Thermochimica Acta, 120 (1987) 261–278
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ABSOLUTE ELECTRODE POTENTIALS IN DIOXANE–WATER SOLVENT MIXTURES AND TRANSFER FREE ENERGIES OF INDIVIDUAL IONS

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(Received 24 March 1987)

ABSTRACT

Standard e.m.f. values at 25 ° C for the cells Pt, H_2(g, 1 atm) | HI, solvent | AgI, Ag and M, Mx | solvent | AgX, Ag in nine solvent mixtures of dioxane with water, containing up to 80 wt.% dioxane, are reported. The e.m.f. data were used to determine standard absolute potentials of the hydrogen, the Ag, AgX (X ≡ Cl, Br and I) and the M, M^+ (M ≡ Li, Na, K, Rb and Cs) electrodes in these solvents by a new method reported recently. The radii of the solvated cations and their solvation extent in such media have been evaluated. The standard Gibbs free energies of transfer of individual ions from water to the respective solvents have also been computed. The results are interpreted and discussed in terms of the solvation characteristics of the solvents. The data obtained in the dioxane–water solvent system are compared with those in various aqueous protic and aprotic solvent systems.

INTRODUCTION

The study of the thermodynamic properties of individual ions in pure or mixed solvents has recently been a subject of interest. E.m.f. measurements on the cells

Pt, H_2(g, 1 atm) | HX(m), solvent | AgX, Ag   cell I

and

M, MX | solvent | AgX, Ag   cell II

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have been extensively used [1–10] not only to determine the thermodynamics of hydrogen halides and alkali metal halides in aqueous, partially aqueous and non-aqueous media, but also to evaluate the thermodynamics of individual ions in such media. A new method for the determination of absolute electrode potentials and the thermodynamics of individual ions in solution was described recently [1]. This method was successfully applied to cells I and II in various water–organic solvent systems, including both protic and aprotic solvents [1,2]. In the present work, the same procedure is applied to e.m.f. data of these cells in dioxane–water solvents at 25 °C. The studies have been extended to this solvent system, on the one hand, for further verification of the procedure used [1,2] in such media, and on the other hand, for the determination of the standard absolute potentials of the hydrogen, Ag, AgX (X ≡ Cl, Br and I) and M, M^+ (M ≡ Li, Na, K, Rb and Cs) electrodes in each solvent, in order to compute the Gibbs free energies of transfer of the individual ions from water to the respective dioxane–water solvent mixtures, with a view to a comprehensive understanding of the ion–solvent interactions.

To obtain the standard absolute potentials of the hydrogen and the Ag, AgX electrodes, the new procedure [1,2] requires a knowledge of the standard e.m.f. (E_m°) values of cell I, where X ≡ Cl, Br and I, in dioxane–water solvents. Those for X ≡ Cl [3] and X ≡ Br [4] were reported earlier from this laboratory. Therefore, in the present work, we have determined the E_m° values of cell I for X ≡ I (the standard potentials of the Ag, AgI electrode) in nine different dioxane–water solvent mixtures (containing up to 80 wt.% dioxane) from the e.m.f. measurements, at 25 °C of the cell

$$\text{Ag, AgI}\left|\begin{array}{l:l} \mathrm{KI}(x)\ (m) & \mathrm{KCl}(x)\ (m) \\ \mathrm{KNO_3}(1-x)\ (m) & \mathrm{KNO_3}(1-x)\ (m) \\ \text{solvent} & \text{solvent} \end{array}\right|\text{AgCl, Ag} \qquad \text{cell III}$$

which is similar to that recently used [5] for the same purpose.

The standard absolute potentials of M, M^+ electrodes in these nine dioxane–water solvent mixtures have also been determined as before [2] from the e.m.f. measurements performed at 25 °C on the double cell:

$$\text{Ag, AgX}\,|\,\mathrm{MX}(m),\ \mathrm{S}\,|\,\mathrm{M(Hg)}\,|\,\mathrm{MX}(m),\ \mathrm{W}\,|\,\text{AgX, Ag} \qquad \text{cell IV}$$

where M ≡ Li, Na, K, Rb and Cs for X ≡ Cl. S is the mixed solvent, W is water and m is the molality, which varies from 0.01 to 0.10 mol kg^{-1}. The standard e.m.f. (ΔE_m°) of cell IV is the difference between the E_m° values of cell II in water and in the mixed solvent.

However, comparisons have been made between the new values of the standard e.m.f. of cell I as well as of cell IV where possible and those reported previously by other investigators [5–12], in dioxane–water solvents.

EXPERIMENTAL

Dioxane (BDH, AnalaR) was further purified as described earlier [3,4]. It was stored over sodium in an atmosphere of nitrogen, freshly redistilled and used within a few hours. AnalaR and Merck quality alkali metal salts were further purified [2,5,9], dried at 120 °C and kept in a desiccator over phosphorus pentoxide [11]. The water used was deionised water, redistilled twice and stored also under nitrogen [3,4]. Solvents were prepared by mixing dioxane and water in the required proportions by weight. Required sets of solutions in each solvent were prepared by mass dilution from a stock solution prepared from weighed amounts of salt and solvent. All solutions were freshly prepared before taking measurements. Transference of the solutions was made under nitrogen pressure and exposure to air was avoided [5].

The preparation of the electrodes and cell solutions and other general experimental techniques and details have been described elsewhere [2,5,9,13–15]. Exposure of the cells to light was always avoided. The temperature control was carefully maintained at 25 ± 0.01 °C. The e.m.f. values were reproducible to ± 0.05 mV for different solutions. 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 triplicates generally agreed withn ± 0.1 mV.

Incomplete dissociation of alkali metal salts in the media considered could be a source of error [11]. This would be the case especially in media with low dielectric constants. This source of error could be avoided by working at lower salt concentrations [11]. Thus, the e.m.f. values of cells III and IV were measured in nine different dioxane–water solvent mixtures, with six different values of m in the range 0.01–0.10 mol kg^{-1}. For cell III, the e.m.f. measurements were made with seven different values of x (ranging from 0.2 to 0.8) for each value of m.

RESULTS AND DISCUSSION

Standard potential of the Ag, AgI electrode

From the e.m.f. data of cell III at 25 °C, the standard e.m.f. (E_m°) values of this cell in nine dioxane and water solvent mixtures were determined by the extrapolation procedure described earlier [5]. In the dioxane-rich solvents (containing 50 wt.% dioxane or more), corrections have been made as before [4] for the incomplete dissociation of electrolytes in such media of low dielectric constant. The E_m° values of cell III, so calculated at 25 °C, are recorded in Table 1. The average standard deviations in E_m° values of cell III are ± 0.05 mV, ± 0.15 mV and ± 0.20 mV for solvents containing up to 30 wt.% dioxane, 60 wt.% dioxane and 80 wt.% dioxane respectively.

TABLE 1

Values of standard e.m.f., E_m° (V), of cells III and I, where X ≡ I, in dioxane–water solvents at 25 °C and previously reported values [5–8] for comparison

Dioxane (wt.%)	Reference	Cell III E_m°	Cell I, (X ≡ I) $-E_m^\circ$
0	13	—	0.15235
5	This work	0.36987	0.15215
	7	–	0.15274
10	This work	0.36504	0.15202
	5	–	0.1509
	7	–	0.15423
20	This work	0.35434	0.15151
	5	–	0.1519
	6	–	0.15136
	7	–	0.15452
30	This work	0.34349	0.15326
	5	–	0.1557
40	This work	0.33231	0.15869
	5	–	0.1591
45	This work	0.32659	0.16283
	6	–	0.16025
50	This work	0.32100	0.16928
60	This work	0.31135	0.19084
70	This work	0.30212	0.23830
	8	–	0.2243
80	This work	0.28527	0.32546

In any solvent, the E_m° value of cell III is the difference between the E_m° values of cell I for X ≡ Cl and X ≡ I, i.e. the difference between the standard potentials of the Ag, AgCl and Ag, AgI electrodes. Since the standard potentials of the Ag, AgCl electrode in these dioxane–water solvent mixtures were reported earlier [3] from this laboratory, those of the Ag, AgI electrode could be obtained by subtraction. The E_m° values of cell I for X ≡ I, i.e. the standard potentials of the Ag, AgI electrode, so calculated at 25 °C, are thus accurate to ± 0.10 mV, ± 0.20 mV and ± 0.30 mV in solvents containing up to 30 wt.% dioxane, 60 wt.% dioxane and 80 wt.% dioxane respectively. These are also included in Table 1, together with previously reported values [5–8] for comparison.

The standard potential E_m° of the Ag, AgI electrode was determined in 20 and 45 wt.% dioxane–water mixtures by Feakins and Turner [6] and in 5, 10, 15 and 20 wt.% dioxane–water mixtures by Mussini et al. [7], using Owen's borate-buffered cells at 25 °C. Bax et al. [8] determined the E_m° value of the Ag, AgI electrode in a 70 wt.% dioxane–water mixture by comparison with that of the Ag, AgCl electrode known in this solvent. Also the E_m° values of the Ag, AgI electrode were measured in aqueous mixtures containing 10, 20, 30 and 40 wt.% dioxane at 15, 25, 35 and 45 °C by Mishra et al. [5] using cell III. However, discrepancies between the reported values are generally noted (see Table 1); there is as much as a 3.3 mV difference for the 10 wt.% dioxane–water mixture and a 3.16 mV difference for the 20 wt.% dioxane–water mixture.

It can be seen from Table 1 that our new value of E_m° for the 20 wt.% dioxane–water mixture is in better agreement with that obtained by Feakins and Turner [6]. Also, the new E_m° values for the aqueous mixtures containing 20 and 40 wt.% dioxane agree well (within the sums of experimental errors) with those of Mishra et al. [5]. The new value of E_m° for the 10 wt.% dioxane–water mixture is inbetween those of Mishra et al. [5] and Mussini et al. [7]. However, the agreement between the new E_m° values for the rest of the solvent systems and the corresponding reported values is poor. Feakins and Turner [6] reported that their results in the 45 wt.% mixture were slightly less accurate and extrapolation did not therefore appear to be justified. The value of E_m° obtained by Bax et al. [8] in the 70 wt.% mixture is not corrected for ion association. Furthermore, Feakins et al. [9], by their additivity rule, do not support the results obtained by Mussini et al. [7]. Therefore, the new values of E_m° in dioxane–water solvent mixtures should be preferred. The present investigation was thus undertaken not only to check the previous data but also to extend the work to other solvent compositions at 25 °C. This enables us to study solvent effects on the standard absolute electrode potential and related thermodynamic quantities in such media.

Standard absolute potential of the hydrogen and Ag, AgX electrodes

The new recently developed method [1,2] for the determination of absolute electrode potentials and the thermodynamics of individual ions in solution has now been applied to the e.m.f. data of cell I in dioxane–water solvent mixtures. According to this method, the oxidation potential of any electrode varies directly with the radius r of the solvated ion on whose activity the potential depends. Therefore, the cell e.m.f. is proportional to the radius of the solvated ion which is being varied in a series of electrolytes having a common ion [1]. Thus, in any solvent, the plot of the standard e.m.f. (E_m°) values of cell I, containing HCl [3], HBr [4] and HI, against the radius of the solvated anion r_- should yield a straight line according to eqn. (1) at any temperature [1]:

$$E_m^\circ = a_1^\circ r_+ - a_1^\circ r_- \qquad (1)$$

This is readily verified in various dioxane–water solvent mixtures, and the least-squares results at 25 °C are collected in Table 2. In all solvents, perfect straight lines were obtained, and the extent of correlation is indicated by the

TABLE 2

The least-squares results of applying eqn. (1) to the E_m° values of cell I in dioxane–water solvents at 25 °C

Dioxane (wt.%)		5	10	20	30	40	45	50	60	70	80
−Corr (10^{-2})		99.9983	99.9987	99.9994	100.0000	99.9991	99.9991	99.9999	99.9804	99.9964	99.9977
Δ (mV)		−0.75	−0.65	−0.41	+0.05	+0.49	+0.48	+0.18	−2.13	−0.88	−0.67
		+1.26	+1.08	+0.68	−0.09	−0.82	−0.80	−0.30	+3.55	+1.48	+1.11
		−0.50	−0.43	−0.27	+0.04	+0.33	+0.32	+0.12	−1.42	−0.59	−0.45
a_1° (10^{10} V m^{-1})		1.05605	1.04235	1.01201	0.98145	0.94992	0.93357	0.91732	0.88754	0.86236	0.81442
r_+ (10^{-10} m)		2.015	2.014	2.010	2.004	1.993	1.986	1.976	1.943	1.883	1.760
${}^{\mathrm{Ox}}_{\mathrm{L}}E_m^\circ$ (V)		2.12842	2.09903	2.03416	1.96671	1.89347	1.85400	1.81224	1.72483	1.62380	1.43324
${}^{\mathrm{Ox}}_{\mathrm{R}}E_m^\circ$ (V)	Cl	1.91146	1.88666	1.83174	1.77643	1.71936	1.68976	1.66034	1.60645	1.56087	1.47410
	Br	2.05930	2.03259	1.97342	1.91383	1.85235	1.82046	1.78877	1.73071	1.68160	1.58812
	I	2.28107	2.25148	2.18594	2.11993	2.05184	2.01651	1.98140	1.91709	1.86269	1.75915
ΔG_t° (J mol^{-1})	H	2913	5749	12008	18515	25582	29390	33419	41853	51601	69987
	Cl	2447	4840	10139	15475	20982	23837	26676	31876	36273	44645
	Br	2636	5213	10922	16672	22603	25680	28738	34340	39078	48098
	I	2921	5776	12099	18468	25038	28447	31834	38039	43288	53278
	HCl	466	909	1869	3040	4600	5553	6743	9977	15328	25342
	HBr	277	536	1086	1843	2979	3710	4681	7513	12523	21889
	HI	−8	−27	−91	47	544	943	1585	3814	8313	16709

correlation coefficients (corr) and the differences Δ (mV) between the E_m° values obtained experimentally and those calculated from eqn. (2):

$$E_m^\circ = {}^{\mathrm{Ox}}_{\mathrm{L}}E_m^\circ - {}^{\mathrm{Ox}}_{\mathrm{R}}E_m^\circ \tag{2}$$

where ${}^{\mathrm{Ox}}_{\mathrm{L}}E_m^\circ$ and ${}^{\mathrm{Ox}}_{\mathrm{R}}E_m^\circ$ are the oxidation potentials of the left-hand electrode and right-hand electrode respectively [1,2].

Table 2 shows that the value of a_1° decreases with increasing porportion of dioxane in the solvent system. As reported earlier [1,2], the values of a_1° appear to be universal constants for all electrodes and dependent only on the medium at any temperature. However, as the dioxane content of the solvent increases, the radius of the solvated H^+ ion (r_+) decreases, i.e. the extent of solvation of the protons decreases, and the oxidation potentials of both the left-hand and right-hand electrodes, ${}^{\mathrm{Ox}}_{\mathrm{L}}E_m^\circ$ and ${}^{\mathrm{Ox}}_{\mathrm{R}}E_m^\circ$, respectively decrease. These features have recently been observed in aqueous methanol (MeOH), aqueous ethylene glycol (EG) and aqueous propylene glycol (PG) solvent systems [1,2].

The protons therefore, must be less solvated in the mixed solvent than in water, and much less solvated when the dioxane content in the solvent is increased (Table 2). The solvation of protons in aqueous dioxane solvents could be compared also with that in aqueous dimethyl sulphoxide (DMSO) solvents, where the protons become gradually more solvated (r_+ values increase) on the successive addition of DMSO to the aqueous medium [15]. This may reflect the different natures of the dipolar aprotic solvent (DMSO) and the non-polar aprotic solvent (dioxane) in mixtures of each with water.

The standard free energy changes ($\Delta G_{\mathrm{E}}^\circ$) involved in the half-cell reactions are essentially related to the standard absolute electrode potentials (${}^{\mathrm{Ox}}_{\mathrm{E}}E_m^\circ$) by the relation [1,2]

$$\Delta G_{\mathrm{E}}^\circ = -F\,{}^{\mathrm{Ox}}_{\mathrm{E}}E_m^\circ \tag{3}$$

where F is the faraday. Thus, the values of $\Delta G_{\mathrm{E}}^\circ$ could be computed on the molal scale using the ${}^{\mathrm{Ox}}_{\mathrm{E}}E_m^\circ$ values given in Table 2. Since the oxidation potentials of the single electrodes are all positive and decrease with increasing dioxane concentration in the solvent, the values of $\Delta G_{\mathrm{E}}^\circ$ (not included) are all negative and increase with increasing dioxane concentration in the solvent. The standard free energy change associated with the overall cell reaction can then be obtained as the difference between those for the half-cell reactions, both based on the same oxidation potential scale [1,2].

It is noteworthy that while the negative values of E_m° for cell I containing HI appear to pass over a maximum at around 20 wt.% dioxane, the standard absolute potentials of the hydrogen or Ag, AgX electrodes are all positive and decrease directly (in one direction), with increasing amounts of dioxane in the solvent. Since the value of E_m° is the difference between those of ${}^{\mathrm{Ox}}_{\mathrm{L}}E_m^\circ$ and ${}^{\mathrm{Ox}}_{\mathrm{R}}E_m^\circ$ (see eqn. (2)), the rate of variation of each will determine the net rate of variation of E_m° with solvent composition. This can explain the maximum observed at around 20 wt.% dioxane for the E_m° values of cell I containing HI.

Standard transfer free energies of individual ions

The standard Gibbs free energy of transfer is an important index of the differences in interactions of the ions and the solvent molecules in the two different media, and the individual ion free energies of transfer provide a clearer understanding of ion–solvent interactions than do the free energies of transfer of the HX acids or MX electrolytes [16–21]. The values for the standard Gibbs free energy ΔG_t° for the transfer of an individual ion from water to various dioxane–water solvents were calculated [1,2] on the molal scale from the standard absolute electrode potentials in water (${}^{\mathrm{w}}_{\mathrm{E}}E_m^\circ$) and in the respective mixed solvents (${}^{\mathrm{s}}_{\mathrm{E}}E_m^\circ$) using eqn. (4):

$$\Delta G_t^\circ = F\left({}^{\mathrm{w}}_{\mathrm{E}}E_m^\circ - {}^{\mathrm{s}}_{\mathrm{E}}E_m^\circ\right) \tag{4}$$

The values of ΔG_t° calculated at 25 °C on the basis of the oxidation potential scale [1,2] are included in Table 2. These ΔG_t° values are accurate to ± 80 J mol^{-1}. It is evident from Table 2 that for all ions the values of ΔG_t° increase positively with increasing proportion of dioxane in the solvent. The observed positive increase in ΔG_t° values suggests that the transfer of ions from water to the respective dioxane–water solvents is increasingly unfavourable. The positive ΔG_t° values indicate that the ions are in higher free energy states in the mixed solvents than in water, and therefore the transfer process is not spontaneous.

Gibbs free energies of transfer of individual ions from water to any solvent of low dioxane content (up to 20 wt.% dioxane) increase in the order $\mathrm{Cl^-} < \mathrm{Br^-} < \mathrm{H^+} < \mathrm{I^-}$, but to any solvent of higher dioxane content (30–80 wt.% dioxane) the order becomes $\mathrm{Cl^-} < \mathrm{Br^-} < \mathrm{I^-} < \mathrm{H^+}$. Again, the different rates of variation of ${}^{\mathrm{Ox}}_{\mathrm{L}}E_m^\circ$ and ${}^{\mathrm{Ox}}_{\mathrm{R}}E_m^\circ$ with solvent composition are also responsible for these orders. However, this feature, which is verified also by the previous results [5,6,8] in Table 3, is not observed in the data of Mussini et al. [7]. Generally, for the transfer of halide ions to any dioxane–water solvent, the values of ΔG_t° increase in the order $\mathrm{Cl^-} < \mathrm{Br^-} < \mathrm{I^-}$ which is evident in several solvent systems [1,2,15].

Standard Gibbs free energy of transfer of HX acids or MX electrolytes is given [1,2] by eqn. (5):

$$\Delta G_t^\circ(\mathrm{HX\ or\ MX}) = \Delta G_t^\circ(\mathrm{H^+\ or\ M^+}) - \Delta G_t^\circ(\mathrm{X^-}) \tag{5}$$

where $\Delta G_t^\circ(\mathrm{H^+\ or\ M^+})$ and $\Delta G_t^\circ(\mathrm{X^-})$ are the standard Gibbs transfer free energies on the molal scale of $\mathrm{H^+}$ or $\mathrm{M^+}$ and $\mathrm{X^-}$ ions respectively. The values of ΔG_t° for halogen acids, calculated using eqn. (5) at 25 °C are also included in Table 2. The standard free energies of transfer for the pair of ions ($\mathrm{H^+I^-}$) are found to be negative for solvents of low dioxane content.

TABLE 3

The least-squares results of applying eqn. (1) to the previous e.m.f. data [5–8] of cells I in dioxane–water solvent mixtures at 25 °C

Dioxane (wt.%)		5 [7]	10 [5]	10 [7]	15 [7]	20 [5]	20 [6]	20 [7]	30 [5]	40 [5]	45 [6]	70 [8]
$-$Corr (10^{-2})		99.9992	99.9972	99.9992	99.9999	99.9995	99.9990	100.0000	99.9961	99.9968	99.9969	99.9927
Δ (mV)		-0.50	-0.95	-0.50	-0.18	-0.38	-0.54	$+0.04$	-1.05	0.93	-0.88	-1.20
		$+0.84$	$+1.59$	$+0.83$	$+0.30$	$+0.63$	$+0.90$	-0.07	$+1.76$	$+1.55$	$+1.46$	$+2.01$
		-0.34	-0.63	-0.33	-0.12	-0.25	-0.36	$+0.03$	-0.70	-0.62	-0.58	-0.80
a_I° (10^{10} V m^{-1})		1.05603	1.04058	1.05150	1.03520	1.01373	1.01203	1.02176	0.98980	0.95126	0.92439	0.82242
r_+ (10^{-10} m)		2.015	2.014	2.013	2.011	2.010	2.010	2.009	2.002	1.992	1.986	1.886
$^{\mathrm{Ox}}_{\mathrm{L}}E^\circ_m$ (V)		2.12796	2.09612	2.11667	2.08165	2.03750	2.03427	2.05250	1.98156	1.89500	1.83586	1.55133
$^{\mathrm{Ox}}_{\mathrm{R}}E^\circ_m$ (V)	Cl	1.91142	1.88345	1.90321	1.87371	1.83484	1.83177	1.84938	1.79153	1.72178	1.67315	1.48859
	Br	2.05927	2.02913	2.05042	2.01864	1.97676	1.97346	1.99242	1.93010	1.85496	1.80257	1.60373
	I	2.28103	2.24765	2.27123	2.23603	2.18965	2.18598	2.20699	2.13796	2.05472	1.99669	1.77644
ΔG_t°	H	2997	6012	4086	7465	11668	11980	10278	17065	25417	31123	58576
(J mol^{-1})	Cl	2489	5124	3281	6128	9814	10111	8475	13993	20723	25415	43222
	Br	2681	5521	3535	6601	10574	10892	9131	15076	22326	27380	36565
	I	2971	6116	3916	7313	11712	12066	10114	16700	24731	30330	51581
	HCl	508	888	805	1337	1854	1869	1803	3072	4694	5708	15354
	HBr	316	491	551	864	1094	1088	1147	1989	3091	3743	12011
	HI	26	-104	170	152	-44	-86	164	365	686	793	6995

They decrease to a negative minimum at around 20 wt.% dioxane and thereafter increase positively with increasing dioxane amounts in the solvent. But in the case of H^+Cl^- and H^+Br^-, the values of ΔG_t° are all positive and increase with increasing dioxane concentration in the solvent. However, this behaviour indicates that the combined effects of the solvent and solute properties do not favour the transfer of HCl and HBr to any solvent, and HI to solvents of 30 wt.% dioxane or more, while they increasingly favour the transfer of HI to solvents of low dioxane content, the transfer being most favourable to the 20 wt.% dioxane–water solvent.

It is interesting to note from eqn. (5) that the net value of ΔG_t° of HX is thus determined by the rate of increase in the positive values of ΔG_t° of both H^+ and X^- ions with increasing dioxane concentration in the solvent. This is responsible for the minimum observed at around 20 wt.% dioxane for the ΔG_t° values of HI. Furthermore, the values of ΔG_t° decrease in the order HCl > HBr > HI for the transfer to any solvent. This is expected since the value of ΔG_t° for the transfer of halide ion to any solvent increases from Cl^- through Br^- to I^-.

The new method and previous e.m.f. data of cell I in dioxane–water solvents

The new method for the determination of absolute electrode potentials as well as transfer free energies of individual ions [1,2] has been applied also to the previous e.m.f. data for the halogen acids [5–8] in dioxane–water mixtures. The least-squares results of applying eqn. (1) to the e.m.f. data are listed in Table 3. The same interesting general features and trends seen in Table 2 are again observed, leading to the same conclusions. However, the results obtained from the e.m.f. data of Mussini et al. [7] show disagreement with other results [5,6,8]. For example, for solvents of low dioxane content (containing up to 20 wt.% dioxane), their values [7] for the transfer free energies of I^- ions are always less than those of H^+ ions so that the values of ΔG_t° for H^+I^- are all positive. These are 26 J mol^{-1}, 170 J mol^{-1}, 152 J mol^{-1} and 164 J mol^{-1} for the transfer to the aqueous solvents containing 5 wt.%, 10 wt.%, 15 wt.% and 20 wt.% dioxane respectively. This irregular and peculiar order of positive values contradicts all other data [5,6,8] as well as the new values obtained in the present work.

Standard e.m.f. of cell IV in dioxane–water solvent mixtures

The e.m.f. values of cell IV, ΔE, at various molalities, were treated as previously mentioned [9,14,20,21] to give the standard e.m.f. values ΔE_m° (Table 4). Mean deviations from the final extrapolation lines were normally 0.1 mV or less for the different solvents. The values of ΔE_m° are accurate to ±0.1 mV, ±0.2 mV and ±0.3 mV or better for solvents containing up to 30 wt.%, 60 wt.% and 80 wt.% dioxane respectively.

TABLE 4

Values of standard e.m.f., ΔE_m° (mV), of cell IV in dioxane–water solvents at 25 °C and previously reported values [9–11] for comparison

Dioxane (wt.%)	Reference	LiCl	NaCl	KCl	RbCl	CsCl
5	This work	6.40	7.45	7.65	7.50	6.95
	11	–	–	–	7.89	–
10	This work	13.20	15.75	16.00	15.20	14.70
	9	13.15	15.75	15.91	14.57	14.25
	11	13.44	17.35	–	15.26	–
20	This work	28.20	33.70	34.50	34.00	32.55
	9	28.23	33.58	34.61	34.61	32.70
	10	–	–	33.80	34.69	–
	11	28.19	35.13	–	34.04	–
30	This work	46.00	55.55	56.45	56.50	53.30
	11	45.97	55.51	–	55.69	–
40	This work	67.40	81.95	83.65	84.50	78.70
	9	69.32	81.86	83.56	84.48	78.64
	11	67.21	81.09	–	82.03	–
45	This work	80.20	97.05	99.30	101.95	93.55
	10	–	–	99.60	97.14	–
	11	–	–	–	98.87	–
50	This work	94.35	114.00	117.05	121.95	110.50
	11	94.10	114.05	–	114.81	–
60	This work	128.10	152.80	156.20	168.05	147.70
	11	–	–	–	155.37	–
70	This work	167.05	195.10	200.10	220.70	189.20
	10	–	–	227.70	219.42	–
	11	–	–	–	220.73	–
80	This work	209.70	241.15	247.90	277.20	234.60
	11	–	–	–	275.56	–

In a comparison between amalgam and glass electrode results, Clune et al. [12] reported that the agreement between the results with the two types of electrode seems excellent at relatively low concentrations of organic solvent, say up to 40 wt.%, particularly for an unreactive solvent like *t*-butanol, and more work is therefore needed at the higher concentrations of organic solvent. In the dioxane–water system (solvents containing 10, 20 and 40 wt.% dioxane), values of ΔG_t° obtained with glass electrodes [11] and with amalgam electrodes [9] for LiCl, NaCl and RbCl show that the agreement is, on average, ± 97 J (± 1 mV) which is satisfactory and within the sums of experimental errors [12].

Many comparisons are possible over wider ranges of solvent composition. The new values of ΔE_m° for cell IV in dioxane–water solvent mixtures at 25 °C are recorded in Table 4, together with the previous data [9–11] using both amalgam electrodes [9,10] and glass electrodes [11] for comparison. In general, the agreement between our results and those obtained by the other investigators is acceptable, being practically always within the combined precision limits of their and our measurements. Especially for the 70 wt.% dioxane–water mixture, the value of Smits et al. [11], corrected for association, is in better agreement with the new value and both approach more closely the value reported by Bax et al. [10]. In general, the values of ΔE_m° reported by Smits et al. [11], using glass electrodes, are in good agreement with those obtained using amalgam electrodes (the new values as well as those of Feakins et al. [9] and Bax et al. [10]) in solvents of low dioxane content. However, the agreement between the new values and those previously reported for KCl in 70 wt.% dioxane–water solvent [10] and for RbCl in aqueous solvent mixtures with 50, 60 and 80 wt.% dioxane content [11] is poor. These reported values [10,11] were not corrected for the incomplete dissociation of KCl and RbCl in these media of low dielectric constant. Thus, since our new values of ΔE_m° in dioxane-rich solvents are all corrected for the incomplete dissociation of electrolytes in such media of low dielectric constant, they should be preferred. However, in the present investigation, in view of recent technical developments with the amalgam electrodes and their use in e.m.f. measurements [14,20–22] to obtain more accurate results, the standard e.m.f.s of the double cell IV have been determined at 25 °C by the procedure adopted recently [14,20,21], a method which is generally recognized as being the most reliable [20,21]. In addition, all the precautions we have taken in the experimental work make ours the more reliable.

The overall spontaneous reaction of cell IV is the transfer of 1 mol of the alkali metal halide from the mixed solvent to water. Thus, from ΔE_m° values, standard Gibbs free energies of transfer (ΔG_t°) of MX from water to the appropriate solvent could be computed ($\Delta G_t^\circ = F\Delta E_m^\circ$). The ΔG_t° values (not included) are correct to better than ± 10 J mol^{-1}, ± 20 J mol^{-1} and ± 30 J mol^{-1} for solvents containing up to 30 wt.%, 60 wt.% and 80 wt.% dioxane respectively. The increasingly positive ΔE_m° and thus ΔG_t° values of alkali metal halides indicate that the dissolution of these salts is not favoured by the addition of dioxane to water. This behaviour is of course the result of the combined effects of reduced dielectric constants and overall interactions of the cations and anions with the dioxane–water solvents relative to that with water. However, the individual ionic contributions to the total ΔG_t° values are naturally more conveniently interpreted in terms of the solvation characteristics of the solvents.

Standard absolute potential of M, M^+ electrodes and transfer free energies of M^+ ions

The value of ΔE_m° is the difference between the E_m° values of cell II in water, ${}^{W}E_m^\circ$, and in the respective dioxane–water solvent, ${}^{S}E_m^\circ$, i.e.

$$\Delta E_m^\circ = {}^{W}E_m^\circ - {}^{S}E_m^\circ \qquad (6)$$

TABLE 5

Values of the standard e.m.f., E_m° (V), of the cell M, MX | solvent | AgX, Ag in dioxane–water solvent mixtures at 25 °C

Dioxane (wt.%)	0	5	10	20	30	40	45	50	60	70	80
MX											
LiCl	3.2667	3.2603	3.2535	3.2385	3.2207	3.1993	3.1865	3.1723	3.1386	3.0996	3.0570
LiBr	3.1169	3.1124	3.1076	3.0968	3.0833	3.0663	3.0558	3.0439	3.0143	2.9789	2.9430
LiI	2.8923	2.8907	2.8887	2.8843	2.8772	2.8668	2.8597	2.8513	2.8279	2.7978	2.7719
NaCl	2.9352	2.9277	2.9194	2.9015	2.8796	2.8532	2.8381	2.8212	2.7824	2.7401	2.6940
NaBr	2.7854	2.7799	2.7735	2.7598	2.7422	2.7203	2.7074	2.6928	2.6581	2.6194	2.5800
NaI	2.5608	2.5581	2.5546	2.5473	2.5361	2.5208	2.5114	2.5001	2.4717	2.4383	2.4090
KCl	3.1472	3.1395	3.1312	3.1127	3.0907	3.0635	3.0479	3.0301	2.9910	2.9471	2.8993
KBr	2.9974	2.9917	2.9852	2.9710	2.9533	2.9305	2.9172	2.9017	2.8667	2.8263	2.7852
KI	2.7728	2.7699	2.7663	2.7585	2.7472	2.7310	2.7211	2.7090	2.6803	2.6452	2.6142
RbCl	3.1475	3.1400	3.1323	3.1135	3.0910	3.0630	3.0456	3.0256	2.9795	2.9268	2.8703
RbBr	2.9978	2.9922	2.9864	2.9718	2.9536	2.9300	2.9149	2.8971	2.8552	2.8061	2.7563
RbI	2.7731	2.7704	2.7675	2.7593	2.7475	2.7305	2.7188	2.7045	2.6688	2.6250	2.5853
CsCl	3.1454	3.1384	3.1307	3.1128	3.0921	3.0667	3.0518	3.0349	2.9977	2.9562	2.9108
CsBr	2.9956	2.9906	2.9847	2.9711	2.9547	2.9337	2.9211	2.9064	2.8734	2.8354	2.7967
CsI	2.7710	2.7688	2.7658	2.7586	2.7486	2.7342	2.7251	2.7138	2.6870	2.6543	2.6257

TABLE 6

Standard absolute potentials of M, M^+ electrodes, radii of solvated cations and their solvation extent in dioxane–water solvent mixtures, and standard transfer free energies of individual cations from water to these solvents, at 25 °C

Dioxane (wt.%)		5	10	20	30	40	45	50	60	70	80
${}^{\mathrm{Ox}}_{\mathrm{L}}E^\circ_m$ (V)	Li	5.1717	5.1401	5.0702	4.9971	4.9186	4.8762	4.8327	4.7450	4.6605	4.5311
	Na	4.8392	4.8061	4.7332	4.6561	4.5726	4.5279	4.4815	4.3888	4.3010	4.1681
	K	5.0510	5.0178	4.9444	4.8671	4.7829	4.7376	4.6904	4.5974	4.5079	4.3734
	Rb	5.0515	5.0190	4.9452	4.8674	4.7824	4.7353	4.6859	4.5859	4.4877	4.3444
	Cs	5.0499	5.0173	4.9445	4.8685	4.7860	4.7416	4.6952	4.6041	4.5170	4.3849
r_+ (10^{-10} m)	Li	4.897	4.931	5.010	5.092	5.178	5.223	5.268	5.346	5.404	5.564
	Na	4.582	4.611	4.677	4.744	4.814	4.850	4.885	4.945	4.987	5.118
	K	4.783	4.814	4.886	4.959	5.035	5.075	5.113	5.180	5.227	5.370
	Rb	4.783	4.815	4.887	4.959	5.034	5.072	5.108	5.167	5.204	5.334
	Cs	4.782	4.813	4.886	4.961	5.038	5.079	5.118	5.187	5.238	5.384
S_e (10^{-10} m)	Li	4.30	4.33	4.41	4.49	4.58	4.62	4.67	4.75	4.80	4.96
	Na	3.63	3.66	3.73	3.79	3.86	3.90	3.94	3.99	4.04	4.17
	K	3.45	3.48	3.56	3.63	3.71	3.74	3.78	3.85	3.90	4.04
	Rb	3.30	3.34	3.41	3.48	3.55	3.59	3.63	3.69	3.72	3.85
	Cs	3.09	3.12	3.20	3.27	3.35	3.39	3.43	3.50	3.55	3.69
ΔG°_t ($\mathrm{J\ mol^{-1}}$)	Li	3002	6051	12796	19851	27421	31512	35715	44172	52327	64814
	Na	3103	6297	13326	20772	28825	33138	37611	46555	55034	67849
	K	3121	6320	13403	20858	28988	33354	37904	46882	55515	68499
	Rb	3108	6244	13355	20864	29071	33610	38378	48026	57504	71327
	Cs	3055	6195	13215	20555	28511	32800	37273	46063	54465	67217

The values of ${}^{W}E_m^\circ$ of cell II have been recently reported [1,2,15] and thus, those of ${}^{S}E_m^\circ$ could be computed in the mixed solvents for cell II containing MX ≡ LiCl, NaCl, KCl, RbCl and CsCl. These are recorded in Table 5. From a knowledge of the computed values of the standard absolute potential of the Ag, AgCl electrode (Table 2) in each solvent, those of Li,Li^+, Na,Na^+, K,K^+, Rb,Rb^+ and Cs,Cs^+ electrodes (${}^{Ox}_{L}E_m^\circ$) could be obtained from ${}^{S}E_m^\circ$ values of cell II containing LiCl, NaCl, KCl, RbCl and CsCl respectively, by using eqn. (2). Thus, the values of ${}^{Ox}_{L}E_m^\circ$ calculated at 25 °C are listed in Table 6. The radius of the solvated cation (r_+) in the standard state can thus be obtained [1,2] in each solvent. The solvation extent (S_e) was calculated as the difference between the r_+ values obtained and the ionic radii of non-solvated ions in the aqueous medium [1,2]. The values of r_+ and S_e are also given in Table 6.

The standard transfer Gibbs free energy of individual cations from water to the respective dioxane–water solvents were computed (Table 6) using eqn. (4). These are accurate to ± 80 J mol^{-1}. Furthermore, by coupling the standard absolute potentials (${}^{Ox}_{L}E_m^\circ$) of M, M^+ (M ≡ Li, Na, K, Rb or Cs) electrodes with those (${}^{Ox}_{R}E_m^\circ$) of Ag, AgX (X ≡ Br or I) electrodes using eqn. (2), the values of E_m° for cell II containing MX electrolytes could be computed. All the E_m° values of cell II in various dioxane–water solvents at 25 °C are collected in Table 5.

Table 6 shows that ${}^{Ox}_{L}E_m^\circ$ values decrease with increasing dioxane content in the solvent. This is reflected by the increasingly positive values of ΔG_t° for cations in the same direction. In any solvent, the irregular order of variation in 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. The values of r_+ and S_e increase with increasing proportion of dioxane in the solvent. As the water content of the solvent decreases, the water molecules in the solvation sheath around the M^+ ion are gradually replaced by dioxane molecules of larger size (compared with those of water). Therefore, the increasing r_+ and thus S_e values were expected. However, the values of r_+ indicate that, so far as any M^+ ion is concerned, water is a weaker solvating agent than the dioxane–water solvents.

The successive substitution of water molecules by the larger-sized dioxane molecules in the solvation sheath, on the gradual addition of dioxane to the solvent, is supported by the very interesting feature seen in Table 6. In any solvent, the extent of solvation (S_e) increases in the expected well-known order, $Cs^+ < Rb^+ < K^+ < Na^+ < Li^+$, and the Li^+ ion is always highly solvated. Similar results were also obtained for the alkali metal ions in the MeOH–water, EG–water, PG–water [1,2] and DMSO–water [15] solvent systems.

An assessment of ΔG_t° for the individual ions is necessary in order to draw meaningful conclusions about these results and hence about ion–solvent interactions in these solvents. The values of ΔG_t° show a qualitative resemblance to other mixed-solvent systems [1,2,15] in that all the values are positive and increase, i.e. ion transfer becomes increasingly less favourable, with rising organic content of the solvent. Now, if the transfer behaviour of the individual ions is compared, for example, with that in MeOH–water solvents [1] at the corresponding solvent compositions, the smaller positive values of ΔG_t° obtained in MeOH–water solvents suggest that the ion affinity of these solvents is greater than that of dioxane–water solvents.

However, the values of ΔG_t° for cations do not follow such a regular order in any solvent (Table 6). If ΔG_t° values for the individual M^+ ions are examined as a function of S_e (i.e. as we proceed from Li^+ through Na^+, K^+ and Rb^+ to Cs^+), the pattern is very similar to that found for transfers from water to MeOH–water [1] and DMSO–water [15] solvent systems. There is a marked rise in ΔG_t° from Li^+ to Na^+ and a fall from Rb^+ to Cs^+ with a maximum (for K^+ in solvents of low dioxane content) that shifts (to Rb^+ in solvents of high dioxane content) as the proportion of dioxane is increased. While the shifting of the maximum to Rb^+ occurs around 90 wt.% MeOH and 50 wt.% DMSO in the MeOH–water and DMSO–water systems respectively, it occurs at a dioxane content as low as 30 wt.% dioxane in the dioxane–water system. Nevertheless, the essential similarity in the profiles of ΔG_t° against S_e points to a common cause for the resulting behaviour of these simple ions in these solvent systems [15].

Solvation characteristics of the solvents and $\Delta(G)_t^\circ$ values

Another important feature noticed in MeOH–water, EG–water, PG–water [1,2] and now in dioxane–water solvent systems, on the one hand, is the increased desolvation of the proton (r_+ values decrease), and on the other hand, the increased solvation of the M^+ ions (r_+ values increase) with increasing amounts of the organic solvent. Thus, if the solvation of ions is concerned, r_+ values should reflect the solvating capacities of the solvent concerned and water towards the ion. The increasing r_+ values for all M^+ ions presumably indicate that the dioxane–water solvents possess greater solvating capacities (which increase with increasing dioxane amounts in the solvent) towards ions than water. The opposite is the case for protons. Nevertheless, both ${}^{Ox}_{L}E_m^\circ$ values for the hydrogen electrode (reversible with respect to H^+ ions) and M, M^+ electrodes (reversible with respect to M^+ ions) decrease with increasing dioxane concentration in the solvent. Thus, as it is apparent from this relationship that if the single electrode potential is largely influenced by the value of a_l°, values of ${}^{Ox}_{L}E_m^\circ$ as well as of ΔG_t° should not reflect the solvating capacities of the solvent concerned and water towards the ion. This may be so because, although r_+ values decrease for protons and increase for M^+ ions, ΔG_t° values for the transfer of a proton or any M^+ ion increase with increasing dioxane content in the solvent. Thus, the increasingly positive values of ΔG_t° for all (H^+ and M^+) ions presumably indicate that there is no relationship between ΔG_t° values and the solvation of ions.

The new method and e.m.f. data of cell II in dioxane–water solvents

Furthermore, the new method [1,2,15] has been applied to the previous E_m° values of Feakins et al. [9] for cell II containing KCl, KBr and KI in the 20 wt.% dioxane–water mixture (the only available data for alkali metal halides in dioxane–water mixtures can be used for our purpose) to verify its use in such media, and to obtain the absolute potentials of M, M^+ and Ag, AgX electrodes in this solvent and also the transfer free energies of the individual ions for comparison with the new values obtained in the present work. However, the least-squares results of applying eqn. (1) to the E_m° values [9] of cell II show that $-\text{corr}\ (10^{-2}) = 100.0000$, Δ (mV) values for KCl, KBr and KI are -0.11, $+0.18$ and -0.07 respectively and a_1° (10^{10} V m^{-1}) $= 1.01193$. The values of r_+, S_e, ${}^{\text{Ox}}_{\text{L}}E_m^\circ$ and ${}^{\text{Ox}}_{\text{R}}E_m^\circ$ (and thus ΔG_t° values for individual ions) are all almost the same as those obtained in the present work, and thus could be interpreted and discussed in the same manner. However, these results lend further support to the validity of our new values and also to the general applicability of the new method and procedure [1,2,15] in dioxane–water solvent mixtures for the determination of absolute electrode potentials as well as transfer free energies of individual ions.

Moreover, Feakins et al. [9] reported that ΔG_t° values should be additive in the values for the ion constituents. That this is really so, in view of eqn. (5), is realized [1,2,15] in several aqueous, non-aqueous, protic and aprotic solvents. The difference, $\Delta G_t^\circ(\text{MX}) - \Delta G_t^\circ(\text{HX})$, which is $\Delta G_t^\circ(\text{M}^+) - \Delta G_t^\circ(\text{H}^+)$, should be constant (within the experimental error) for any M^+ ion and independent of X (X $\equiv$ Cl, Br or I). This reflects the high degree of consistency between the values of ΔG_t° for the halogen acids and those for the alkali metal halides [9].

Feakins procedure and thermodynamics of single ions

Feakins and coworkers [6,9,12,14,18,19,21] assumed that the free energy of transfer (and thus E_m°) is inversely proportional to the radius of the ion which is being varied in a series of electrolytes having a common ion. However, it should be pointed out that this possibility [1,2] for the variation in the reduction potential of any electrode with $1/r_-$ has also been examined in view of the present e.m.f. data of cells I and II in dioxane–water solvents. Again, the results gave the same conclusions as those which have already been obtained in our previous work [1,2,15] in several solvent systems including protic, aprotic, partially aqueous and non-aqueous solvents. The same important and interesting general features [1,2,15] have been apparent again in the present work, and thus provide further strong evidence that the plots of standard e.m.f. and transfer free energy or entropy against the reciprocal of the anionic or cationic radius, used earlier [5–7,9,12,14,18,19,21] to obtain the thermodynamic properties of single ions, cannot be accepted [1,2]. All the results obtained lead to a recognition of the interest, validity and general applicability of our new method [1,2]. Above all, it represents a more exact method for the determination of absolute electrode potentials as well as the thermodynamic properties of individual ions in any solvent without extra thermodynamic assumptions of any type.

ACKNOWLEDGEMENT

The authors are very indebted to Mrs. Laila Abu Elela for encouragement, many helpful suggestions and fruitful discussions.

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