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GIBBS FREE ENERGIES OF TRANSFER OF THE ALKALI-METAL CHLORIDES FROM WATER INTO *t*-BUTYL ALCOHOL–WATER MIXTURES

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ABSTRACT

The standard Gibbs free energies of transfer $\Delta G_t^{\ominus}$ of the alkali-metal chlorides MCl from water (W) into 5–90 wt.% *t*-butyl alcohol (TBA)–water mixtures (S) were determined from EMF measurements performed on the double cell

$$\text{Ag, AgCl}\,|\,\text{MCl}(m),\ \text{S}\,|\,\text{M(Hg)}\,|\,\text{MCl}(m),\ \text{W}\,|\,\text{AgCl, Ag}$$

at 25 ° C in the molality range of MCl from 0.001–0.100 mol kg^{-1}. The value of $\Delta G_t^{\ominus}$ rises from Li^+ to Na^+ and falls from K^+ to Cs^+, with a maximum between Na^+ and K^+ whose position depends on the solvent composition. The standard potentials of the cell

$$\text{M}\,|\,\text{MCl}(m),\ \text{S}\,|\,\text{AgCl, Ag}$$

in these 10 TBA–water mixtures were also determined. The results have been interpreted and discussed in terms of solute–solvent interactions.

INTRODUCTION

As far as electrochemical methods are concerned, amalgam electrodes have been considered for a long time to be the most reliable means for the determination of alkali-metal ion activity in solution [1–3]. Clune et al. [1] used amalgam electrodes to determine the standard free energy of transfer $\Delta G_t^{\ominus}$ of the alkali-metal chlorides MCl from water into aqueous mixtures containing up to 50 wt.% of *t*-butyl alcohol (TBA). They compared their results with those of Pointud et al. [2], who used glass electrodes to study

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mixtures containing up to 40 wt.% of TBA. The two sets of results agreed on average to within ±88 J (equivalent to ±0.9 mV). In summary [1], the agreement between 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 TBA. It is perhaps least satisfactory for Cs^+. Smits et al. [3] reported the free energy of transfer of RbCl from water to a large number of organic solvent–water mixtures, measured using glass electrodes. They compared their results, where possible, with those obtained by other workers using classical techniques. With some exceptions, the agreement was satisfactory [3].

However, for the TBA–water solvent system, there are no comparisons possible over wider ranges of solvent composition. More work is therefore needed at the higher concentrations of the organic solvent. In this paper, we report and discuss briefly measurements of the free energy of transfer of the alkali-metal chlorides from water into 10 TBA–water mixtures ranging in composition from 5–90 wt.% TBA. In view of recent technical developments with amalgam electrodes and their use in EMF measurements [4–7] to obtain more accurate results, the standard EMF values ($\Delta E_m^\ominus$) of the double cell

$$\text{Ag, AgCl} \,|\, \text{MCl}(m),\ \text{S} \,|\, \text{M(Hg)} \,|\, \text{MCl}(m),\ \text{W} \,|\, \text{AgCl, Ag} \qquad \text{(I)}$$

have been determined at 25 °C by the procedure adopted recently [4–7], a method which is generally recognized as being the most reliable [6,7]. Here M ≡ Li, Na, K, Rb or Cs and m is the molality, which varies from 0.001 mol kg^{-1} to 0.100 mol kg^{-1}. The overall spontaneous cell reaction is the transfer of 1 mol of the alkali-metal chloride from the TBA–water mixture (S) to water (W). Thus, from $\Delta E_m^\ominus$ values, Gibbs free energies of transfer ($\Delta G_t^\ominus$) of MCl from water to the appropriate solvent can be computed [4–7].

EXPERIMENTAL

Water was deionized and doubly distilled. TBA (BDH grade) was further purified as previously [8]. AnalaR and Merck quality alkali-metal chlorides were further purified, dried and stored for a few days as mentioned earlier [4,5]. All other materials were as used previously [2,4,5]. The EMF measurements, as well as other experimental details and mathematical treatment of the results, were essentially similar to those described elsewhere [4,5]. The temperature was carefully controlled at 25.00 ± 0.05 °C. The equilibrium criterion was an EMF constant to within ±0.1 mV during 30 min. The EMF measurements were made in triplicate, and the mean values of these observations recorded. The triplicate values generally agreed within ±0.15 mV.

RESULTS AND DISCUSSION

The EMF values of cell I, for different molalities m of MCl in different solvents, were analysed in the manner previously described [4–7] for amalgam cells to yield the standard EMF values $\Delta E_m^{\ominus}$ which are given in Table 1. These values are accurate to better than ± 0.15 and ± 0.25 mV for solvents containing up to 50 wt.% and 90 wt.% of TBA, respectively.

Standard Gibbs transfer free energies

The standard Gibbs free energy change $\Delta G_t^{\ominus}$ accompanying the transfer process

$$\mathrm{MCl(W)} = \mathrm{MCl(S)} \tag{1}$$

has been computed from

$$\Delta G_t^{\ominus} = F\Delta E_x^{\ominus}, \tag{2}$$

where $\Delta E_x^{\ominus}$ is the standard EMF of cell I on the mole fraction scale. The $\Delta E_x^{\ominus}$ values, computed from $\Delta E_m^{\ominus}$ values (Table 1) by using the usual relation [9], were utilized to compute the $\Delta G_t^{\ominus}$ values presented in Table 2. These values are accurate to better than ± 15 J mol^{-1} and ± 25 J mol^{-1} for solvents containing up to 50 wt.% and 90 wt.% of TBA, respectively. The use of standard potentials on the mole fraction scale serves to eliminate the free energy change contribution due to the concentration changes accompanying the transfer of MCl from one solvent to another [9].

It is evident from Table 2 that the standard Gibbs free energy of transfer $\Delta G_t^{\ominus}$ becomes more and more positive with the increase of TBA content in the medium. The positive $\Delta G_t^{\ominus}$ values suggest that the electrolyte is in a higher free energy state in TBA–water mixtures than in water, so that any

TABLE 1

Values of $\Delta E_m^{\ominus}$ (mV) for cell I in *t*-butyl alcohol–water mixtures at 25 ° C

TBA (wt.%)	LiCl	NaCl	KCl	RbCl	CsCl
5	8.92	11.32	11.10	10.32	9.78
10	18.08	22.49	22.38	21.06	19.84
20	37.67	43.73	44.49	42.57	39.03
30	57.03	63.97	64.81	61.00	58.34
40	78.00	84.98	86.52	83.09	77.18
50	101.82	109.68	112.24	107.71	96.73
60	130.59	143.96	147.93	141.26	118.01
70	168.21	191.53	195.97	187.52	144.15
80	221.89	263.25	271.50	255.45	177.02
90	297.46	363.74	377.02	352.91	218.14

TABLE 2

Standard free energies of transfer $\Delta G_t^\ominus$ (J mol^{-1}) of MCl and HCl from water into *t*-butyl alcohol–water mixtures at 25 °C, on the mole fraction scale

TBA (wt.%)	HCL [a]	LiCl	NaCl	KCl	RbCl	CsCl
5	234	670	901	880	805	753
10	470	1354	1780	1769	1642	1524
20	897	2821	3405	3479	3293	2952
30	1339	4226	4895	4976	4609	4352
40	1886	5738	6411	6560	6229	5659
50	2678	7466	8224	8471	8034	6975
60	3893	9598	10888	11271	10627	8384
70	5664	12488	14738	15166	14351	10166
80	7801	16797	20788	21584	20035	12468
90	10218	23032	29427	30709	28382	15379

[a] From ref. 8.

MCl has more affinity for water than for TBA–water mixtures. The transfer of MCl from water to TBA–water mixtures is, therefore, not a spontaneous process with the solute in the standard state in either medium. Thus, the increasingly positive $\Delta G_t^\ominus$ values of alkali-metal chlorides indicate that the dissolutions of these salts are not favoured by addition of TBA to water. This behaviour is of course the combined effects of decreased dielectric constants and overall interactions of the cations and anions with the alcoholic solvents relative to those with water.

It is generally recognized that changes of Gibbs free energies for the transfer from one medium to another are closely associated with changes in solute solvation [10]. Sharma and Ahluwalia [11] suggested that the transfer of structure breaking solutes should be accompanied by a positive free energy change, thereby making the transfer of these solutes from water to the mixed solvents thermodynamically unfavourable. The positive $\Delta G_t^\ominus$ values, therefore, suggest that any MCl behaves as a structure breaker in water.

The values for $\Delta G_t^\ominus$(HCl) in TBA–water mixtures on the mole fraction scale, reported by Elsemongy [8], are also included in Table 2. All the data for $\Delta G_t^\ominus$ indicate that the transfer process of HCl or MCl is non-spontaneous and the more so the higher the TBA content in the mixed solvent. Since this non-spontaneity is less pronounced for the HCl electrolyte, it can be concluded that the obtained results indicate greater non-spontaneity for the transfer process of M^+ ion in comparison to that of H^+ ion, although these (H^+ and M^+) ions are all preferentially hydrophilic in nature.

In any mixed solvent, the values of $\Delta G_t^\ominus$ for MCl, and thus for M^+ ions, do not follow such a regular order. With the Cl^- ion being common, the observed order of $\Delta G_t^\ominus$(HCl or MCl) should necessarily reflect the corresponding order for the H^+ or alkali-metal M^+ ions. However, there is a marked rise in $\Delta G_t^\ominus$ from H^+ through Li^+ to Na^+ and a fall from K^+ through Rb^+ to Cs^+ with a maximum (for Na^+ in solvents of low TBA content) that shifts (to K^+ in solvents of high TBA content) as the proportion of TBA is increased. This pattern is very similar to that found for transfers from water to methanol–water [12,13], dimethyl sulphoxide–water [5] and dioxan–water [4] solvent systems. While the shifting of the maximum occurs around 90 wt.% methanol, 50 wt.% dimethyl sulphoxide and 30 wt.% dioxan in the methanol–water, dimethyl sulphoxide–water and dioxan–water systems respectively, it occurs at a TBA content as low as 20 wt.% in the TBA–water system. Nevertheless, the essential similarity in the profiles of $\Delta G_t^\ominus$ points to a common cause for the resulting behaviour of these simple ions in these solvent systems. However, this behaviour is extensively explained and discussed in terms of the acid–base theory of ionic solvation [13,14].

Comparison with previous work

A comparison may now be made between our new values for the Gibbs free energy of transfer of MCl from water into TBA–water mixtures and those obtained previously by different investigators [1–3]. Clune et al. [1] and Pointud et al. [2] both reported their $\Delta G_t^\ominus(\mathrm{MCl})$ values on the molal scale (m), whereas Smits et al. [3] reported their values of $\Delta G_t^\ominus(\mathrm{RbCl})$ on the molar scale (c). These were converted to the molal scale using eqn. (3)

$$\Delta G_t^\ominus(\mathrm{MCl})_m = \Delta G_t^\ominus(\mathrm{MCl})_c + 11\,415 \log_{10}(d_s/d_w) \text{ J mol}^{-1} \qquad (3)$$

Thus, to avoid any approximations and to get a more precise and accurate comparison, all the $\Delta G_t^\ominus(\mathrm{MCl})$ values are expressed on the molal scale and collected in Table 3. It is evident from this table that the agreement between our new results and those obtained by other workers is acceptable in most cases, being practically always within the combined precision limits of their and our measurements. However, the new values of $\Delta G_t^\ominus$ for LiCl in 10% TBA and for NaCl in 20% TBA are slightly lower, whereas those for LiCl and CsCl in 40% TBA are slightly higher, than those of Clune et al. [1] obtained using amalgam electrodes. For the $\Delta G_t^\ominus$ values obtained using glass electrodes, although there are good agreements between all the values of Smits et al. [3], reported for RbCl in 5–80% TBA solvents, and the new values, those of Pointud et al. [2] for LiCl and KCl in 30% and 40% TBA and for RbCl in 40% TBA are slightly lower, whereas those for NaCl in 20% TBA and CsCl in 20% and 30% TBA are slightly higher, than the new values. However, all the precautions we have taken in the experimental work [4,5] make our values the more reliable, and to be preferred.

TABLE 3

Values of standard molal free energies of transfer (in J mol^{-1}) of alkali-metal chlorides from water to *t*-butyl alcohol–water mixtures at 25 °C and previously reported values [1–3] for comparison

TBA (wt.%)	Source	LiCl	NaCl	KCl	RbCl	CsCl
5	This work	861	1092	1071	996	944
	Ref. 1	–	1100	1075	1000	935
	Ref. 2	850	1100	1080	990	980
	Ref. 3	–	–	–	992	–
10	This work	1744	2170	2159	2032	1914
	Ref. 1	1850	2175	2165	2035	1910
	Ref. 2	1710	2170	2160	2050	1970
	Ref. 3	–	–	–	2030	–
20	This work	3635	4219	4293	4107	3766
	Ref. 1	3655	4395	4295	4115	3795
	Ref. 2	3630	4370	4300	4100	3970
	Ref. 3	–	–	–	4130	–
30	This work	5503	6172	6253	5886	5629
	Ref. 1	5530	6155	6270	5875	5650
	Ref. 2	5320	6210	6070	5870	5740
	Ref. 3	–	–	–	5910	–
40	This work	7526	8199	8348	8017	7447
	Ref. 1	7385	8240	8365	8035	7370
	Ref. 2	7210	8180	8110	7850	7680
	Ref. 3	–	–	–	7950	–
50	This work	9824	10582	10829	10392	9333
	Ref. 1	9845	10565	10807	10390	9320
	Ref. 3	–	–	–	10400	–
60	This work	12600	13890	14273	13629	11386
	Ref. 3	–	–	–	13700	–
70	This work	16230	18480	18908	18093	13908
	Ref. 3	–	–	–	18100	–
80	This work	21409	25400	26196	24647	17080
	Ref. 3	–	–	–	24700	–
90	This work	28700	35095	36377	34050	21047

Standard potential of the cell M | MCl(m),S | AgCl,Ag

The value of $\Delta E_m^\ominus$ (Table 1) is the difference between the $E_m^\ominus$ values of cell II

$$\mathrm{M}\,|\,\mathrm{MCl}(m),\ \mathrm{S}\,|\,\mathrm{AgCl},\ \mathrm{Ag} \qquad \text{(II)}$$

TABLE 4

Values of the standard EMF $E_m^\ominus$ (V) of the cell M|MCl(m), solvent|AgCl, Ag in *t*-butyl alcohol–water mixtures at 25 °C

TBA (wt.%)	LiCl	NaCl	KCl	RbCl	CsCl
0 [a]	3.2667	2.9352	3.1472	3.1475	3.1454
5	3.2578	2.9239	3.1361	3.1372	3.1356
10	3.2486	2.9127	3.1248	3.1264	3.1256
20	3.2290	2.8915	3.1027	3.1049	3.1064
30	3.2097	2.8712	3.0824	3.0865	3.0871
40	3.1887	2.8502	3.0607	3.0644	3.0682
50	3.1649	2.8255	3.0350	3.0398	3.0487
60	3.1361	2.7912	2.9993	3.0062	3.0274
70	3.0985	2.7437	2.9512	2.9600	3.0012
80	3.0448	2.6720	2.8757	2.8921	2.9684
90	2.9692	2.5715	2.7702	2.7946	2.9273

[a] From ref. 4.

in water, ${}^{w}E_m^\ominus$, and in the respective TBA–water solvents, ${}^{s}E_m^\ominus$, i.e.

$$\Delta E_m^\ominus = {}^{w}E_m^\ominus - {}^{s}E_m^\ominus \qquad (4)$$

The values of ${}^{w}E_m^\ominus$ for cell II have been reported recently [4], and so those of ${}^{s}E_m^\ominus$ could be computed in the mixed solvents for cell II containing MCl ≡ LiCl, NaCl, KCl, RbCl or CsCl. These are recorded in Table 4. Since the ${}^{s}E_m^\ominus$ values of cell II are related to the solvation energies of non-protogenic solutes, such as MCl, in a simple manner, their determination in different solvents seems to be equally important with regard to the general phenomenon of ion–solvent interaction [14]. With that end in view, we have computed ${}^{s}E_m^\ominus$ values of cell II in aqueous mixtures of TBA at 25 °C.

In the literature, it is frequently noticeable that some researchers [7,9,10,14] have determined the standard potential of $M|M^+$ (M ≡ Li, Na, K, Rb or Cs) electrodes, in various solvents, using the values of $E_m^\ominus$ for cell II and the standard potentials of cell III

$$\text{Pt, } H_2|HCl(m),S|AgCl,Ag \qquad \text{(III)}$$

which are incorrectly taken to be the standard potentials of the Ag,AgCl electrode, not only in all solvent systems and in all solvent compositions, but also at all temperatures. This means that the standard hydrogen electrode potential is zero in all solvents and at all temperatures, which is, of course, not the case [12]. It is well known that any electrode potential varies with temperature as well as with solvent composition, in any solvent system. Thus, the difference between the EMF values of cells II and III gives the difference between the oxidation potentials of the $M|M^+$ and $H_2|H^+$ electrodes, as indicated by eqn. (5)

$${}_{II}E_m^\ominus - {}_{III}E_m^\ominus = E^\ominus_{M|M^+} - E^\ominus_{H_2|H^+} \qquad (5)$$

These invalid calculations [7,9,10,14] are therefore responsible for the peculiar trends observed for the variation of standard potential of $M|M^+$ electrodes [7], although the EMF values of cell II or cell III vary monotonically with solvent composition in any solvent system.

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