

GIBBS FREE ENERGIES OF TRANSFER OF INDIVIDUAL IONS FROM WATER INTO WATER-UREA MIXTURES

MAHMOUD M. ELSEMONGY *

Chemistry Department, Faculty of Education, Umm Al-Qura University, Al-Taif City, Shihar (Saudi Arabia)

AHMED A. ABDEL-KHALEK

Chemistry Department, Faculty of Science, Cairo University, Beni-Suef City (Egypt)

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ABSTRACT

The use of a new method for the determination of the absolute electrode potentials and the thermodynamics of individual ions in various solvent systems has been extended to solvents of higher dielectric constant than water, formed by adding structure-breaking urea to water. Standard e.m.f. values are reported at 25 °C for the cell: Pt,H₂ (g, 1 atm)/HX (m), water-urea/AgX,Ag, where X=Cl, Br and I, in eight different aqueous solvents containing up to 40 wt.% urea. The standard e.m.f. values were used to determine not only the standard transfer Gibbs free energy ΔG_t° for halogen acids from water into water-urea mixtures but also the standard absolute potentials E° of the hydrogen and the Ag,AgX electrodes in these solvents as well as the values of ΔG_i° for the individual H⁺ and X⁻ ions. These data, together with the reported values of ΔG_i° (MCl), enabled us to evaluate values of E° for the M/M⁺ (M = Li, Na, K, Rb and Cs) electrodes, the radii of the solvated cations and the extent of their solvation in such media, and values of ΔG_i° for the individual M⁺ ions. The results are discussed and compared with those in various aqueous solvent systems.

INTRODUCTION

A new method for the determination of the absolute electrode potential and the thermodynamics of individual ions has been applied [1–4] to e.m.f. data of various cells in different aqueous and non-aqueous solvent systems. Thermodynamic quantities for the transfer of individual ions from water into a water-cosolvent mixture have been determined [1–4] for cosolvents such as methanol, ethanol, propan-2-ol, ethan-1,2-diol, propan-1,2-diol, dimethyl sulphoxide, dioxane and acetone. All these cosolvents decrease the dielectric constant and enhance the structure when added to water [5,6]. In

* To whom correspondence should be addressed.

contrast, when structure-breaking urea [5] is added to water the dielectric constant of the mixture increases. It is of considerable interest, therefore, to determine Gibbs free energies of transfer, ΔG_t° , for H^+ , X^- (where $X = Cl, Br$ and I) and M^+ (where $M = Li, Na, K, Rb$ and Cs) ions and to compare the order of these values in water-urea mixtures with those in other aqueous solvents [1-4]. Thus, in the present paper, the new method [1] is further applied to the e.m.f. data of the cell

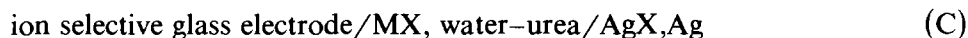


in the aqueous mixtures of urea, on the one hand for verification of its use in such media, on the other hand to obtain standard absolute electrode potentials in each solvent as well as ΔG_t° values for individual ions from water into each solvent. Therefore we have determined the standard e.m.f. (E_m°) values of cell A, where $X = Cl, Br$ and I , in eight different aqueous solvents containing up to 40 wt.% urea, at five intervals, from the e.m.f. measurements at 25°C.

Earlier, E_m° values have been determined for cell A in four aqueous solvents containing 11.52, 20.31, 29.64 and 36.83 wt.% urea for $X = Cl$ by Ahmed and Saleh [7] and for $X = Cl, Br$ and I by Kundu and Mazumdar [8]. Thermodynamic quantities of transfer of alkali metal chlorides from water into these four solvents have been obtained from E° values for the amalgam cell



for $M = Li, Na, K, Rb$ and Cs by Das and Kundu [9], and into solvents containing up to 40 wt.% urea from E° values for the cell



where $X = Cl$, for $M = Rb$ by Smits et al. [10] and for $M = Li, Na, K, Rb$ and Cs by Pointud and Juillard [11]. The latter data [11] have been used in the present work to determine the standard absolute potentials of the M/M^+ electrodes in water-urea mixtures and the values of ΔG_t° for the individual M^+ ions.

EXPERIMENTAL

Urea (analytical reagent, BDH) was used without further purification. Water was first deionized, distilled from alkaline $KMnO_4$, and then distilled twice under a nitrogen atmosphere prior to use. Solvent mixtures of various compositions were made up by weight. All solutions were freshly prepared before taking measurements. The cell design, general experimental procedure and mathematical treatment of the results have been described earlier [7,8,12-14]. Constant e.m.f. readings to ± 0.1 mV for 1 h were taken to be

the criterion of equilibrium in most of the solvents. 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 within ± 0.1 mV. The temperature of the measuring cells was carefully maintained at $25 \pm 0.01^\circ\text{C}$.

RESULTS

The standard e.m.f. of cell A on the molal scale, E_m° , for each water-urea mixture has been determined as before [7,8,12-14] and these values are presented in Table 1. The values of E_m° are accurate to better than ± 0.2 mV. The standard molal Gibbs free energies of transfer, ΔG_t° , of 1 mol of HCl, HBr or HI from water into any mixture, calculated from the E_m° values in water (w) and in the solvent (s) mixture using eqn. (1), are also included in Table 1:

$$\Delta G_t^\circ = F(^w E_m^\circ - ^s E_m^\circ) \quad (1)$$

where F is the faraday and m refers to the molal concentration scale. Since the values of E_m° in water [1] and in the water-urea mixtures are accurate to within ± 0.05 mV and ± 0.2 mV respectively, the values of ΔG_t° are therefore accurate to ± 0.02 kJ mol $^{-1}$. In water-urea mixtures, the agreement is generally good between the new values of $^s E_m^\circ$ or ΔG_t° (Table 1) and those obtained earlier [7,8], since most of the earlier values lie on the same curve showing the variation of $^s E_m^\circ$ or ΔG_t° with solvent composition.

TABLE 1

Values of standard e.m.f., E_m° (V), for cell A in water-urea mixtures, and the standard molal Gibbs free energies (kJ mol $^{-1}$) of transfer of halogen acids from water into these mixtures, at 25°C

Urea (wt.%)	HCl		HBr		HI	
	E_m°	ΔG_t°	E_m°	ΔG_t°	E_m°	ΔG_t°
0	0.22236	0	0.07105	0	-0.15235	0
5	0.2405	-1.75	0.0904	-1.87	-0.1329	-1.88
10	0.2566	-3.31	0.1069	-3.46	-0.1155	-3.56
15	0.2678	-4.38	0.1187	-4.59	-0.1030	-4.77
20	0.2765	-5.22	0.1281	-5.50	-0.0929	-5.74
25	0.2838	-5.93	0.1356	-6.23	-0.0842	-6.58
30	0.2908	-6.60	0.1430	-6.94	-0.0758	-7.39
35	0.2975	-7.25	0.1505	-7.66	-0.0675	-8.19
40	0.3040	-7.87	0.1573	-8.33	-0.0596	-8.95

TABLE 2
The least-squares results of applying eqn. (2) to the E_m° values of cell A in water-urea mixtures at 25 °C

Parameter	Urea (wt.%)									
	0	5	10	15	20	25	30	35	40	99.9993
-Corr (10^{-2})	99.9991	99.9997	99.9996	99.9997	99.9998	99.9995	99.9993	99.9994	99.9993	99.9993
Δ (mV) X = Cl	-0.6	-0.3	-0.4	-0.3	-0.3	-0.4	-0.5	-0.4	-0.5	-0.5
X = Br	+0.9	+0.5	+0.6	+0.5	+0.5	+0.7	+0.8	+0.7	+0.8	+0.8
X = I	-0.4	-0.2	-0.2	-0.2	-0.2	-0.3	-0.3	-0.3	-0.3	-0.3
a° (10^{10} V m $^{-1}$)	1.0701	1.0665	1.0627	1.0589	1.0551	1.0510	1.0468	1.0424	1.0381	1.0381
r_+ (10^{-10} m)	2.017	2.035	2.051	2.063	2.072	2.080	2.087	2.095	2.102	2.102
${}^{\text{ox}}E_s^\circ$ (V) s = m	2.1586	2.1707	2.1798	2.1841	2.1859	2.1858	2.1850	2.1839	2.1825	2.1825
s = c	2.1585	2.1710	2.1805	2.1851	2.1872	2.1875	2.1870	2.1862	2.1852	2.1852
s = x	2.0554	2.0684	2.0785	2.0837	2.0866	2.0876	2.0879	2.0880	2.0878	2.0878
${}^{\text{ox}}E_m^\circ$ (V) X = Cl	1.9368	1.9304	1.9236	1.9166	1.9097	1.9024	1.8947	1.8868	1.8790	1.8790
X = Br	2.0866	2.0798	2.0723	2.0649	2.0574	2.0495	2.0413	2.0327	2.0244	2.0244
X = I	2.3113	2.3037	2.2955	2.2873	2.2789	2.2702	2.2611	2.2516	2.2424	2.2424
ΔG_f° (H^+) _s (kJ mol $^{-1}$) s = m	0	-1.16	-2.05	-2.46	-2.63	-2.62	-2.55	-2.44	-2.31	-2.31
s = c	0	-1.20	-2.11	-2.56	-2.77	-2.79	-2.75	-2.67	-2.57	-2.57
s = x	0	-1.25	-2.23	-2.73	-3.01	-3.10	-3.13	-3.14	-3.12	-3.12
ΔG_f° (X $^-$) (kJ mol $^{-1}$) X = Cl	0	0.62	1.28	1.95	2.62	3.32	4.06	4.83	5.57	5.57
X = Br	0	0.66	1.38	2.10	2.82	3.58	4.38	5.20	6.01	6.01
X = I	0	0.73	1.53	2.32	3.13	3.97	4.85	5.76	6.65	6.65

Absolute electrode potentials and Gibbs free energies

According to the new method [1], the cell e.m.f. is linearly related to the radius of the solvated ion which is being varied in a series of electrolytes having a common ion. Thus, in any water-urea mixture, the plot of the standard e.m.f. (E_m°) values of cell A, containing HCl, HBr and HI, against the radius of the solvated anions (r_-) should yield a straight line according to

$$E_m^\circ = a^\circ r_+ - a^\circ r_- \quad (2)$$

where a° appears to be a universal constant for all electrodes, and depends only on the medium, at any temperature [1-4]. This holds in all water-urea mixtures, and the least-squares results at 25°C are given in Table 2. In all solvents, perfect straight lines were obtained, and the extent of correlation is indicated by the correlation coefficients (corr) and the differences, Δ (mV), between the E_m° values obtained experimentally and those calculated using the equation

$$E_m^\circ = {}_L^{\text{ox}}E_m^\circ - {}_R^{\text{ox}}E_m^\circ \quad (3)$$

where ${}_L^{\text{ox}}E_m^\circ$ and ${}_R^{\text{ox}}E_m^\circ$ are the oxidation potentials of the left and right electrodes respectively [1-4]. Thus the standard absolute potential of the H_2/H^+ and Ag,AgX ($\text{X} = \text{Cl, Br and I}$) electrodes, the radius r_+ of the solvated H^+ ion, in the standard state, have been computed as before [1-4] (Table 2).

The values of the standard Gibbs free energy $\Delta G_i^\circ(i)$ for the transfer of an individual ion from water into water-urea mixtures were computed [1-4] on the molal scale from the standard absolute electrode potentials in water (${}_E^{\text{w}}E_m^\circ$) and in the respective solvents (${}_E^{\text{s}}E_m^\circ$) (Table 2) using the equation

$$\Delta G_i^\circ(i) = F({}_E^{\text{w}}E_m^\circ - {}_E^{\text{s}}E_m^\circ) \quad (4)$$

The values of $\Delta G_i^\circ(i)$, for H^+ , Cl^- , Br^- and I^- ions, so calculated at 25°C are also included in Table 2. These are accurate to better than $\pm 0.05 \text{ kJ mol}^{-1}$.

Standard molal Gibbs free energies of transfer for alkali metal chlorides from water into water-urea mixtures, reported by Pointud and Juillard [11], have been used to compute values for $\Delta G_i^\circ(\text{M}^+)$. For each electrolyte, two series of measurements were made [11]: the first for mixtures containing 5, 15, 25 and 35 wt.% urea, and the second for mixtures containing 10, 20, 30 and 40 wt.% urea. All the data lie on the same curve relating $\Delta G_i^\circ(\text{MCl})$ with solvent composition, and the agreement is within 0.1 kJ mol^{-1} [11]. The values reported [11] for the second series are the best fit values to this curve. Therefore it is very reasonable to interpolate for values of the first series using large-scale plots. Thus, for transfer to the eight water-urea mixtures,

TABLE 3

Standard absolute potentials ($^{\circ}E_m^{\circ}$) of M/M^+ electrodes, radii r_+ of solvated cations and their solvation extent S_c in water-urea mixtures, and standard transfer Gibbs free energies ΔG_t° of individual cations from water into these mixtures, at 25°C

Parameter	M	Urea (wt.%)									
		0	5	10	15	20	25	30	35	40	
$^{\circ}E_m^{\circ}$ (V)	Li	5.2035	5.1975	5.1911	5.1843	5.1770	5.1693	5.1613	5.1529	5.1437	
	Na	4.8720	4.8653	4.8582	4.8506	4.8423	4.8332	4.8238	4.8137	4.8033	
	K	5.0840	5.0769	5.0694	5.0614	5.0527	5.0431	5.0334	5.0226	5.0115	
	Rb	5.0843	5.0775	5.0701	5.0623	5.0536	5.0444	5.0347	5.0243	5.0136	
	Cs	5.0822	5.0774	5.0718	5.0656	5.0585	5.0505	5.0421	5.0329	5.0230	
r_+ (10^{-10} m)	Li	4.863	4.873	4.885	4.896	4.907	4.918	4.931	4.943	4.955	
	Na	4.553	4.562	4.571	4.581	4.590	4.599	4.608	4.618	4.627	
	K	4.751	4.760	4.770	4.780	4.789	4.798	4.808	4.818	4.827	
	Rb	4.751	4.761	4.771	4.781	4.790	4.799	4.810	4.820	4.829	
	Cs	4.749	4.761	4.772	4.784	4.795	4.805	4.817	4.828	4.839	
S_c (10^{-10} m)	Li	4.26	4.27	4.28	4.30	4.31	4.32	4.33	4.34	4.35	
	Na	3.60	3.61	3.62	3.63	3.64	3.65	3.66	3.67	3.68	
	K	3.42	3.43	3.44	3.45	3.46	3.47	3.48	3.49	3.50	
	Rb	3.27	3.28	3.29	3.30	3.31	3.32	3.33	3.34	3.35	
	Cs	3.06	3.07	3.08	3.09	3.10	3.12	3.13	3.14	3.15	
ΔG_t° (kJ mol $^{-1}$)	Li	0	0.58	1.20	1.85	2.56	3.30	4.07	4.88	5.76	
	Na	0	0.64	1.33	2.06	2.86	3.74	4.65	5.62	6.62	
	K	0	0.68	1.41	2.18	3.02	3.94	4.88	5.92	7.00	
	Rb	0	0.66	1.37	2.13	2.96	3.86	4.78	5.79	6.83	
	Cs	0	0.47	1.00	1.60	2.28	3.06	3.86	4.75	5.71	

values for $\Delta G_i^\circ(M^+)$, where $M = \text{Li, Na, K, Rb and Cs}$, are computed [1-4] using

$$\Delta G_i^\circ(\text{MX}) = \Delta G_i^\circ(M^+) - \Delta G_i^\circ(\text{X}^-) \quad (5)$$

where $\text{X} = \text{Cl}$, using values for $\Delta G_i^\circ(\text{Cl}^-)$ in Table 2 derived from the present data. All the values for $\Delta G_i^\circ(M^+)$ on the molal scale are listed in Table 3.

The standard absolute potentials of the M/M^+ (where $M = \text{Li, Na, K, Rb and Cs}$) electrodes in each mixture ${}^s E_m^\circ$ have been evaluated from the values of $\Delta G_i^\circ(M^+)$ (Table 3) using eqn. (4) and the values of ${}^w E_m^\circ$ reported previously [1-4]. The radii r_+ of the solvated cations and their solvation extent S_e , in each mixture, were computed as before [1-4]. All these results are also included in Table 3.

The standard absolute oxidation potential of any electrode, and the value of $\Delta G_i^\circ(i)$ for any individual ion, can be computed on the molar (c) and on the mole fraction (x) scales with the help of the usual relations [4,15]. As examples, the values of ${}^{\text{ox}} E_L^\circ$ for the hydrogen electrode and $\Delta G_i^\circ(\text{H}^+)$ values computed at 25°C are also included in Table 2.

Further, by coupling the standard absolute potentials (${}^{\text{ox}} E_m^\circ$) of M/M^+ electrodes with those (${}^{\text{ox}} E_m^\circ$) of Ag,AgX electrodes, using eqn. (3), the values of E_m° for cell C, containing MX ($M = \text{Li, Na, K, Rb and Cs}$ for $\text{X} = \text{Cl, Br}$

TABLE 4

Values of standard e.m.f., E_m° (V), of cell C in water-urea mixtures at 25°C

MX	Urea (wt.%)								
	0	5	10	15	20	25	30	35	40
LiCl	3.2667	3.2671	3.2675	3.2677	3.2673	3.2669	3.2666	3.2661	3.2647
LiBr	3.1169	3.1177	3.1187	3.1194	3.1196	3.1198	3.1200	3.1201	3.1194
LiI	2.8922	2.8938	2.8956	2.8971	2.8980	2.8991	2.9002	2.9012	2.9014
NaCl	2.9352	2.9349	2.9347	2.9340	2.9327	2.9309	2.9291	2.9269	2.9243
NaBr	2.7854	2.7855	2.7859	2.7857	2.7850	2.7837	2.7825	2.7810	2.7790
NaI	2.5607	2.5616	2.5627	2.5634	2.5634	2.5630	2.5627	2.5621	2.5609
KCl	3.1472	3.1465	3.1458	3.1447	3.1430	3.1408	3.1387	3.1358	3.1324
KBr	2.9974	2.9972	2.9970	2.9965	2.9953	2.9936	2.9921	2.9899	2.9871
KI	2.7726	2.7732	2.7738	2.7741	2.7737	2.7729	2.7723	2.7710	2.7691
RbCl	3.1475	3.1471	3.1466	3.1457	3.1440	3.1420	3.1400	3.1375	3.1345
RbBr	2.9977	2.9978	2.9978	2.9974	2.9963	2.9949	2.9935	2.9916	2.9892
RbI	2.7730	2.7738	2.7746	2.7750	2.7747	2.7742	2.7737	2.7727	2.7712
CsCl	3.1454	3.1469	3.1483	3.1490	3.1489	3.1481	3.1474	3.1461	3.1440
CsBr	2.9956	2.9976	2.9995	3.0007	3.0012	3.0010	3.0009	3.0002	2.9987
CsI	2.7708	2.7736	2.7763	2.7783	2.7796	2.7803	2.7810	2.7813	2.7807

TABLE 5

Standard molal Gibbs free energies (kJ mol^{-1}) of transfer for alkali metal halides from water into water-urea mixtures at 25°C

MX	Urea (wt.%)							
	5	10	15	20	25	30	35	40
LiCl	-0.04	-0.08	-0.10	-0.06	-0.03	0.01	0.06	0.19
LiBr	-0.08	-0.18	-0.25	-0.26	-0.28	-0.30	-0.31	-0.24
LiI	-0.15	-0.33	-0.47	-0.57	-0.67	-0.78	-0.88	-0.89
NaCl	0.03	0.05	0.11	0.24	0.42	0.59	0.80	1.05
NaBr	-0.02	-0.05	-0.04	0.04	0.16	0.28	0.42	0.62
NaI	-0.09	-0.20	-0.26	-0.27	-0.23	-0.20	-0.14	-0.03
KCl	0.06	0.13	0.23	0.40	0.62	0.82	1.09	1.42
KBr	0.02	0.03	0.08	0.20	0.36	0.51	0.72	0.99
KI	-0.06	-0.12	-0.14	-0.11	-0.03	0.03	0.16	0.34
RbCl	0.04	0.09	0.18	0.34	0.53	0.72	0.96	1.25
RbBr	-0.01	-0.01	0.03	0.14	0.27	0.41	0.59	0.82
RbI	-0.08	-0.16	-0.20	-0.17	-0.11	-0.07	0.03	0.17
CsCl	-0.15	-0.28	-0.35	-0.34	-0.27	-0.20	-0.07	0.13
CsBr	-0.20	-0.38	-0.50	-0.54	-0.52	-0.51	-0.45	-0.30
CsI	-0.27	-0.53	-0.72	-0.85	-0.91	-0.99	-1.01	-0.95

and I) electrolytes, could be computed. Thus all the values of E_m° of this cell in water-urea mixtures so computed at 25°C are collected in Table 4.

Furthermore, the values of ΔG_t° for all other alkali metal halides than MCl could be also obtained from the E_m° values of cell C in water and in water-urea mixtures (Table 4) using eqn. (1). These are tabulated in Table 5. For further verification of the accuracy of our calculations, the values of $\Delta G_t^\circ(\text{MX})$ computed from $\Delta G_t^\circ(\text{i})$ values (Tables 2 and 3) using eqn. (5), are exactly the same as those reported in Table 5.

DISCUSSION

The values of E_m° (Table 1) for cell A, containing HCl, HBr or HI in water-urea mixtures, increase monotonically with increasing urea concentration in the solvent, i.e. with increasing dielectric constant of the solvent. Nevertheless, the values of ${}^{\text{ox}}E_m^\circ$ ($X = \text{Cl}, \text{Br}$ or I) decrease, whereas those of ${}^{\text{ox}}E_m^\circ$ increase to a maximum at around 20 wt.% urea and thereafter decrease, with successive addition of urea to the solvent (Table 2). The rates of decreasing a° value and of increasing r_+ value determine the net rate of

variation of $a^\circ r_+$ (i.e. ${}^{\circ}E_m^{\circ}$) with solvent composition. This can explain the maximum observed at around 20 wt.% urea for the absolute potential of the hydrogen electrode (Table 2).

Table 1 shows that as the proportion of urea increases, ΔG_i° values for HCl, HBr and HI become increasingly negative, indicating increased stabilization in the mixed solvents, possibly because of the increased dielectric constant and the increased basicity of the solvents as compared to water. The increasingly negative values of ΔG_i° at any solvent composition, however, are of the order HCl < HBr < HI, which suggests that halide ions are hydrophilic, H^+ solvophilic and that the relative hydrophilicity of X^- increases with increasing radius of X^- .

As expected, it is evident from Table 2 that the values of $\Delta G_i^\circ(X^-)$ are increasingly positive with increasing urea concentration in the solvent, and at any solvent composition, their relative magnitudes are in the order Cl < Br < I. Increasing positive values of $\Delta G_i^\circ(X^-)$ are indicative of stronger affinity of X^- towards water than towards aqueous urea solutions. However, the negative values of $\Delta G_i^\circ(H^+)$, which are fairly small, decrease, pass through a minimum at around 20 wt.% urea and thereafter increase with successive addition of urea. This can explain the initial sharp fall followed by the smaller downward trend in the variation of ΔG_i° for HCl, HBr or HI with solvent composition.

The negative values of $\Delta G_i^\circ(H^+)$ suggest that successive addition of urea imparts increasing basicity to the aqueous solution, with a maximum at around 20 wt.% urea. This is due to the larger proton affinity of urea than of water. This is also in agreement with the reported views [8,16,17] regarding the structure of aqueous urea solutions. Studies on the thermodynamics of ionization of water in aqueous urea solutions [16] show that in the water-rich region (0–15 wt.% urea), urea molecules do not enhance the formation of bulky ice-like structures in water but possibly occupy interstitial spaces between the bulky ice-like species and between dense species of water, forming a regular solution [8,17]. At higher concentrations of urea (15–30 wt.% urea), however, urea–water clusters form, causing a shifting of the bulky/dense water equilibria to the right which is related to structure breaking of water as in Frank and Franks model [17], referred to in various experimental work [8,16,17]. At urea concentrations above 30 wt.%, the urea–water clusters undergo disruption, possibly owing to increasing packing imbalance similar to that observed in higher concentrations of aqueous alcohol solvents [8,16].

As the concentration of urea increases, the radius (r_+) of the solvated H^+ ion increases, i.e. the solvation extent of the protons increases (Table 2). This is similar to that found in the water–dimethyl sulphoxide (DMSO) system [2], but the H^+ ions are more solvated in water–urea than in water–DMSO solvents, i.e. urea is a more basic solvent for H^+ than DMSO. On the contrary, in all other solvent systems [1,3,4], the protons are less solvated in

the aqueous solvents than in water, and much less solvated by increasing cosolvent content in the mixture.

It is evident from Table 3 that, as the concentration of urea increases, the oxidation potentials of the alkali metal electrodes (${}_L^{\text{ox}}E_m^\circ$) decrease, and the radius r_+ of the solvated M^+ ion and thus its solvation extent S_e increase. In any solvent, the irregular order of variation of ${}_L^{\text{ox}}E_m^\circ$ value, 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. In addition, although the observed Gibbs free energy change does not seem to be clearly related to the size of the solvated cation involved, the extent of solvation of these cations increases in the order $\text{Cs}^+ < \text{Rb}^+ < \text{K}^+ < \text{Na}^+ < \text{Li}^+$, and the Li^+ ion is always highly solvated in all solvents. This well-known order of increasing extent of solvation of the alkali metal ions is always found in all solvent systems [1-4].

The values of $\Delta G_t^\circ(M^+)$ are weak but show a qualitative resemblance to other solvent systems [1-4] in that all the values are positive and increase, i.e. ion transfer becomes increasingly unfavourable, by adding urea to the solvent. In any solvent, the relative order of non-spontaneity for the cations is $\text{Li}^+ < \text{Na}^+ < \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$, i.e. there is a marked rise in ΔG_t° from Li^+ through Na^+ to K^+ and thereafter a fall from K^+ through Rb^+ to Cs^+ with a maximum for K^+ , at least in this range of solvent composition studied. This pattern is similar to that found for transfers from water into several solvent systems [1-4].

As found earlier [4], whatever the concentration scale (molal, molar or mole fraction) used, the same general trend of variation of standard absolute electrode potential or standard Gibbs free energy for the transfer of an individual ion with solvent composition is noticed. The maximum in the hydrogen electrode potential and the minimum in the negative $\Delta G_t^\circ(\text{H}^+)$ values are displaced from 20 wt.% urea on the molal scale to 25 or 35 wt.% urea for the values computed on the molar or the mole fraction scales respectively (Table 2).

Increased solvation of both H^+ and M^+ ions (r_+ value increases), with increasing amounts of urea in the solvent, is noticed. Nevertheless, the values of $\Delta G_t^\circ(i)$ for these ions show different trends with solvent composition. This presumably indicates, and proves again [3,4], that there is no relationship between ΔG_t° values and the solvation of ions.

Generally, the values of $\Delta G_t^\circ(i)$ for all individual ions, obtained in the present work in water-urea mixtures, are all relatively small compared to those found in other solvent systems [1-4]. Although values of ΔG_t° for M^+ and X^- ions show the same general trend in the variation with solvent composition as found earlier [1-4], those for the proton, $\Delta G_t^\circ(\text{H}^+)$, reflect clearly the different nature of the solvents of higher dielectric constant than water, formed by adding structure-breaking urea to water.

The trend in the variation of E_m° values for cell C containing MX

electrolytes (Table 4), is reflected in that of $\Delta G_i^\circ(\text{MX})$ values (Table 5), with solvent composition. Table 5 shows that $\Delta G_i^\circ(\text{MX})$ values of transfer, whether positive or negative, are very weak, but always significant. The value of ΔG_i° increases positively for NaCl, KCl, KBr and RbCl, decreases and passes through minima and thereafter increases for LiCl, LiBr, NaBr, NaI, KI, RbBr, RbI, CsCl, CsBr and CsI, or decreases negatively for LiI. These features can be explained in view of eqn. (5) where the value of ΔG_i° for any electrolyte is equal to the difference between those for positive and negative ions, which are very close to each other (Tables 2 and 3) leading to relatively small positive or negative values for $\Delta G_i^\circ(\text{MX})$. The net rate of variation of ΔG_i° is thus determined by the difference between the rates of variation of two positive values with increasing urea concentration in the solvent.

The transfer behaviour of electrolytes is generally dictated by the relative magnitudes of $\Delta G_i^\circ(i)$ of the oppositely charged ions. This is also responsible for the observed difference in the transfer behaviour of HX and MX into urea–water mixtures; this difference is associated with the affinity of H^+ ions towards water–urea mixtures compared to that of M^+ ions towards water (Tables 2 and 3).

The new method and previous data in water–urea mixtures

The new method for the determination of absolute electrode potential, as well as transfer free energies of individual ions, has also been applied to previous E_m° data for the halogen acids in water–urea mixtures containing 11.52, 20.31, 29.64 and 36.83 wt.% urea, reported by Kundu and Mazumdar [8]. Using the data of Das and Kundu [9] for alkali metal chlorides in the same four solvents, ${}^{\text{ox}}E_m^\circ$ values for the M/M^+ electrodes, the radii of solvated cations and the extent of their solvation and $\Delta G_i^\circ(\text{M}^+)$ values have been computed. Further, the data of Smits et al. [10] for RbCl in water–urea mixtures have been used, together with the present data in Table 2, to evaluate ${}^{\text{ox}}E_m^\circ$, r_+ , S_e and ΔG_i° values for Rb^+ . In all cases, all the results (not included to save space) show the same general features and trends observed in the present work, leading to the same conclusions. Thus the whole of the obtained results in water–urea mixtures, lend another proof and extra confidence to the general applicability of the new method [1–4] applied to the e.m.f. data of cells in media of higher dielectric constant than that of water, and hence, more reliability in the evaluated data.

Other $\Delta G_i^\circ(i)$ values for single ions

Wells and coworkers [5,6] determined the free energy of transfer for the proton from water into water-rich mixtures of several cosolvents by the spectrophotometric solvent-sorting method using trace additions of 4-

nitroaniline. For the water–urea mixtures [5], the same broad dispersion of values for $\Delta G_i^\circ(i)$ has been found, generally comparable with the distribution found in aqueous mixtures with a dielectric constant less than that of water: $\Delta G_i^\circ(i)$ is negative for cations and positive for anions [5,6]. The values obtained by Wells and coworkers [5] for ΔG_i° decrease monotonically for H^+ , decrease to minima and thereafter increase for Li^+ , Na^+ , K^+ , Rb^+ and Cs^+ , and increase to maxima and thereafter decrease for Cl^- , Br^- and I^- ; the extrema are at around 20 wt.% urea. However, Blandamer et al. [18] examined the method used by Wells and coworkers [5,6]; they show that the treatment is in error, and advance reasons for rejecting the estimates offered by Wells and coworkers [5,6] for single-ion transfer parameters. In addition, we have also reported [4] some other comments on the procedure of Wells and coworkers [5,6].

Kundu and Mazumdar [8] determined $\Delta G_i^\circ(i)$ values for the individual H^+ and X^- ions by the method of simultaneous extrapolation. Their values for $\Delta G_i^\circ(H^+)$ are negative and decrease monotonically, whereas those for $\Delta G_i^\circ(X^-)$ are positive and increase monotonically also, as the proportion of urea increases. However, this method, which depends on $1/r$ relationships, has recently been criticized and proved to be unacceptable [2,3].

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