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STANDARD ABSOLUTE POTENTIALS OF M; M^+ AND Ag, AgX; X^- ELECTRODES IN ETHYLENE GLYCOL + WATER SOLVENTS AND RELATED TRANSFER FREE ENERGIES

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ABSTRACT

From EMF measurements performed on the double cell Ag, AgX; MX (m), S; M (Hg); MX (m), W; AgX, Ag, the standard absolute potentials of M; M^+ (M = Li, Na and K) and Ag, AgX (X = Cl, Br and I) electrodes in ethylene glycol and its aqueous mixtures over the full composition range of the solvent, have been determined at 25°C by a new procedure. The radii of solvated cations and their solvation extent in these media have been computed. The standard Gibbs energies of transfer, ΔG_t^0, of alkali-metal halides from water to the glycolic solvents have been obtained from the EMF data. The individual ionic contributions to ΔG_t^0 have also been evaluated, employing a recent method without any extra-thermodynamic assumptions. The observed increase in ΔG_t^0 values of the alkali-metal M^+ or halide X^- ions with increasing concentration of glycol and their relative order in any solvent has been discussed and analyzed with respect to ion solvation.

INTRODUCTION

Kundu et al. [1] determined the standard potentials (E_m^0) of M; M^+ (M = Li, Na and K) electrodes in ethylene glycol (EG) and its aqueous mixtures (containing 30, 50, 70 and 90 wt.% EG) from EMF measurements at 25°C of the cell

$$\text{M (Hg); MBr (m), solvent; AgBr, Ag} \tag{A}$$

at different molalities (m) of HBr in each solvent, and of the cell

$$\text{M (Hg); MBr (m), water; AgBr, Ag} \tag{B}$$

at $m = 0.10$, 0.20 and 0.50 mol kg^{-1} in water, using an amalgam of the same

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composition as for cell (A). The activities of the amalgams used were evaluated from the EMF's of cell (B), the E_m^0 values of M; M^+ and Ag, AgBr electrodes in water, and the activity coefficients at the respective concentrations of MBr in water [1]. These values were utilized to compute the EMF's of the cell

M; MX, solvent; AgX, Ag (C)

where X = Br. The $(E_m^0)_{M;M^+}$ values in each solvent were computed from those of cell (C), using the reported E_m^0 values of the Ag, AgBr electrode in the respective solvents. As reported [1], the maximum probable uncertainty involved in the values of $(E_m^0)_{M;M^+}$ is of the order of ± 1.5 mV, since the mean uncertainty involved in the determination of the activity of amalgams corresponds to an error of the order of ± 1 mV. This is expected in view of a long series of calculations; each step provides an error which may increase more and much more in following steps.

In the present investigation, in view of recent technical developments with the amalgam electrodes and their use in EMF measurements [2–6] to get more accurate results, the standard EMF's (ΔE_m^0) of the double cell

Ag, AgX; MX (m), S; M (Hg); MX (m), W; AgX, Ag (D)

have been determined at 25°C by the procedure adopted recently [3–7], a method which is generally recognized as being the most reliable one [3,4]. In cell (D), M = Li, Na and K for X = Cl and M = K for X = Br and I, where *m* varies from 0.02 to 0.20 mol kg^{-1}.

The overall spontaneous cell reaction is the transfer of 1 mole of the alkali-metal halide from the glycolic solvent (s) to water (w). Thus, from ΔE_m^0 values, Gibbs energies of transfer (ΔG_t^0) of MX from water to the appropriate solvent can be computed. Moreover, in order to draw meaningful conclusions about these results and hence about ion–solvent interactions in these solvents, dissection of ΔG_t^0 of the electrolytes to individual ion contribution is necessary. We have, therefore, estimated ΔG_t^0 values by employing the recent method developed by Elsemongy [8]. It has the advantage that it does not involve any extra-thermodynamic assumptions. Very recently, it has been proved to be applicable in all solvents of any composition [9]. Thus, a new procedure [8,9] has been used to determine the standard absolute potentials of M; M^+ and Ag, AgX electrodes in EG + water solvents.

EXPERIMENTAL

EG (A.R., Merck) was further purified by the method described earlier [1]. Deionized water was distilled from alkaline $KMnO_4$ and redistilled before use. Solvents were prepared by mixing EG and water in the required proportions by weight. The salts, LiCl, NaCl, KCl, KBr and KI (all G.R., Merck), were used after drying at 200–300°C and cooling in a vacuum desiccator over silica gel. Required sets of solutions in each solvent were prepared by mass dilution from a stock solution prepared from weighed amounts of salt and solvent. For the highly hygroscopic LiCl, owing to weighing under nitrogen, the concentrations of the stock solution, which was used in the preparation of cell solutions, were determined by potentiometric titration with a standard $AgNO_3$ solution.

The Ag, AgCl electrodes were of thermal electrolytic type whereas the Ag, AgBr and Ag, AgI electrodes were of thermal type [4]. Electrodes having bias potential 0.1 mV were used. Alkali-metal amalgams were prepared and pretreated as before [1,10]. The experimental set-up comprised two cell vessels [1,5a,10], one containing a solution in water and the other an equimolal solution in the glycolic solvent, with the cylindrical amalgam reservoir working as the dropping amalgam electrode [1,10]. The whole assembly was maintained at 25 ± 0.05°C. A K-4 (Leeds and Northrup) potentiometer and a moving coil galvanometer (Cambridge Instrument Co.) were used for measurements. In all other experimental details, previous techniques and procedures were followed [1,5,10].

RESULTS AND DISCUSSION

The observed EMF values (ΔE) of cell (D), for different molalities (m) of MX in different solvents, were analyzed in the way previously described [4,5,7] for amalgam cells to yield ΔE_m^0 values. These are given in Table 1. The values of ΔE_m^0 are correct to better than ± 0.2, ± 0.3, ± 0.4 and ± 0.5 mV for solvents containing up to 30, 60, 80 and 100% EG, respectively.

The standard free energy change ΔG_t^0, accompanying the transfer process MX (w) $\rightarrow$ MX (s), has been computed from eqn. (1). The values of ΔG_t^0(MX) so calculated at 25°C, on the molal scale, are also included in Table 1.

$$\Delta G_t^0(\mathrm{MX}) = F \Delta E_m^0 \qquad (1)$$

The average uncertainties being about ± 0.02, ± 0.03, ± 0.04 and ± 0.05 kJ mol^{-1} for solvents containing up to 30, 60, 80 and 100% EG, respectively.

A new procedure [8] has been followed in order to obtain the standard absolute potential of M; M^+ and Ag, AgX electrodes in these solvents, as well as the individual ionic contributions to ΔG_t^0 (Tables 2 and 3, without any extra-thermodynamic assumption. This procedure depends on the fact that there are generally two possibilities (I and II) for the variation of the electrode potential with the radius of the solvated ion, r, on whose activity the potential depends, i.e., either the oxidation potential varies directly with r (case I), or the reduction potential varies inversely with r (case II).

TABLE 1

Values of ΔE^0 (V) of cell (D) and ΔG_t^0 (kJ mol^{-1}) of MX in ethylene glycol + water solvents at 25°C

Wt.% glycol	LiCl	NaCl	KCl	KBr	KI
ΔE^0 values					
10	0.0076	0.0072	0.0088	0.0076	0.0044
20	0.0164	0.0156	0.0173	0.0141	0.0086
30	0.0261	0.0248	0.0270	0.0222	0.0136
40	0.0366	0.0348	0.0370	0.0310	0.0193
50	0.0492	0.0457	0.0486	0.0411	0.0266
60	0.0643	0.0593	0.0606	0.0518	0.0339
70	0.0835	0.0727	0.0756	0.0626	0.0396
80	0.1009	0.0864	0.0875	0.0735	0.0449
90	0.1228	0.1041	0.1076	0.0857	0.0565
100	0.1462	0.1245	0.1258	0.1002	0.0672
ΔG_t^0 values					
10	0.73	0.69	0.85	0.73	0.42
20	1.58	1.51	1.67	1.36	0.83
30	2.52	2.39	2.61	2.14	1.31
40	3.53	3.36	3.57	2.99	1.86
50	4.75	4.41	4.69	3.97	2.57
60	6.20	5.72	5.85	5.00	3.27
70	8.06	7.01	7.29	6.04	3.82
80	9.74	8.34	8.44	7.09	4.33
90	11.85	10.04	10.38	8.27	5.45
100	14.11	12.01	12.14	9.67	6.48

Therefore, the standard EMF (E_m^0) of a cell, which is the difference between two oxidation or reduction potentials, is given as either

$$E_m^0 = {}^{\mathrm{Ox}}_{\mathrm{L}}E_m^0 - {}^{\mathrm{Ox}}_{\mathrm{R}}E_m^0 = a_1^0 r_+ - a_1^0 r_- \tag{2-I}$$

or,

$$E_m^0 = {}^{\mathrm{Red}}_{\mathrm{R}}E_m^0 - {}^{\mathrm{Red}}_{\mathrm{L}}E_m^0 = a_2^0/r_- - a_2^0/r_+ \tag{2-II}$$

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

The value of ΔE_m^0 (given in Table 1) is the difference between the E_m^0 values of cell (C) in water and in the respective glycolic solvent, i.e.,

$$\Delta E_m^0 = {}^{\mathrm{w}}E_m^0 - {}^{\mathrm{s}}E_m^0 \tag{3}$$

The values of ${}^{\mathrm{w}}E_m^0$ of cell (C) have been recently obtained [8], and thus, those of ${}^{\mathrm{s}}E_m^0$ could be calculated in the respective glycolic solvents for cell (C) containing MX = LiCl, NaCl, KCl, KBr or KI (Table 4). Therefore, accord-

TABLE 2

Absolute electrode potential, radius of solvated cation and extent of solvation in ethylene glycol + water solvents and transfer free energies ΔG_t^0 (kJ mol^{-1}), of individual ions from water to these solvents, at 25 °C, all calculated by method I

	Wt.% glycol =	10	20	30	40	50	60	70	80	90	100
$-$Corr (10^{-2})		99.9998	100.0000	99.9999	99.9994	99.9991	99.9980	99.9989	99.9943	99.9985	99.9970
a_1^0 (10^{10} V m^{-1})		1.0573	1.0450	1.0315	1.0191	1.0067	0.9930	0.9666	0.9470	0.9246	0.9032
r_+ (10^{-10} m)	M = Li	4.893	4.920	4.952	4.980	5.006	5.035	5.103	5.153	5.210	5.265
	Na	4.579	4.604	4.632	4.656	4.680	4.706	4.771	4.818	4.872	4.922
	K	4.778	4.805	4.835	4.862	4.887	4.918	4.987	5.040	5.098	5.156
S_e (10^{-10} m)	M = Li	4.29	4.32	4.35	4.38	4.41	4.44	4.50	4.55	4.61	4.66
	Na	3.63	3.65	3.68	3.71	3.73	3.76	3.82	3.87	3.92	3.97
	K	3.45	3.47	3.50	3.53	3.56	3.59	3.66	3.71	3.77	3.83
${}^{\text{Ox}}_{\text{L}}E_m^0$ (V)	M = Li	5.1727	5.1418	5.1076	5.0747	5.0396	4.9996	4.9328	4.8799	4.8175	4.7553
	Na	4.8416	4.8110	4.7773	4.7450	4.7116	4.6731	4.6121	4.5629	4.5046	4.4455
	K	5.0518	5.0213	4.9869	4.9543	4.9202	4.8831	4.8206	4.7726	4.7137	4.6570
${}^{\text{Ox}}_{\text{R}}E_m^0$ (V)	X = Cl	1.9136	1.8915	1.8669	1.8445	1.8221	1.7973	1.7496	1.7141	1.6735	1.6348
	Br	2.0616	2.0378	2.0114	1.9872	1.9631	1.9363	1.8849	1.8467	1.8030	1.7613
	I	2.2837	2.2572	2.2280	2.2012	2.1745	2.1448	2.0879	2.0455	1.9971	1.9509
$\Delta G_t^0(+)_m$	M = Li	2.939	5.922	9.220	12.395	15.777	19.635	26.087	31.191	37.211	43.208
	Na	2.899	5.848	9.102	12.223	15.440	19.155	25.041	29.790	35.412	41.121
	K	3.065	6.014	9.326	12.471	15.761	19.342	25.372	30.009	35.687	41.155
$\Delta G_t^0(-)_m$	X = Cl	2.200	4.339	6.704	8.866	11.027	13.428	18.028	21.453	25.365	29.101
	Br	2.371	4.675	7.223	9.552	11.880	14.466	19.423	23.113	27.327	31.352
	I	2.626	5.177	8.000	10.580	13.160	16.024	21.515	25.601	30.270	34.729

TABLE 3

Absolute electrode potential, radius of solvated cation and extent of solvation in ethylene glycol + water solvents, and transfer free energies, ΔG_t^0 (kJ mol^{-1}), of individual ions from water to these solvents, at 25 °C, all calculated by method II

	Wt.% glycol =	10	20	30	40	50	60	70	80	90	100
Corr (10^{-2})		99.8867	99.8826	99.8869	99.8948	99.8982	99.9069	99.9005	99.9244	99.8517	99.8370
a_2^0 (10^{-10} V m)		4.1471	4.0992	4.0462	3.9976	3.9492	3.8961	3.7923	3.7169	3.6255	3.5420
r_+ (10^{-10} m)	M = Li	4.285	4.159	4.026	3.913	3.814	3.711	3.485	3.342	3.178	3.044
	Na	6.512	6.259	5.995	5.779	5.581	5.386	4.942	4.674	4.378	4.149
	K	4.863	4.707	4.545	4.408	4.284	4.150	3.865	3.679	3.478	3.309
S_e (10^{-10} m)	M = Li	4.88	3.56	3.43	3.31	3.21	3.11	2.89	2.74	2.58	2.44
	Na	5.56	5.31	5.05	4.83	4.63	4.44	3.99	3.72	3.43	3.20
	K	3.53	3.38	3.22	3.08	2.95	2.82	2.53	2.35	2.15	1.98
$-{}^{\mathrm{Red}}_{\mathrm{L}}E_m^0$ (V)	M = Li	0.9679	0.9856	1.0051	1.0215	1.0356	1.0499	1.0880	1.1123	1.1409	1.1636
	Na	0.6368	0.6549	0.6749	0.6918	0.7076	0.7234	0.7673	0.7953	0.8281	0.8538
	K	0.8529	0.8709	0.8902	0.9069	0.9218	0.9389	0.9813	1.0103	1.0423	1.0703
${}^{\mathrm{Red}}_{\mathrm{R}}E_m^0$ (V)	X = Cl	2.2912	2.2647	2.2355	2.2086	2.1819	2.1525	2.0952	2.0535	2.0030	1.9569
	Br	2.1267	2.1021	2.0750	2.0501	2.0253	1.9980	1.9448	1.9061	1.8592	1.8164
	I	1.9200	1.8978	1.8733	1.8508	1.8284	1.8037	1.7557	1.7208	1.6785	1.6398
$\Delta G_t^0(+)_m$	M = Li	1.920	3.628	5.509	7.092	8.452	9.832	13.508	15.852	18.612	20.802
	Na	1.959	3.705	5.635	7.265	8.790	10.314	14.550	17.251	20.416	22.896
	K	1.785	3.522	5.384	6.995	8.433	10.083	14.174	16.972	20.059	22.761
$\Delta G_t^0(-)_m$	X = Cl	2.653	5.210	8.028	10.623	13.199	16.036	21.564	25.588	30.460	34.908
	Br	2.470	4.844	7.458	9.861	12.254	14.888	20.021	23.754	28.280	32.409
	I	2.219	4.361	6.725	8.896	11.057	13.440	18.072	21.439	25.520	29.254

TABLE 4

Values of E_m^0 (V) of cell (C) in ethylene glycol + water solvents at 25 °C and previously reported [1] values, for comparison

Wt.% glycol	M = Li			M = Na			M = K		
	X = Cl	X = Br	X = I	X = Cl	X = Br	X = I	X = Cl	X = Br	X = I
0	3.2667	3.1169	2.8923	2.9352	2.7854	2.5608	3.1472	2.9974	2.7727
10	3.2591	3.1110	2.8890	2.9280	2.7800	2.5580	3.1384	2.9898	2.7683
20	3.2503	3.1040	2.8846	2.9196	2.7733	2.5538	3.1299	2.9833	2.7641
30	3.2406	3.0962	2.8796	2.9104	2.7660	2.5494	3.1202	2.9752	2.7591
Ref. 1	3.239	3.095	2.879	2.910	2.766	2.550	3.119	2.975	2.759
40	3.2301	3.0875	2.8735	2.9004	2.7578	2.5438	3.1102	2.9664	2.7534
50	3.2175	3.0766	2.8651	2.8895	2.7486	2.5371	3.0986	2.9563	2.7461
Ref. 1	3.217	3.076	2.865	2.889	2.748	2.537	3.098	2.957	2.746
60	3.2024	3.0634	2.8548	2.8759	2.7369	2.5283	3.0866	2.9456	2.7388
70	3.1832	3.0479	2.8449	2.8625	2.7272	2.5242	3.0716	2.9348	2.7331
Ref. 1	3.183	3.047	2.845	2.864	2.728	2.526	3.070	2.934	2.732
80	3.1658	3.0332	2.8343	2.8488	2.7163	2.5174	3.0597	2.9239	2.7278
90	3.1439	3.0145	2.8203	2.8311	2.7017	2.5075	3.0396	2.9117	2.7162
Ref. 1	3.144	3.014	2.826	2.835	2.705	2.517	3.044	2.914	2.726
100	3.1205	2.9941	2.8044	2.8107	2.6842	2.4945	3.0214	2.8972	2.7055
Ref. 1	3.121	2.996	2.804	2.811	2.686	2.494	3.022	2.897	2.705

ing to eqns. (2-I) and (2-II), the plot of E_m^0 of cell (C), containing KCl, KBr and KI, against r_- (method I) or against $1/r_-$ (method II) gave practically perfect straight lines, in each solvent. The least-squares results of applying eqns. (2-I) and (2-II) to the E_m^0 values of cell (C) in EG + water solvents at 25 °C, are summarized in Tables 2 and 3, respectively. Thus as before [8], the standard absolute potential of the K; K^+ (${}_{\mathrm{L}}E_m^0$) and Ag, AgX (${}_{\mathrm{R}}E_m^0$) electrodes, the radius of the solvated K^+ ion (r_+) and thus its solvation extent (S_e), in the standard state, have been computed by both methods I and II. As expected [8], different values based on different, oxidation or reduction, potential scales are obtained. Of course, only one set of the data should be credited. So, we will go on through the present data, taking into account the results of calculations by both methods (I and II), in order to decide which set must be considered and credited.

Now, from the knowledge of the values of the standard absolute potential of the Ag, AgCl electrode in each solvent, those of Li; Li^+ and Na; Na^+ electrodes could be obtained from the E_m^0 values of cell (C) containing LiCl and NaCl, respectively. Thus, the radii of the solvated cations (Li^+ and Na^+ ions) and their solvation extent as well as the individual ionic contributions to ΔG_t^0 values of electrolytes, for each solvent, were calculated as before [8]. These are also included in Tables 2 and 3.

Inspection of Tables 2 and 3 reveals the following results:

(1) In all solvents, eqn. (2-I) fits better than eqn. (2-II), as indicated from the correlation coefficients (corr).

(2) The radii of the solvated cations (r_+) and thus the solvation extent (S_e), calculated by method I increase, whereas those by method II decrease, with increasing the EG content 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 the more polar glycol molecules (since the dipole moment of EG is larger than that of water [1]) of larger size (compared to that of water). Therefore, the increasing r_+ and thus S_e values, obtained by method I, were expected. The successive substitution of water dipoles by the larger sized glycol dipoles in the solvation sheath, on gradual addition of glycol to the solvent, is supported by the very interesting feature seen in Table 2. In any solvent, the extent of solvation (S_e) increases in the expected well-known order; $K^+ < Na^+ < Li^+$, and the Li^+ ion is always highly solvated. On the other hand, results of method II (Table 3) show that the expected order of increasing solvation, in any solvent, is inverted for Li^+ and Na^+ ions. As it is well known [11,12], this is not the case. Thus, this interesting feature, again [8,9], gave further evidence for the validity and general applicability of method I and, at the same time, shed more light on the inapplicability of method II for such calculations. Similar results have been obtained for the alkali-metal ions, Li^+, Na^+, K^+, Rb^+ and Cs^+, in methanol + water solvents [8]. Therefore, the set of data obtained from method I calculations (Table 2) and their results should be credited.

(3) The values of standard absolute electrode potentials are all collected in Tables 2 and 3. As the EG content of the solvent increases, the oxidation potentials of both left and right electrodes, ${}^{\mathrm{Ox}}_{\mathrm{L}}E^0_m$ and ${}^{\mathrm{Ox}}_{\mathrm{R}}E^0_m$, respectively, decrease (as indicated by the results of method I, Table 2), whereas the reduction potentials (computed by method II, Table 3) decrease positively for the right electrode and negatively for the left one.

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

By coupling the standard absolute potentials of M; M^+ (M = Li or Na) with Ag, AgX (X = Br or I) electrodes, the values of E^0_m for cell (C) containing MX (LiBr, LiI, NaBr or NaI) electrolytes were also computed at 25 °C. Thus, all values of E^0_m of cell (C) in various EG + water solvents are collected in Table 4, together with the previously reported data [1], for comparison. However, good agreement is noticed in several places. In view of the more accurate results of our EMF measurements, the new values of E^0_m should be preferred.

Kundu et al. [1] computed the standard potentials of M; M^+ electrodes, in each solvent, from values of E_m^0 of cell (C) using their reported E_m^0 values of Ag, AgBr electrode in the respective solvent. Their calculated $E^0_{\mathrm{M;M^+}}$ values decrease to minima at around 70% EG, and thereafter increase with increasing EG content in the solvent [1]. Such calculations cannot be accepted. It is impractical to calculate, or to compare, $E^0_{\mathrm{M;M^+}}$ values in different EG + water solvents in this manner, because such values were calculated on the basis that all refer to the same zero reference point of standard hydrogen electrode potential in all the solvents, which is not the case [8]. Now, it is evident that the standard hydrogen electrode potential is not zero either at all temperatures or in all solvents [8]. Thus, it is not convenient to compare electrode potentials on the hydrogen potential scale, in different solvents nor in different compositions of the same solvent system. The comparison should be made between the absolute electrode potentials or between the E_m^0 values of cells, where the value of the reference potential is cancelled. This fact is reflected by the decreasing E_m^0 values of cell (C) containing any electrolyte, as indicated by the data of Kundu et al. [1] as well as our new data (Table 4), and also by our standard absolute electrode potentials (Tables 2 and 3), which decrease directly with increasing EG concentration in the solvent.

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The increasingly positive ΔG_t^0 values of alkali-metal halides (Tables 1 and 5) indicate that the dissolutions of these salts are not favored by addition of EG to water. This behavior is of course the combined effects of decreased dielectric constants and the overall interactions of the cations and anions with the glycolic solvents relative to that with water. However, the individual ionic contributions to total ΔG_t^0 values are naturally more convenient for interpretation in terms of solvation characteristics of the solvents. These are computed, as before [8], and included in Tables 2 and 3.

It is evident [8] that the standard Gibbs free energy of transfer, $\Delta G_t^0(\mathrm{MX})$, is given, according to methods I and II, by

$$\Delta G_t^0(\mathrm{MX}) = \Delta G_t^0(\mathrm{M^+}) - \Delta G_t^0(\mathrm{X^-}) \tag{4-I}$$

or,

$$\Delta G_t^0(\mathrm{MX}) = \Delta G_t^0(\mathrm{X^-}) - \Delta G_t^0(\mathrm{M^+}) \tag{4-II}$$

where $\Delta G_t^0(\mathrm{M^+})$ and $\Delta G_t^0(\mathrm{X^-})$ are the standard Gibbs transfer free energies, on the molal scale, of M^+ and X^- ions, respectively [8].

However, it should be pointed out that whatever the method of calculation used (I or II), the same value of standard Gibbs transfer free energy, $\Delta G_t^0(\mathrm{MX})$, or cell EMF ($E_m^0$), is always obtained. This important fact can be

TABLE 5

Values of ΔG_t^0 (kJ mol^{-1}) of MX in ethylene glycol + water solvents at 25 °C, calculated by methods I and II

Wt.% glycol	Method	LiCl	LiBr	LiI	NaCl	NaBr	NaI	KCl	KBr	KI
10	I	0.739	0.568	0.313	0.699	0.528	0.273	0.865	0.694	0.439
	II	0.733	0.550	0.299	0.694	0.511	0.260	0.868	0.685	0.434
20	I	1.583	1.247	0.745	1.509	1.173	0.671	1.675	1.339	0.837
	II	1.582	1.216	0.733	1.505	1.139	0.656	1.688	1.322	0.839
30	I	2.516	1.997	1.220	2.398	1.879	1.102	2.622	2.103	1.326
	II	2.519	1.949	1.216	2.393	1.823	1.090	2.644	2.074	1.341
40	I	3.529	2.843	1.815	3.357	2.671	1.643	3.605	2.919	1.891
	II	3.531	2.769	1.804	3.358	2.596	1.631	3.628	2.866	1.901
50	I	4.750	3.897	2.617	4.413	3.560	2.280	4.734	3.881	2.601
	II	4.747	3.802	2.605	4.409	3.464	2.267	4.766	3.821	2.624
60	I	6.207	5.169	3.611	5.727	4.689	3.131	5.914	4.876	3.318
	II	6.204	5.056	3.608	5.722	4.574	3.126	5.953	4.805	3.357
70	I	8.059	6.664	4.572	7.013	5.618	3.526	7.344	5.949	3.857
	II	8.056	6.513	4.564	7.014	5.471	3.522	7.390	5.847	3.898
80	I	9.738	8.078	5.590	8.337	6.677	4.189	8.556	6.896	4.408
	II	9.736	7.902	5.587	8.337	6.503	4.188	8.616	6.782	4.467
90	I	11.846	9.884	6.941	10.047	8.085	5.142	10.322	8.360	5.417
	II	11.848	9.668	6.908	10.044	7.864	5.104	10.401	8.221	5.461
100	I	14.107	11.856	8.479	12.020	9.769	6.392	12.054	9.803	6.426
	II	14.106	11.607	8.452	12.012	9.513	6.358	12.147	9.648	6.493

noticed in Tables 2–5, where the calculated values of ΔG_t^0(MX), or E_m^0 of cell (C), from the corresponding individual values of methods I or II, agree very well within the experimental errors. This also supports the reliability of the calculations (see Table 5).

Although the transfer free energies calculated by method I are based on the oxidation potential scale, whereas those calculated by method II are based on the reduction potential scale, the transfer free energies of ions from water to glycolic solvents show the same trend, with increasing glycol concentration in the solvent. Tables 2 and 3 show that the values of ΔG_t^0 of all ions are increasingly positive indicating that the transfer of the cations or anions is increasingly non-spontaneous. For the alkali-metal M^+ ions, the relative order of non-spontaneity, in water-rich solvents, is $Na^+ < Li^+ < K^+$, whereas that in EG-rich solvents is $Na^+ < K^+ < Li^+$, as dictated by results of method I (Table 2). On the other hand, those of method II (Table 3) show the reversed indicated orders in water- and EG-rich solvents. In all cases, it appears that the position of the Li^+ ion is anomalous. The apparent anomaly in the position of Li^+ ion in glycolic solvents, however, may be associated partly with the larger contribution of a Born-type electrostatic effect [12] and partly with the decreased ion–dipole interaction resulting from the steric inhibition experienced by the larger sized glycol dipoles in solvating the smaller sized Li^+ ion, compared to that in water [1]. Such irregular orders have been observed earlier [1,4,7] in other aquo–organic solvents. On the other hand, for the halide ions, the relative order of non-spontaneity, in any solvent, is $Cl^- < Br^- < I^-$ as obtained from results of method I; whereas this order is reversed as dictated by those of method II.

The results of method I show that the non-spontaneity of the transfer of the alkali-metal cations or halide ions to any solvent increases with increasing ionic size, as indicated from the radii of the solvated cations (r_+ values in Table 2), whereas those of method II (Table 3) show the same order for

TABLE 6

Absolute electrode potential, radius of solvated cation and solvation extent in ethylene glycol + water solvents and transfer free energies of individual ions from water to these solvents, at 25 °C, all calculated using the data reported by Kundu et al. [1], ΔG_t^0 (kJ mol^{-1})

Wt.% glycol		30	50	70	90	100
Results of method I						
$-$Corr (10^{-2})		99.9999	100.0000	99.9995	99.9959	99.9965
a_1^0 (10^{10} V m^{-1})		1.0296	1.0079	0.9671	0.9082	0.9046
r_+ (10^{-10} m)	M = Li	4.959	5.009	5.107	5.273	5.254
	Na	4.639	4.683	4.776	4.933	4.912
	K	4.842	4.891	4.990	5.163	5.145
S_e (10^{-10} m)	M = Li	4.36	4.41	4.51	4.67	4.65
	Na	3.69	3.73	3.83	3.98	3.96
	K	3.51	3.56	3.66	3.83	3.81
${}^{\mathrm{Ox}}_{\mathrm{L}}E_m^0$ (V)	M = Li	5.101	5.037	4.930	4.786	4.762
	Na	4.772	4.709	4.611	4.477	4.452
	K	4.981	4.918	4.817	4.686	4.663
${}^{\mathrm{Ox}}_{\mathrm{R}}E_m^0$ (V)	X = Cl	1.8635	1.8243	1.7504	1.6438	1.6373
	Br	2.0077	1.9654	1.8858	1.7710	1.7639
	I	2.2239	2.1771	2.0889	1.9617	1.9539
$\Delta G_t^0(+)_m$	M = Li	9.542	15.677	26.005	39.955	42.196
	Na	9.349	15.387	24.847	37.832	40.169
	K	9.542	15.580	25.330	38.025	40.169
$\Delta G_t^0(-)_m$	X = Cl	7.031	10.820	17.950	28.231	28.861
	Br	7.575	11.656	19.338	30.414	31.093
	I	8.391	12.912	21.420	33.690	34.442

TABLE 6 (continued)

Wt.% glycol		30	50	70	90	100
Results of method II						
Corr (10^{-2})		99.8836	99.8828	99.8938	99.9188	99.8337
a_2^0 (10^{-10} V m)		4.0386	3.9535	3.7938	3.5638	3.5466
r_+ (10^{-10} m)	M = Li	3.972	3.781	3.456	3.017	3.055
	Na	5.874	5.515	4.876	4.087	4.166
	K	4.504	4.268	3.854	3.296	3.340
S_e (10^{-10} m)	M = Li	3.37	3.18	2.86	2.42	2.46
	Na	4.92	4.57	3.93	3.14	3.22
	K	3.17	2.94	2.52	1.97	2.01
$-{}^{\text{Red}}_{\text{L}}E_m^0$ (V)	M = Li	1.016	1.043	1.096	1.180	1.163
	Na	0.687	0.715	0.777	0.871	0.853
	K	0.896	0.924	0.983	1.080	1.064
${}^{\text{Red}}_{\text{R}}E_m^0$ (V)	X = Cl	2.2313	2.1842	2.0960	1.9690	1.9595
	Br	2.0711	2.0274	1.9455	1.8276	1.8188
	I	1.8697	1.8303	1.7564	1.6499	1.6420
$\Delta G_t^0(+)_m$	M = Li	5.627	8.273	13.340	21.513	19.847
	Na	5.820	8.563	14.498	23.636	21.873
	K	5.627	8.370	14.016	23.443	21.873
$\Delta G_t^0(-)_m$	X = Cl	8.446	12.983	21.497	33.754	34.671
	Br	7.840	12.051	19.954	31.330	32.182
	I	7.077	10.880	18.014	28.284	29.053

the alkali-metal cations, but an opposite order for the halide ions, and in both cases, Li^+ ion seems to show some abnormality in this respect. The different orders obtained by results of method II may lend further evidence against the applicability of method II for such calculations. Now, there is every reason that method I should be applied to the EMF data for determination of absolute electrode potentials as well as thermodynamic properties of single ions in solution [8,9], and that its set of data should be credited.

PREVIOUS EMF DATA AND THE NEW PROCEDURE

However, the new procedure of determination of absolute electrode potential as well as transfer free energies of single ions has been applied to the previous data of Kundu et al. [1]. The least-squares results are collected in Table 6. The same trends are generally observed, except that the values of r_+, and thus S_e, show slight maxima and minima at around 90% EG for results of method I and II, respectively. Also, the values of ${}^{\text{Red}}_{\text{L}}E_m^0$ pass through minima which are reflected by maxima in $\Delta G_t^0(M^+)$ values in the same region of 90% EG. Such extrema (maxima and minima) are not observed in our results. Again, the same interesting features seen in Table 6 lead to the same conclusions.

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REFERENCES

1 K.K. Kundu, A.K. Rakshit and M.N. Das, Electrochim. Acta, 17 (1972) 1921.

2 J. Radosevic and I. Mekjavic, Electrochim. Acta, 28 (1983) 1435, and references therein.

3 D. Feakins, R.D. O'Neill, W.E. Waghorne and A.J.I. Ward, J. Chem. Soc., Faraday Trans. 1, 78 (1982) 1431, and references therein.

4 K. Das, A.K. Das and K.K. Kundu, Electrochim. Acta, 26 (1981) 471, and references therein.

5 K. Bose and K.K. Kundu, (a) J. Solution Chem., 8 (1979) 175; (b) Can. J. Chem., 57 (1979) 2476.

6 D. Feakins, B.E. Hickey and P.J. Voice, J. Chem. Soc., Faraday Trans. 1, 75 (1979) 907.

7 D. Feakins and P.J. Voice, J. Chem. Soc., Faraday Trans. 1, 68 (1972) 1390; 69 (1973) 1711.

8 M.M. Elsemongy, Thermochim. Acta, 80 (1984) 239.

9 M.M. Elsemongy and F.M. Reicha, Thermochim. Acta, 103 (1986) 371.

10 I.N. Basu Mullick and K.K. Kundu, Can. J. Chem., 58 (1980) 79.

11 R.G. Bates, in J.F. Coetzee and C.D. Ritchie (Eds.), Solute–Solvent Interactions, Dekker, New York, 1969.

12 D. Feakins, in F. Franks (Ed.), Physico-Chemical Processes in Mixed Aqueous Solvents, Heinemann, London, 1969, and references therein.