

In both cases I and II the radius of the solvated H^+ ion decreases, while that of the solvated Zn^{2+} or Cd^{2+} ion increases slightly, with increasing

TABLE 2

The least-squares results of applying eqns. (1) to the e.m.f. data of cell (ii) in an aqueous medium at 20–40 °C reported by Elsemongy et al. [16]

Temperature (°C)	20	25	30	35	40
Case I					
– Corr (10^{-2})	99.9988	99.9991	99.9992	99.9993	99.9994
Δ (mV) X = Cl	–0.63	–0.56	–0.53	–0.48	–0.44
Br	+1.05	+0.94	+0.87	+0.80	+0.73
I	–0.42	–0.38	–0.35	–0.32	–0.29
a_1^\ominus (10^{10} V m $^{-1}$)	1.07463	1.07006	1.06536	1.06077	1.05612
r_+ (10^{-10} m)	2.019	2.017	2.015	2.013	2.010
${}^{\text{ox}}E_m^\ominus$ (V)	2.17000	2.15861	2.14684	2.13515	2.12319
${}^{\text{R}}E_m^\ominus$ (V) X = Cl	1.94508	1.93682	1.92830	1.91999	1.91158
Br	2.09552	2.08662	2.07745	2.06850	2.05944
I	2.32120	2.31134	2.30117	2.29126	2.28123
Case II					
Corr (10^{-2})	99.9011	99.8988	99.8976	99.8961	99.8947
Δ (mV) X = Cl	+5.40	+5.44	+5.45	+5.46	+5.48
Br	–9.70	–9.77	–9.78	–9.81	–9.83
I	+4.30	+4.33	+4.34	+4.35	+4.36
a_2^\ominus (10^{-10} V m)	4.21605	4.19804	4.17952	4.16146	4.14317
r_+ (10^{-10} m)	2.009	2.007	2.005	2.003	2.000
${}^{\text{red}}E_m^\ominus$ (V)	2.09836	2.09156	2.08461	2.07804	2.07152
${}^{\text{R}}E_m^\ominus$ (V) X = Cl	2.32931	2.31936	2.30913	2.29915	2.28904
Br	2.16208	2.15284	2.14334	2.13408	2.12470
I	1.95187	1.94354	1.93496	1.92660	1.91813
a_2^\ominus/a_1^\ominus (10^{-20} m 2)	3.92326	3.92318	3.92310	3.92306	3.92301

temperature. This trend was noticed earlier [4,5] for the H^+ ion and alkali metal ions in several solvent systems. However, the values of r_+ reflect the extent of solvation of the cations. The extent of solvation S_e has been calculated [4] as the difference between the r_+ values obtained and the Pauling ionic radii [14] of nonsolvated ions in the aqueous medium. These are 0.74 and 0.97 (both in 10^{-10} m) for the Zn^{2+} and Cd^{2+} ions respectively. Thus the extent of solvation values S_e (10^{-10} m) for Zn^{2+} and Cd^{2+} ions respectively are 4.72 and 3.72 in case I and 0.84 and 0.23 in case II. The values of r_+ and S_e for the Zn^{2+} and Cd^{2+} ions are greater in case I than in case II and in both cases they are greater for the Zn^{2+} ion than the Cd^{2+} ion, at each temperature. However, these values can be compared with those for the K^+ and Rb^+ ions computed earlier [4] as 3.42 and 3.27 in case I and 3.70 and 3.55 in case II respectively. In the Periodic Table of elements K and Zn are in the fourth period, while Rb and Cd are in the fifth period, in groups IA and IIB respectively. In an aqueous medium at 25 °C, the Zn^{2+} and Cd^{2+} ions are known [17] to be more solvated than the K^+ and Rb^+ ions

TABLE 3

The least-squares results of applying eqns. (1) to the e.m.f. data of cell (ii) in an aqueous medium at 20–40 °C reported by Robinson and Stokes [11]

Temperature (°C)	20	25	30	35	40	
Case I						
–Corr (10^{-2})	99.9991	99.9993	99.9994	9.9995	99.9995	
Δ (mV)	X = Cl	–0.54	–0.47	–0.44	–0.42	–0.42
	Br	+0.90	+0.79	+0.74	+0.71	+0.70
	I	–0.36	–0.31	–0.29	–0.28	–0.28
a_1^\ominus (10^{10} V m $^{-1}$)		1.07431	1.06981	1.06529	1.06105	1.05660
r_+ (10^{-10} m)		2.019	2.017	2.015	2.013	2.010
${}^{\text{ox}}E_m^\ominus$ (V)		2.16953	2.15822	2.14678	2.13573	2.12411
${}^{\text{red}}E_m^\ominus$ (V)	X = Cl	1.94450	1.93635	1.92818	1.92051	1.91245
	Br	2.09491	2.08613	2.07732	2.06905	2.06037
	I	2.32051	2.31079	2.30103	2.29187	2.28226
Case II						
Corr (10^{-2})		99.8980	99.8956	99.8947	99.8941	99.8939
Δ (mV)	X = Cl	+5.48	+5.52	+5.53	+5.52	+5.50
	Br	–9.84	–9.92	–9.92	–9.91	–9.87
	I	+4.36	+4.39	+4.40	+4.39	+4.38
a_2^\ominus (10^{-10} V m)		4.21467	4.19689	4.17913	4.16247	4.14501
r_+ (10^{-10} m)		2.009	2.007	2.005	2.003	2.000
${}^{\text{red}}E_m^\ominus$ (V)		2.09749	2.09086	2.08435	2.07854	2.07248
${}^{\text{ox}}E_m^\ominus$ (V)	X = Cl	2.32855	2.31872	2.30891	2.29971	2.29006
	Br	2.16137	2.15225	2.14315	2.13460	2.12564
	I	1.95124	1.94300	1.93478	1.92707	1.91898
a_2^\ominus/a_1^\ominus (10^{-20} m 2)		3.92314	3.92302	3.92300	3.92298	3.92297

respectively, and the K^+ and Zn^{2+} ions are more solvated than the Rb^+ and Cd^{2+} ions respectively. The results of case I are in agreement with, and support, these well-known orders of increasing solvation [17], while those of case II show that $S_e(\text{K}^+) > S_e(\text{Zn}^{2+})$ and $S_e(\text{Rb}^+) \gg S_e(\text{Cd}^{2+})$, i.e. the expected order is reversed for Zn^{2+} and K^+ ions and for Cd^{2+} and Rb^+ ions, which is not the case [17]. This very interesting feature sheds more light on, and adds further strong evidence to, the validity of results obtained in case I, based on the oxidation potential scale, and, at the same time, proves that all results obtained in case II, based on the reduction potential scale, i.e. on $1/r$ relationships, are invalid.

As expected, the standard absolute oxidation potentials computed in case I increase in the order ${}^{\text{ox}}E_m^\ominus(\text{Ag}, \text{AgCl}) < {}^{\text{ox}}E_m^\ominus(\text{Ag}, \text{AgBr}) < {}^{\text{ox}}E_m^\ominus(\text{H}_2 | \text{H}^+) < {}^{\text{ox}}E_m^\ominus(\text{Ag}, \text{AgI}) < {}^{\text{ox}}E_m^\ominus(\text{Cd}(\text{Hg}) | \text{Cd}^{2+}) < {}^{\text{ox}}E_m^\ominus(\text{Zn}(\text{Hg}) | \text{Zn}^{2+})$, whereas the standard absolute reduction potentials in case II decrease in the same order, at each temperature. However, both the oxidation and reduction electrode potentials decrease with increasing temperature. For the electrode

TABLE 4
Standard molal absolute electrode potentials and radii of solvated cations in an aqueous medium at 0–40 °C

Temp. (°C)	Case I				Case II					
	$\frac{\text{ox}}{\text{R}} E_m^\ominus$ X = Cl	$\frac{\text{ox}}{\text{L}} E_m^\ominus$ M = Zn	$\frac{\text{ox}}{\text{L}} E_m^\ominus$ M = Cd	r_+ M = Zn	r_+ M = Cd	$\frac{\text{red}}{\text{R}} E_m^\ominus$ X = Cl	$\frac{\text{red}}{\text{L}} E_m^\ominus$ M = Zn	$\frac{\text{red}}{\text{L}} E_m^\ominus$ M = Cd	r_+ M = Zn	r_+ M = Cd
0	1.97829	–	2.55980	–	4.6841	2.36926	–	1.78775	–	1.1994
5	1.97002	–	2.55041	–	4.6865	2.35931	–	1.77892	–	1.2003
10	1.96174	2.95691	2.54074	5.4564	4.6884	2.34934	1.35417	1.77034	1.5701	1.2010
15	1.95342	2.94534	2.53097	5.4582	4.6903	2.33933	1.34741	1.76178	1.5712	1.2017
20	1.94508	2.93357	2.52089	5.4597	4.6916	2.32930	1.34081	1.75349	1.5722	1.2022
25	1.93672	2.92157	2.51062	5.4608	4.6927	2.31925	1.33440	1.74535	1.5729	1.2026
30	1.92833	2.90936	2.50008	5.4617	4.6933	2.30917	1.32814	1.73742	1.5735	1.2028
35	1.91992	2.89694	2.48947	5.4622	4.6939	2.29906	1.32204	1.72951	1.5738	1.2030
40	1.91149	2.88430	2.47879	5.4623	4.6944	2.28893	1.31612	1.72163	1.5739	1.2032

reactions, either the oxidation potential or the reduction potential would decrease with increasing temperature. This indicates that only one set of these results (either those of case I or those of II) can be accepted and considered for the evaluation of the thermodynamics of individual ions.

The standard absolute electrode potentials and their temperature coefficients are essentially related to the standard thermodynamic functions involved in the half-cell reactions and also to the thermodynamic quantities for the transfer of individual ions from water into respective solvents. The temperature range should be sufficient to give significant accuracy in the values of the thermodynamic quantities which depend on the temperature coefficients of the potential. The reported [11] standard e.m.f. values of cell (i) at 0–40 °C where $M = \text{Zn}$ or Cd and $X = \text{Cl}$ were thus used to obtain more accurate ${}_L E_m^\ominus$ values over a wider range of temperatures than that given in Table 1, using our previously reported [5] least-squares values of ${}_R E_m^\ominus$ where $X = \text{Cl}$, computed from data at 12 different temperatures in the range 0–55 °C, and applying eqns. (13–I) and (13–II). The radii r_+ of the solvated Zn^{2+} and Cd^{2+} cations were also calculated by means of eqns. (5–I) and (5–II). The results calculated in this way at each temperature in cases I and II are collected in Table 4.

The standard absolute potential ${}_E E_m^\ominus$ of each electrode obtained in the aqueous medium (Table 4) at different temperatures were fitted by the method of least-squares to

$${}_E E_m^\ominus = a - bT - cT^2 \quad (22)$$

The values of the parameters a , b and c are recorded in Table 5 for each electrode over the indicated temperature range in cases I and II. The maximum difference $\Delta(\text{mV})$ between the values of ${}_E E_m^\ominus$ calculated using eqn. (22) and the experimental values (Table 4) is included in Table 5 for each electrode.

Standard thermodynamic functions for the half-cell reactions

The standard free energy ΔG_E^\ominus , enthalpy ΔH_E^\ominus , and entropy ΔS_E^\ominus changes associated with the half-cell reactions were computed [4] on the molal scale. The results at 25 °C are also included in Table 5. The values of ΔG_E^\ominus are accurate to $\pm 50 \text{ J mol}^{-1}$. Although the values obtained in case I are based on the oxidation potential scale whereas those in case II are based on the reduction potential scale, the thermodynamic functions for the half-cell reactions are all negative. However, since the oxidation reactions of the half-cells are known [4,11,17] to be exothermic and accompanied by an entropy decrease, the ΔH_E^\ominus and ΔS_E^\ominus values must be negative, and the oxidation potentials of the single electrodes should decrease with increasing temperature. This is in agreement with the results obtained in case I and, at the same time, contradict those of case II. Thus the set of data obtained in

TABLE 5

Values of the parameters a , b and c of eqn. (22) for the evaluation of E_m^\ominus in an aqueous medium at the indicated temperature range, and the standard molal thermodynamic functions of the half-cell reactions at 25 °C

Electrode	Temp. range (°C)	a (V)	b (10^{-4} V K $^{-1}$)	c (10^{-7} V K $^{-2}$)	Δ (mV)	$-\Delta G_E^\ominus$ (kJ mol $^{-1}$)	$-\Delta H_E^\ominus$ (kJ mol $^{-1}$)	$-\Delta S_E^\ominus$ (J K $^{-1}$ mol $^{-1}$)
Case I								
H $_2$ H $^+$	0-55	2.53955	2.4637	34.5993	0.18	208.3	274.7	222.8
Zn(Hg) Zn $^{2+}$	10-40	3.26225	-1.3513	42.8571	0.01	563.8	703.0	467.1
Cd(Hg) Cd $^{2+}$	0-40	2.75885	-4.0805	41.6033	0.13	484.5	603.7	400.0
Ag,AgCl	0-55	2.39263	13.8332	4.8903	0.18	186.9	235.0	161.6
Ag,AgBr	0-55	2.57855	14.9630	5.1647	0.20	201.3	253.2	174.0
Ag,AgI	0-55	2.85545	16.5212	5.8101	0.22	223.0	280.5	192.8
Case II								
H $_2$ H $^+$	0-55	2.71893	28.3618	-24.5361	0.22	201.8	241.3	132.5
Zn(Hg) Zn $^{2+}$	10-40	1.73962	14.4781	-3.0124	0.34	257.6	330.5	244.7
Cd(Hg) Cd $^{2+}$	0-40	2.27102	18.7723	-3.8795	0.55	336.9	431.6	317.6
Ag,AgCl	0-55	2.87339	17.0365	5.1970	0.22	223.8	281.7	194.3
Ag,AgBr	0-55	2.66805	15.8758	4.7223	0.21	207.7	261.5	180.3
Ag,AgI	0-55	2.40804	14.2918	4.3296	0.18	187.5	236.1	162.8

case I, based on the oxidation potential scale, are valid. This conclusion is further confirmed by another important feature seen in Table 5. For the left-hand electrode reaction all the thermodynamic functions ($-\Delta G_E^\ominus$, $-\Delta H_E^\ominus$ and $-\Delta S_E^\ominus$) obtained in case I increase in the order $H_2|H^+ < Cd(Hg)|Cd^{2+} < Zn(Hg)|Zn^{2+}$, which is the increasing order of the standard e.m.f. values of cells joining one of these electrodes with, for example, the $Ag, AgCl$ electrode, i.e. cells containing HCl , $CdCl_2$ or $ZnCl_2$; these are 0.222 34 V, 0.573 90 V and 0.984 85 V respectively, at $25^\circ C$. On the other hand, the increasing order of these functions in case II is $H_2|H^+ < Zn(Hg)|Zn^{2+} < Cd(Hg)|Cd^{2+}$, i.e. the expected order is reversed for the Zn and Cd electrodes. This is further strong evidence against the validity of the set of data obtained in case II, based on the reduction potential scale, i.e. results based on $1/r$ relationships.

Effect of temperature on electrode potential

In this respect, it should be pointed out that a comparison between values of the electrode potential should be made between either cell potentials or absolute electrode potentials. Both decrease with increasing temperature in any solvent, as is evident from all reported E_m^\ominus values for different cells, including cells (i) and (ii), and from absolute electrode potentials [4,5] in addition to those recorded in Tables 1–4. Višić and Mekjavić [13] compared the standard potentials of the $Zn(Hg)|Zn^{2+}$ electrode derived from the standard e.m.f. values of cell (i) and those of cell (ii) where $X = Cl$, i.e. the standard potentials of the $Ag, AgCl$ electrode on the hydrogen scale. The values thus calculated in aqueous medium for $M = Zn$ or Cd and $X = Cl, Br$ or I at $0-40^\circ C$ are given in Table 6. This table shows that while the standard potential of the Zn electrode decreases, that of the Cd electrode increases, although all cell e.m.f. values decrease with increasing temperature. It is well-known that both the Zn and Cd electrodes behave in the same manner and would show similar trends with increasing temperature, which is reflected from the cell e.m.f. values [11–13] and the absolute potentials in Tables 1–4. Such calculations and comparisons (Table 6), which occur frequently in the literature [7–13], are not valid and lead to serious confusion. This is due to the misuse of the standard e.m.f. of cell (ii) as the standard potential of the Ag, AgX electrode, i.e. putting the standard hydrogen electrode potential equal to zero in all solvents and at all temperatures. This is, of course, impossible and is not the case [1–6]. For the same reason, contradictions are also apparent in several solvent systems. For example, Višić and Mekjavić [13] obtained the same value of the potential for the $Zn(Hg)|Zn^{2+}$ electrode in 30% 2-propanol at two different temperatures (30 and $40^\circ C$) and a value in 50% 2-propanol at $40^\circ C$ which is not in accordance with the general trend of variation of potential with temperature, and as a result believed that the values of potential might not be fully

TABLE 6

Standard potentials (V) of $M(\text{Hg})|M^{2+}$ electrodes in an aqueous medium at 0–40 °C calculated using the E_m^\ominus values of cell (ii) as if they were the right-hand Ag,AgX electrode potentials

Temp. (°C)	Zn(Hg) Zn ²⁺				Cd(Hg) Cd ²⁺	
	X = Cl [11]	Cl [13]	Br [11]	I [11]	Cl [11]	Br [11]
0	–	–	–	–	0.34496	–
5	–	–	–	0.7647	0.34626	0.3451
10	0.76475	–	–	0.7642	0.34758	0.3468
15	0.76335	–	–	0.7637	0.34898	0.3484
20	0.76292	0.7627	0.76312	0.7632	0.35024	0.3499
25	0.76251	0.7623	0.76257	0.7627	0.35156	0.3514
30	0.76199	0.7617	0.76212	0.7623	0.35271	0.3528
35	0.76137	–	0.76169	0.7618	0.35390	0.3541
40	0.76073	0.7603	0.76126	0.7612	0.35522	0.3555

reliable. As will be seen later in Table 8, the oxidation potential of the Zn electrode (like the cell e.m.f.) decreases monotonically with increasing temperature.

Effect of solvent on electrode potential

The e.m.f. data [12,13] of cells (i) in different aqueous, protic and aprotic solvents have been used not only to determine the single electrode potentials and the thermodynamic properties of single ions, but also to study the effects of solvent on these properties. The standard absolute potential of the Zn electrode can be obtained (using eqn. (13)) from the E_m^\ominus values of cells (i) containing ZnCl_2 in methanol-, 2-propanol-, acetone- and dioxane-water solvents and from the values of the standard absolute potential of the Ag,AgCl electrode in each solvent. These were recently reported for methanol- [4], acetone- and dioxane-water solvents [6]. Those in 2-propanol-water solvents can now be obtained by applying eqns. (1-I) and (1-II) to the reported e.m.f. data (E_m^\ominus values) of cell (ii), where $X = \text{Cl, Br}$ [18] and I [19], in these solvents. The least-squares results in cases I and II are given in Table 7. This table again shows the same interesting features observed recently [4–6] in different solvent systems, and all prove that the set of data obtained in case I, based on the oxidation potential scale, should be accepted, whereas those based on the reduction potential scale (results based on $1/r$ relationships [20]) are invalid and cannot be accepted. In view of this conclusion, and to save space, the standard absolute electrode potentials in various solvent systems and the related thermodynamic quantities were computed on the oxidation potential scale only. The results are given in Tables 8 and 9.

TABLE 7

The least-squares results of applying eqns. (1) to the standard e.m.f. data [18,19] of cell (ii) in 2-propanol + water solvents at 25 °C

2-Propanol (%)	0 [4]	10	20	30	50	
Case I						
-Corr (10^{-2})	99.9991	99.9993	99.9999	99.9993	99.9967	
Δ (mV)	X = Cl	-0.56	-0.47	-0.13	+0.45	+0.93
	Br	+0.94	+0.79	+0.21	-0.74	-1.54
	I	-0.38	-0.31	-0.08	+0.30	+0.62
a_1^\ominus (10^{10} V m $^{-1}$)		1.07006	1.05181	1.02711	0.99248	0.93648
r_+ (10^{-10} m)		2.017	2.013	2.010	2.007	1.992
${}^L E_m^\ominus$ (V)		2.15861	2.11729	2.06437	1.99186	1.86512
${}^R E_m^\ominus$ (V)	X = Cl	1.93682	1.90377	1.85907	1.79639	1.69503
	Br	2.08662	2.05103	2.00286	1.93534	1.82614
	I	2.31134	2.27191	2.21856	2.14376	2.02280
Case II						
Corr (10^{-2})		99.8988	99.8959	99.8833	99.8594	99.8349
Δ (mV)	X = Cl	+5.44	+5.42	+5.61	+5.95	+6.08
	Br	-9.77	-9.74	-10.07	-10.68	-10.92
	I	+4.33	+4.31	+4.46	+4.73	+4.84
a_2^\ominus (10^{-10} V m)		4.19804	4.12629	4.02886	3.89212	3.67171
r_+ (10^{-10} m)		2.007	2.003	2.000	1.997	1.981
${}^L E_m^\ominus$ (V)		2.09156	2.06030	2.01485	1.94938	1.85333
${}^R E_m^\ominus$ (V)	X = Cl	2.31936	2.27972	2.22589	2.15035	2.02857
	Br	2.15284	2.11605	2.06608	1.99596	1.88293
	I	1.94354	1.91032	1.86521	1.80191	1.69986
a_2^\ominus/a_1^\ominus (10^{-20} m 2)		3.9232	3.9230	3.9225	3.9216	3.9208

It is evident from Table 8 that the potential ${}^L E_m^\ominus$ of the Zn electrode decreases both with increasing temperature and with increasing cosolvent content in the mixture. At any temperature, the effect of the solvent on ${}^L E_m^\ominus$ is more pronounced in 2-propanol–water than in methanol–water and in acetone–water than in dioxane–water solvents. The different nature of these protic and aprotic solvents is reflected by the radii of the solvated Zn^{2+} cations. As the cosolvent content increases, the values of r_+ increase monotonically in acetone– and dioxane–water solvents, pass through a maximum in methanol–water and pass through a minimum in 2-propanol–water solvents. These extrema shift to a lower alcohol content as the temperature increases.

Standard thermodynamic functions of the half-cells in various solvents

The standard thermodynamic functions for the electrode reactions of cell (i) were computed [4], using eqns. (3–I) and (7–I) and the results at 25 °C are recorded in Table 9. The free energy changes ΔG^\ominus , which are all

TABLE 8

Standard molal absolute potential ${}^{\circ}E_m^{\ominus}$ (V) of Zn(Hg)|Zn²⁺ electrode and radius r_+ (10^{-10} m) of solvated Zn²⁺ cation in water–cosolvent mixtures at different temperatures

Cosolvent (wt.%)		0	10	20	30	50
Methanol–water solvents [12]						
25 °C	${}^{\circ}E_m^{\ominus}$	2.9215	2.8761	2.8311	2.7830	2.6877
	r_+	5.4612	5.4688	5.4691	5.4577	5.4416
30 °C	${}^{\circ}E_m^{\ominus}$	2.9102	2.8673	2.8234	2.7771	2.6824
	r_+	5.4637	5.4684	5.4671	5.4533	5.4344
35 °C	${}^{\circ}E_m^{\ominus}$	2.8987	2.8584	2.8157	2.7705	2.6774
	r_+	5.4658	5.4679	5.4648	5.4492	5.4265
40 °C	${}^{\circ}E_m^{\ominus}$	2.8870	2.8487	2.8079	2.7632	2.6729
	r_+	5.4676	5.4675	5.4619	5.4446	5.4164
2-Propanol–water solvents [13]						
20 °C	${}^{\circ}E_m^{\ominus}$	2.9333	2.8843	–	2.7373	2.5927
	r_+	5.4596	5.4543	–	5.4891	5.5177
25 °C	${}^{\circ}E_m^{\ominus}$	2.9214	2.8701	–	2.7247	2.5818
	r_+	5.4610	5.4574	–	5.4907	5.5139
30 °C	${}^{\circ}E_m^{\ominus}$	2.9091	2.8557	–	2.7120	2.5713
	r_+	5.4616	5.4598	–	5.4911	5.5101
40 °C	${}^{\circ}E_m^{\ominus}$	2.8838	2.8266	–	2.6869	2.5502
	r_+	5.4615	5.4645	–	5.4916	5.5023
Acetone–water solvents [12]						
25 °C	${}^{\circ}E_m^{\ominus}$	2.9215	2.8509	2.7782	2.6999	–
	r_+	5.4612	5.4878	5.5299	5.5864	–
Dioxane–water solvents [12]						
25 °C	${}^{\circ}E_m^{\ominus}$	2.9215	2.8650	2.8014	2.7339	–
	r_+	5.4612	5.4971	5.5364	5.5712	–

negative, become less negative on increasing the cosolvent content in the mixture of any solvent system. The negative values of ΔG^{\ominus} are greater in methanol–water than in 2-propanol–water and in dioxane–water than in acetone–water solvents of any composition, for both left-hand and right-hand electrode reactions. In water–methanol solvents the standard enthalpy ΔH^{\ominus} and entropy ΔS^{\ominus} changes of both reactions increase negatively and the value of ΔS_R^{\ominus} becomes positive in 50% methanol, while the negative values of ΔH^{\ominus} and ΔS^{\ominus} in 2-propanol–water pass through maxima at around 10–20% 2-propanol on increasing the alcohol concentration in the solvent.

Standard transfer thermodynamic quantities of individual ions

The standard transfer thermodynamic quantities of individual ions on transfer from water into aqueous organic mixed solvents were computed on

TABLE 9

Standard thermodynamic functions of the left-hand (L) and right-hand (R) electrode reactions in various solvents, and standard thermodynamic quantities for transfer of Zn^{2+} and Cl^- ions from water into the respective solvents, all at 25°C [ΔG^\ominus and ΔH^\ominus (kJ mol⁻¹); ΔS^\ominus (J K⁻¹ mol⁻¹)]

Cosolvent (wt.%)	0	10	20	30	50
Methanol-water solvents [12]					
$-\Delta G_L^\ominus$	563.8	555.0	546.3	537.1	518.6
$-\Delta H_L^\ominus$	695.9	654.0	636.8	589.1	563.4
$-\Delta S_L^\ominus$	443.1	332.2	303.5	174.4	150.1
$-\Delta G_R^\ominus$	186.9	183.7	180.8	178.1	172.5
$-\Delta H_R^\ominus$	235.0	214.6	206.3	182.8	169.5
$-\Delta S_R^\ominus$	161.6	103.6	85.4	15.8	-10.0
$\Delta G_i^\ominus (\text{Zn}^{2+})$	0	8.8	17.4	26.7	45.1
$\Delta H_i^\ominus (\text{Zn}^{2+})$	0	41.9	59.1	106.8	132.5
$\Delta S_i^\ominus (\text{Zn}^{2+})$	0	111.0	139.6	268.7	293.1
$\Delta G_i^\ominus (\text{Cl}^-)$	0	3.2	6.1	8.8	14.4
$\Delta H_i^\ominus (\text{Cl}^-)$	0	20.5	28.8	52.2	65.5
$\Delta S_i^\ominus (\text{Cl}^-)$	0	58.0	76.2	145.8	171.6
2-Propanol-water solvents [13]					
$-\Delta G_L^\ominus$	563.7	553.8	-	525.8	498.2
$-\Delta H_L^\ominus$	706.7	720.5	-	671.3	620.5
$-\Delta S_L^\ominus$	479.7	558.9	-	488.1	410.2
$-\Delta G_R^\ominus$	186.9	183.7	179.4	173.3	163.6
$-\Delta H_R^\ominus$	235.0	244.0	243.6	222.4	196.6
$-\Delta S_R^\ominus$	161.6	202.3	215.4	164.6	110.7
$\Delta G_i^\ominus (\text{Zn}^{2+})$	0	9.9	-	37.9	65.5
$\Delta H_i^\ominus (\text{Zn}^{2+})$	0	-13.7	-	35.4	86.2
$\Delta S_i^\ominus (\text{Zn}^{2+})$	0	-79.2	-	-8.4	69.5
$\Delta G_i^\ominus (\text{Cl}^-)$	0	3.2	7.5	13.5	23.3
$\Delta H_i^\ominus (\text{Cl}^-)$	0	-8.9	-8.6	12.6	38.4
$\Delta S_i^\ominus (\text{Cl}^-)$	0	-40.7	-53.8	-3.0	50.9
Acetone-water solvents [12]					
$-\Delta G_L^\ominus$	563.8	550.1	536.1	521.0	-
$-\Delta G_R^\ominus$	186.9	181.5	175.6	168.9	153.9
$\Delta G_i^\ominus (\text{Zn}^{2+})$	0	13.6	27.7	42.8	-
$\Delta G_i^\ominus (\text{Cl}^-)$	0	5.4	11.3	18.0	33.0
Dioxane-water solvents [12]					
$-\Delta G_L^\ominus$	563.8	552.8	540.6	527.6	-
$-\Delta G_R^\ominus$	186.9	182.0	176.7	171.4	160.2
$\Delta G_i^\ominus (\text{Zn}^{2+})$	0	10.9	23.2	36.2	-
$\Delta G_i^\ominus (\text{Cl}^-)$	0	4.8	10.1	15.5	26.7

the molal scale using eqns. (20-I) and (21-I) as before [4], and the results at 25°C are also included in Table 9. The ΔG_i^\ominus (i) values are accurate to ± 100 J mol⁻¹.

The free energies of transfer of Zn^{2+} and Cl^- ions are all positive and increase with increasing cosolvent content in the mixture. The positive values of $\Delta G_t^\ominus(i)$ support the view that the transfer of ions from water to the respective solvents is not favoured, i.e. the ions are hydrophilic. Free energies of transfer may be simply interpreted by assuming that the Zn^{2+} or Cl^- ions interact more strongly with water molecules than with protic or aprotic cosolvent molecules in their aqueous mixtures, without reference to any special structural properties of water or the cosolvent studied. This is also confirmed by the results of the ion n.m.r. studies [21] which have shown that ions have a preference for water around them in water-methanol mixtures.

For the transfer of Zn^{2+} and Cl^- ions into methanol-water solvents the values of ΔG_t^\ominus are lower, whereas those of ΔH_t^\ominus and ΔS_t^\ominus are higher, than the corresponding values for transfer into 2-propanol-water solvents. Dioxane-water solvents have lower $\Delta G_t^\ominus(\text{Zn}^{2+})$ and $\Delta G_t^\ominus(\text{Cl}^-)$ than acetone-water solvents. Although the values of ΔG_t^\ominus for Zn^{2+} and Cl^- ions generally increase monotonically with increasing methanol or 2-propanol content in the solvent, the values of ΔH_t^\ominus and ΔS_t^\ominus show different trends with solvent composition. They vary monotonically in the methanol-water system whereas they show marked fluctuations in the 2-propanol-water system. The single-ion ΔH_t^\ominus values (Table 9) exhibit negative minima at 10–20 wt.% 2-propanol and thereafter a steady increase with increasing 2-propanol content in the solvent. Such fluctuations are not unexpected in view of the well-known variations of a number of physical and thermodynamic properties of aqueous 2-propanol mixtures with composition [22], as well as variations of kinetic parameters with composition [23]. As usual, the entropy fluctuations (as $-T\Delta S_t^\ominus$) mirror the fluctuations in ΔH_t^\ominus for single ions.

The structural features of the ion-solvent interactions in mixed solvents are reflected by $\Delta H_t^\ominus(i)$ and $\Delta S_t^\ominus(i)$ values. The positive entropy and enthalpy for transfer of ions from water into alcoholic solvents can be attributed to greater structure-breaking by the ion in these solvents than in water. Any methanolic solvent, or the 50% 2-propanolic solvent, is therefore a more structured solvent than water. The negative $\Delta S_t^\ominus(i)$ and $\Delta H_t^\ominus(i)$ values for the water-rich 2-propanolic solvents assume that ions are more effective at breaking the structure in water than in these solvents. This is further supported by the view [17,20] that the structure-forming processes are exothermic and accompanied by an entropy decrease, and the structure-breaking processes are endothermic, leading to an entropy increase.

Although methanol shows no peak in the ultrasonic absorption when mixed with water, the peak observed for 2-propanol at 15–20% [24] is in agreement with, and supports, our results obtained on the basis of the oxidation potential scale. On the other hand, the values for $\Delta G_t^\ominus(i)$ based on the reduction potential scale, i.e. $1/r$ relationships, show extrema or

sharp changes at around 10% 2-propanol and also show some tendency for this at around 20–30% methanol [8,9]. Furthermore, single-ion Gibbs energies for transfer from water into methanol–water solvents obtained by Abraham et al. [7] are all positive while those obtained by numerous workers [8–13,20] are all negative for Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Ag^+ , Zn^{2+} , Cd^{2+} and Ba^{2+} ions, although all are based on $1/r$ relationships. This could be explained, as before [4], in view of eqn. (19). If the value of ΔG_i^\ominus for an electrolyte were the sum of the values for the ion constituents [7–13], this would mean that while one value of $\Delta G_i^\ominus(i)$ is based on the oxidation potential scale, the second is based on the reduction potential scale, i.e. on two different scales. This is, of course, impractical. Therefore, all the reported [8–13,20] $\Delta G_i^\ominus(i)$ values are in fact positive for both anions and cations.

Finally, the interesting general features observed in this work provide further strong evidence and support the validity and general applicability of the new method [4] for the determination of absolute electrode potentials as well as thermodynamic properties of individual ions in any solvent without extra thermodynamic assumptions of any type.

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