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TRANSFER FREE ENERGIES OF IONS FROM WATER TO *N,N*-DIMETHYLFORMAMIDE AND ITS AQUEOUS MIXTURES, BASED ON Ph_4AsBPh_4 AND Ph_4SbBPh_4 ASSUMPTIONS

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ABSTRACT

Standard free energies of transfer, $\Delta^s_w G_t^\ominus$, of some ions from water to DMF and its aqueous mixtures have been evaluated experimentally at 25 °C using the asymmetric reference electrolytes (RE = Ph_4AsBPh_4 and Ph_4SbBPh_4). $\Delta^s_w G_t^\ominus$ of RE and the corresponding tetraphenyl derivatives of the ions under consideration have been derived from the measured solubilities. The transfer free energies of the ions in mixed H_2O–DMF solvents are discussed.

INTRODUCTION

Standard free energies of transfer are useful in establishing a universal scale of activity, acidity or electrode potential as well as in understanding the relative solvation of ions in different solvents [1]. The methods used for evaluating these quantities are based on extra-thermodynamic assumptions. The various extra-thermodynamic assumptions involved in different methods [1–4] and the relatively sound theoretical basis have favoured the use of the reference electrolyte (RE) method and also, to some extent, the ferrocene/ferrocinium (foc/fic$^+$) method [5]. Consequently, the RE methods used here have the following relationships between the transfer free energies ($\Delta^s_w G_t^\ominus$) of the reference cations and reference anions [6,7]

$$\Delta^s_w G_t^\ominus(Ph_4As^+) > \Delta^s_w G_t^\ominus(Ph_4B^-) \quad (1)$$

$$\Delta^s_w G_t^\ominus(Ph_4Sb^+) > \Delta^s_w G_t^\ominus(Ph_4B^-) \quad (2)$$

and do not have equal free-energy values as has been maintained previously in the literature.

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MATERIALS AND METHODS

N,*N*-dimethylformamide (BDH, Spectrosol) was used without purification other than adding a molecular sieve as a dehydrating agent. Methods of purification of the salts Ph_4SbBPh_4 (TPAnTPB), $KBPh_4$ (KTPB), $RbBPh_4$ (RTPB) and $CsBPh_4$ (CTPB) have been described in previous work [8]. Saturated solutions were prepared by gently shaking the suspensions of the salts for one week in an Assistant shaking water bath and then allowing them to equilibrate at 25 °C. The solubility was measured either gravimetrically or spectrophotometrically, as explained in ref. 7, by evaporating 1–2 ml of the saturated solutions on small aluminium disks of diameter 3 cm beneath an IR lamp. The evaporated residues were determined by direct weighing when possible or, if quantities were insufficient, were dissolved in ethanol (BDH) and determined spectrophotometrically using a Jobin–Yvon JY 100 spectrophotometer.

RESULTS AND DISCUSSION

The different physical properties of aqueous DMF solutions at 25 °C are presented in Table 1. This table gives the measured values of the density (ρ) [9] and the dielectric constants (ϵ) [1]. The partial molal diameters (σ_o) and the scaled particle theory diameters (σ_{SPT}), evaluated using the relationship [10,11] $\sigma_{SPT} = (0.09275 \pm 0.0084)\sigma_o - (0.8465 \pm 0.0084) \times 10^{-8}$ cm for

TABLE 1

Physical parameters of mixed DMF–H_2O solvents: density ρ; partial molar diameter σ_o; scaled particle theory diameter σ_{SPT}; and the solvated radii of tetraphenyl derivatives [a]

x_s DMF	ρ (g cm^{-3})	ϵ	σ_o	σ_{SPT}	r KTPB	r RTPB	r CTPB
0	0.9971	78.5	3.855	2.729	8.380	8.530	8.740
0.025	0.9970	–	3.952	2.819	8.429	8.579	8.789
0.0909	0.9967	–	4.184	3.034	8.644	8.794	9.004
0.135	0.9965	65.1	4.325	3.165	8.775	8.925	9.135
0.189	0.9961	62.5	4.489	3.318	8.927	9.078	9.288
0.260	0.9938	57.8	4.689	3.503	9.113	9.263	9.473
0.353	0.9875	53.2	4.935	3.731	9.341	9.491	9.701
0.483	0.9776	48.2	5.249	4.023	9.633	9.783	9.993
0.590	0.9680	44.1	5.490	4.246	9.856	10.006	10.216
0.677	0.9628	42.0	5.669	4.412	10.022	10.172	10.382
0.785	0.9555	40.5	5.880	4.607	10.217	10.367	10.577
0.882	0.9492	39.2	6.059	4.774	10.384	10.534	10.743
1.0	0.9440	36.8	6.262	4.962	10.540	10.690	10.900

[a] ρ and ϵ values are taken from ref. 9. All the diameters and radii in this table are in Å.

TABLE 2

Molal solubilities S, activity coefficients $\gamma_{\pm}$ and solubility products of tetraphenyl derivatives at 25 ° C

x_s	KTPB			RTPB			CTPB		
DMF	S	$\log \gamma_{\pm}$	pK_{sp}	S	$\log \gamma_{\pm}$	pK_{sp}	S	$\log \gamma_{\pm}$	pK_{sp}
0	1.445×10^{-4}	-6.085×10^{-3}	7.692	6.026×10^{-3}	-3.929×10^{-3}	8.448	1.95×10^{-5}	-2.235×10^{-3}	9.424
0.0909	2.188×10^{-3}	−0.024	5.368	1.00×10^{-3}	−0.016	6.032	3.162×10^{-4}	-9.001×10^{-3}	7.018
0.135	5.888×10^{-3}	−0.0388	4.538	2.754×10^{-3}	−0.0266	5.174	1.148×10^{-3}	−0.0172	5.915
0.189	0.0166	−0.0652	3.690	8.318×10^{-3}	−0.0462	4.252	4.169×10^{-3}	−0.0327	4.825
0.260	0.0501	−0.1133	2.827	0.0219	−0.075	3.469	0.0102	−0.0511	4.085
0.353	0.151	−0.197	2.036	0.063	−0.127	2.654	0.0350	−0.094	3.108
0.483	0.447	−0.338	1.375	0.191	−0.221	1.882	0.096	−0.156	2.353
0.590	0.741	−0.436	1.132	0.331	−0.291	1.542	0.166	−0.206	1.972
0.677	0.933	−0.489	1.038	0.437	−0.335	1.389	0.229	−0.242	1.765
0.785	1.148	−0.542	0.964	0.575	−0.384	1.249	0.302	−0.278	1.596
0.882	0.575	−0.384	0.862	0.661	−0.412	1.184	0.363	−0.305	1.490
1.0	0.716	−0.428	0.719	0.708	−0.426	1.152	0.417	−0.327	1.414

TABLE 3

Molal solubilities S, solvated radii r, activity coefficients $\gamma_{\pm}$, solubility products pK_{sp} and transfer free energies of TPAnTPB from water to mixed DMF–H_2O solvents at 25 °C

x_s DMF	S	r (Å)	$\log \gamma_{\pm}$	pK_{sp}	$\Delta_w^s G_t^{\ominus}$ [a] (kJ mol^{-1})
0	3.171×10^{-9}	11.374	-2.869×10^{-5}	16.997	0
0.0909	1.126×10^{-7}	11.679	-2.065×10^{-4}	13.897	−17.689
0.135	6.332×10^{-7}	11.810	-5.369×10^{-4}	12.396	−26.259
0.189	5.032×10^{-6}	11.963	-1.609×10^{-3}	10.593	−36.547
0.260	4.495×10^{-5}	12.147	-5.243×10^{-3}	8.684	−47.442
0.353	4.031×10^{-4}	12.376	−0.0167	6.756	−58.446
0.483	2.883×10^{-3}	12.668	−0.0191	5.042	−68.228
0.590	7.313×10^{-3}	12.892	−0.0244	4.223	−72.902
0.677	0.0146	13.057	−0.1015	3.468	−77.212
0.785	0.0295	13.252	−0.1270	2.806	−80.989
0.885	0.0527	13.419	−0.1336	2.289	−83.939
1.0	0.0837	13.607	−0.1760	1.803	−86.713

[a] Estimated uncertainty of $\Delta_w^s G_t^{\ominus}$ is ±0.4 kJ mol^{-1}.

DMF–water solvents, are represented in Table 1. This table also includes the solvated radii r, i.e. the distance of closest approach of KTPB, RTPB, CTPB and TPAnTPB in the mixed solvents under consideration, calculated by adding together the crystal radius of the alkali metal ion, the van der Waals radius of the tetraphenylboride ion (TPB$^-$) and the σ_{SPT} of the solvents. In the case of TPAnTPB, the calculated van der Waals radius (8.83 Å) was used. The experimental solubilities S for KTPB, RTPB, CTPB and TPAnTPB in aqueous DMF solutions were measured on the molal scale (converted by dividing the molar solubility by the measured densities of the mixed solvents) and are given in Tables 2 and 3.

The salt activity coefficient ($\gamma_{\pm}$) for the four tetraphenyl electrolytes was measured using the Debye–Hückel equation [12]

$$\log \gamma_{\pm} = -\frac{A z_a z_b \sqrt{S}}{1 + B r \sqrt{S}} \tag{3}$$

where $A = 1.825 \times 10^6\ (T\epsilon)^{3/2}$, $B = 50.29 \times 10^8\ (T\epsilon)^{1/2}$, T is the absolute temperature and ϵ is the dielectric constant of the mixed solvent. The solvated radii (r) for the tetraphenyl derivatives applied in eqn. (3) were taken from Tables 2 and 3. The calculated activity coefficient values for KTPB, RTPB and CTPB salts are given in Table 2 and, for TPAnTPB, in Table 3. The transfer free energies for the tetraphenyl derivatives were estimated using eqn. (4)

$$\Delta_w^s G_t^{\ominus} = 2.303RT\left[\mathrm{p}K_{sp(s)} - \mathrm{p}K_{sp(w)}\right] \tag{4}$$

TABLE 4

Transfer free energies (kJ mol^{-1}) of TPB^-, TPA^+ and $TPAn^+$ ions from water to mixed $DMF-H_2O$ solvents at 25 ° C

x_s DMF	$\Delta^s_w G_t^\ominus$ TPB^-	$\Delta^s_w G_t^\ominus$ TPA^+	$\Delta^s_w G_t^\ominus$ $TPAn^+$	$\Delta^s_w G_t^\ominus$ $TPAn^+$/ $\Delta^s_w G^\ominus$ TPB^-
0	0	0	0	
0.0909	−8.577	−9.205	−9.113	1.0624
0.135	−13.682	−13.598	−12.577	0.9192
0.189	−17.364	−18.619	−19.184	1.105
0.260	−22.175	−23.974	−25.267	1.139
0.353	−26.066	−28.158	−32.379	1.242
0.483	−30.752	−31.840	−37.476	1.219
0.590	−33.263	−34.309	−39.639	1.192
0.677	−34.727	−35.815	−42.484	1.223
0.785	−36.192	−38.074	−44.798	1.237
0.882	−37.238	−39.874	−46.702	1.254
1.0	−38.199	−40.376	−48.513	1.269

where pK_{sp} is the solubility product calculated from eqn. (5), and the subscripts s and w refer to mixed solvent and water respectively

$$pK_{sp} = -2 \log S + 2 \log \gamma_{\pm} \qquad (5)$$

The calculated transfer free energy values are presented in Tables 3 and 5 with an uncertainty of ±0.4 kJ mol^{-1}. The transfer free energies of the tetraphenylantimon cation ($TPAn^+$) in mixed aqueous DMF solvents were evaluated by subtracting $\Delta^s_w G_t^\ominus$ values for TPAnTPB from that of the

TABLE 5

Transfer free energies (kJ mol^{-1}) of KTPB, RTPB, CTPB and their alkali metal ions from water to mixed $DMF-H_2O$ solvents at 25 ° C

x_s DMF	$\Delta^s_w G_t^\ominus$					
	KTPB	K^+	RTPB	Rb^+	CTPB	Cs^+
0	0	0	0	0	0	0
0.0909	−13.263	−4.686	−13.786	−5.209	−16.510	−7.933
0.135	−17.999	−4.318	−18.686	−5.004	−20.025	−6.343
0.189	−22.840	−9.159	−23.945	−10.263	−26.246	−12.565
0.260	−27.765	−10.401	−28.414	−11.049	−30.468	−13.104
0.353	−32.279	−10.104	−33.066	−10.891	−36.045	−13.869
0.483	−36.049	−9.083	−37.472	−11.406	−40.355	−14.288
0.590	−37.438	−6.686	−39.413	−8.661	−42.530	−11.778
0.697	−37.974	−3.247	−40.284	−5.556	−43.710	−8.983
0.785	−38.397	−2.205	−41.083	−4.891	−44.673	−8.481
0.882	−38.974	−1.736	−41.455	−4.217	−45.279	−8.042
1.0	−39.794	−1.594	−41.639	−3.439	−45.714	−7.514

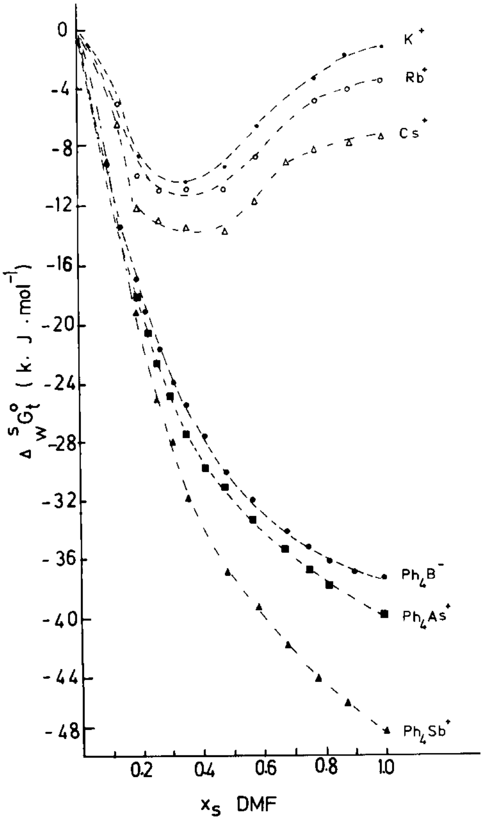


Fig. 1. Transfer free energies of K^+, Rb^+, Cs^+, TPB^-, TPA^+ and $TPAn^+$ ions from water to mixed DMF–H_2O solvents at 25° C.

tetraphenylboride anion (TPB^-) [9]. The results, shown in Table 4, prove that the tetraphenylantimon–tetraphenylboride assumption, like the tetraphenylarsonium–tetraphenylboride assumption, is an asymmetric model with a mean value of 1.1692 for the ratio between the transfer free energy values of $TPAn^+$ to TPB^- (see Table 4).

The single ion transfer free energies for the alkali metal cations K^+, Rb^+ and Cs^+ were evaluated by subtracting the $\Delta^s_w G_t^\ominus$ values for KTPB, RTPB and CTPB from the mean value of the TPB^- cation listed in Table 4, calculated from both the tetraphenylarsonium–tetraphenylboride and tetraphenylantimon–tetraphenylboride electrolyte assumptions. The resulting single ion transfer free energies for K^+, Rb^+ and Cs^+ are listed in Table 5 and presented graphically in Fig. 1. Using the transfer free energy data available in the literature and the reference electrolyte values of TPB^-, TPA^+ and $TPAn^+$ ions evaluated here, the single transfer free energies for many ions from water to pure DMF have been recalculated and are listed in Table 6. All the $\Delta^s_w G_t^\ominus$ data are converted from kcal mol^{-1} to kJ mol^{-1} by

TABLE 6

Transfer free energies (kJ mol^{-1}) for some ions from water to pure DMF using the asymmetric Ph_4AsBPh_4 and Ph_4SbBPh_4 assumptions at 25 °C

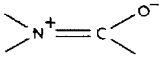
Ion	a	b	c	d	e	f	g	h	i
Cl^-	39.041	37.995	30.234	44.062				51.46	44.062
Br^-	23.769	24.665	14.330	29.158				40.166	29.158
I^-	17.556	17.556	3.460	21.025				23.430	21.025
ClO_4^-	1.347	−0.498							0.427
N_3^-	28.581	38.911							33.746
OAc^-	55.359	65.689							60.526
Li^+	−16.238		20.167					−46.024	−14.032
Tl^+		16.188							16.188
Na^+	−2.222		29.811						−2.222
K^+			−1.594				−1.594	−12.552	−1.594
Rb^+	0.916	−2.489	−1.586				−3.439		−3.439
Cs^+	−6.983		1.377	−7.975			−7.514	−12.552	−7.514
Ag^+	−10.589	−15.046			−20.92	−28.221		−24.686	−28.221
Me_4N^+	−8.054	−4.586							−6.322
Et_4N^+	−7.096	−6.678							−6.887
Pr_4N^+	−20.188	−16.719							−18.451

a: B.G. Cox, Chem. Rev., 9 (1980) 381; b: B.G. Cox, Ann. Rep. Chem. Soc., A (1973) 249; c: K. Das, K. Bose and K.K. Kundu, Electrochim. Acta, 26 (1981) 479; d: E.A. Gomaa, Thermochim. Acta, 120 (1987) 183; e: J. Badoz-Lambling and J.C. Bardin, Electrochim. Acta, 19 (1974) 725; f: experimentally determined in our laboratory; g: this work; h: A.J. Parker, Chem. Rev., 69 (1969) 1; and i: chosen values (mean value or the best determined values).

multiplying by 4.184. The $\Delta^s_w G_t^\ominus$ values for alkali metal cations (Fig. 1), particularly their downward trend in water-rich compositions and upward trend in DMF-rich compositions, appear to suggest that the solvation of these relatively small ions is dictated by the opposing effects of increasingly positive Born-type electrostatic interactions and increasingly negative acid–base-type interactions. Because of the electrostatic interaction of these small cations and also because of possible steric hindrances, the number of hydrogen bonded DMF–H_2O complexes [4] or DMF dipoles interacting with these small sized M^+ ions is much less than that in pure water.

The increase in transfer free energy values of tetraphenyl ions and tetraalkylammonium ions are chiefly due to the large dispersion interactions of the four phenyl groups with the organic co-solvent (Table 6).

The sign, magnitude and order of $\Delta^s_w G_t^\ominus$ values for halide ions indicate that the behaviour of these ions is dictated by the combined effects of increasingly positive acid–base-type interactions [13,14] as well as superimposed soft–soft interactions [15,16], acting in opposite directions.

Generally, in dipolar aprotic solvents like DMF, anions are poorly solvated and are less solvated than cations (see Table 6 and refs. 17 and 18). Owensby et al. [19], suggested that cations should be strongly solvated in highly polar solvents having a negative charge localized on a bare oxygen atom. Also, because of the steric hindrance around positive charge centres in the DMF molecule (), anions should be less easily solvated.

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