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FREE ENERGIES OF TRANSFER FOR SOME MONOVALENT IONS AND Ph_4SbBPh_4 FROM WATER TO ACETONITRILE AND ACETONITRILE–WATER MIXTURES USING THE ASYMMETRIC Ph_4AsBPh_4 ASSUMPTION

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ABSTRACT

From solubility measurements at 25 °C for some tetraphenyl derivatives in water and mixed aqueous acetonitrile solvents, the single-ion free energies of transfer of Cl^-, Br^-, I^-, K^+, Rb^+, Cs^+ and Ph_4Sb^+ from water to acetonitrile and acetonitrile–water mixtures were estimated by using the asymmetric Ph_4AsBPh_4 assumption. Their values were discussed in view of solute–solvent interactions and volcanic-anti-volcanic-shaped relations between the free energies of solvation of a series of salts and the difference of solvation free energies of their ions.

INTRODUCTION

The reference electrolyte Ph_4AsBPh_4 with its cation and anion of similar size, provides the possibility of evaluating single ion thermodynamic quantities in different solvents [1–7]. Although an equal partition of its thermodynamic quantities is generally assumed [1–9], there is strong evidence that a slightly asymmetric partition exists [10–14]. Because the reference cation (Ph_4As^+) differs slightly in volume from that of the reference anion (Ph_4B^-) having the value 9.1 cm^3 mol^{-1}, accurate experimental results were needed to verify the asymmetry in their thermodynamic quantities [13].

The aim of the present work is to determine the free energies of transfer for some tetraphenyl derivatives and their single-ion values from water to acetonitrile and aqueous–acetonitrile mixtures using the asymmetric Ph_4AsBPh_4 assumption. This paper also presents the solubilities and free energies of transfer for Ph_4SbBPh_4 in mixed acetonitrile–water solvents and its suitability as a reference electrolyte for the determination of single ion thermodynamics.

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EXPERIMENTAL

$KBPh_4$, $RbBPh_4$ and $CsBPh_4$ were prepared by adding aqueous solutions of KCl, RbCl and CsCl to $NaBPh_4$ dissolved in water. The precipitates were filtered, crystallized, repeatedly recrystallized in acetone and dried at 100 ° C in an electric oven. Ph_4AsBr and Ph_4AsI were prepared by a similar method by adding aqueous solutions of KBr and KI to Ph_4AsCl dissolved in water. Ph_4SbBPh_4 was prepared by precipitation from water-dissolved Ph_4SbBr and $NaBPh_4$, and the precipitate was then filtered, dried and crystallized in acetonitrile. The water contents of all the prepared tetraphenyl derivatives were determined by Karl–Fischer titration and IR spectra. Only Ph_4AsBr and Ph_4AsI revealed the presence of water, 0.032 and 0.071 mol of water per mol of the corresponding tetraphenyl derivatives respectively. The preparation of saturated solutions and the solubility measurements were carried out as in a previous paper [15]. The experimental values presented in this work are the averages of three separate determinations. The solubility measurements were carried out at a constant temperature of 25 ° C ± 1 ° C.

RESULTS AND DISCUSSION

The standard free energies of transfer $\Delta_w^s G^\ominus(MX)$ from water (w) to organic solvent (s) of $KBPh_4$, $RbBPh_4$, $CsBPh_4$, Ph_4AsCl, Ph_4AsBr and Ph_4AsI were calculated from eqn. (1), where K_{sp} is the solubility product

$$\Delta_w^s G^\ominus(MX) = RT \ln\left[K_{sp}(w)/K_{sp}(s)\right] \tag{1}$$

The solubility products were corrected using activity coefficients ($\gamma_\pm$) calculated from eqn. (2), where a is the solvated radii, A and B are the Debye–Hückel parameters [11] which depend upon the solvent dielectric constant and temperature, and C is the molal solubility

$$\log \gamma_\pm = -\frac{AC^{1/2}}{1 + BaC^{1/2}} \tag{2}$$

Values of A and B were calculated from the experimental dielectric constants of acetonitrile–water mixtures given in ref. 10. The single-ion free energies for halide and alkali metal ions were evaluated by subtracting the free energy values for the tetraphenyl derivatives from the values of the reference cation (Ph_4As^+) and reference anion (Ph_4B^-) using the asymmetric Ph_4AsBPh_4 assumption [10] as explained in eqns. (3) and (4)

$$\Delta_w^s G^\ominus(X^-) = \Delta_w^s G^\ominus(Ph_4AsX) - \Delta_w^s G^\ominus(Ph_4As^+) \tag{3}$$

$$\Delta_w^s G^\ominus(M^+) = \Delta_w^s G^\ominus(MBPh_4) - \Delta_w^s G^\ominus(Ph_4B^-) \tag{4}$$

The results are listed in Table 1.

TABLE 1

Free energies of transfer of some tetraphenyl derivatives and their monovalent single-ion values from water (w) to acetonitrile and acetonitrile–water mixtures at 25 ° C (kJ mol^{-1} in molal scale)

X_s (mole fraction) of acetonitrile)	$KBPh_4$	K^+	$RbBPh_4$	Rb^+	$CsBPh_4$	Cs^+	Ph_4AsCl	Cl^-	Ph_4AsBr	Br^-	Ph_4AsI	I^-
0	0	0	0	0	0	0	0	0	0	0	0	0
0.077	−11.667	−2.511	−12.889	−3.934	−14.898	−5.943	−0.419	13.433	−2.176	11.676	−2.595	11.258
0.128	−18.330	−1.883	−19.460	−3.013	−20.172	−3.725	−0.544	13.852	−3.097	11.299	−4.855	19.251
0.186	−21.807	−4.018	−22.766	−4.896	−23.435	−5.647	−0.669	18.372	−3.934	22.976	−7.533	26.575
0.256	−24.901	−4.227	−25.277	−4.604	−25.194	−4.519	−0.921	21.762	−4.938	17.744	−11.299	11.383
0.292	−26.198	−3.432	−26.533	−3.767	−27.203	−4.436	−0.963	23.855	−5.441	19.460	−13.727	11.090
0.341	−27.286	−2.929	−27.621	−3.264	−27.956	−3.599	−1.046	24.943	−5.859	20.129	−16.824	9.165
0.390	−28.123	−1.967	−28.165	−2.009	−28.793	−2.637	−1.129	26.742	−6.361	21.511	−19.167	8.705
0.446	−28.625	−1.967	−28.625	−1.967	−29.546	−2.888	−1.172	27.956	−6.822	22.306	−20.297	8.830
0.508	−29.044	−1.172	−29.086	−1.214	−30.006	−2.134	−1.256	28.835	−7.282	22.808	−20.841	9.249
0.579	−29.169	−0.167	−29.421	−0.419	−30.551	−1.548	−1.088	30.174	−12.471	18.791	−21.134	10.128
0.661	−29.128	0.837	−29.629	0.335	−30.969	−1.004	−0.544	31.471	−7.784	24.231	−21.259	10.755
0.756	−28.960	1.883	−29.629	1.214	−31.304	−0.460	0.502	33.313	−8.872	23.938	−20.925	11.885
0.868	−28.499	3.222	−28.793	2.929	−31.597	−0.126	2.093	36.200	−9.626	24.482	−18.958	15.149
0.932	−28.165	4.478	−28.165	4.478	−31.722	0.921	3.097	37.623	−10.002	24.524	−17.326	17.200
1.0	−27.705	5.692	−27.035	6.361	−32.015	1.381	5.081	39.339	−10.362	23.913	−14.739	19.536

TABLE 2

Solubilities, solvated radii of Ph_4SbBPh_4 and free energies of transfer of Ph_4SbBPh_4 and Ph_4Sb^+ ion from water (w) to acetonitrile and their mixtures (s) (kJ mol^{-1} in molal scale)

X_s	C	σ_{SPT} (Å)	a (Å)	log $\gamma_\pm$	pK_{sp}	$\Delta^s_w G^\ominus$			
						Ph_4SbBPh_4	Ph_4B^- [a]	Ph_4As^+ [a]	Ph_4Sb^+
0	3.019×10^{-9}	3.854	11.229	-2.810×10^{-5}	17.040	0	0	0	0
0.077	9.333×10^{-8}	4.016	11.378	-1.788×10^{-4}	14.060	−17.012	−8.956	−13.852	−8.056
0.128	1.175×10^{-6}	4.119	11.474	-6.943×10^{-4}	11.861	−29.567	−16.447	−14.396	−13.119
0.186	6.026×10^{-6}	4.238	11.584	-1.747×10^{-3}	10.443	−37.661	−17.869	−19.042	−19.791
0.256	5.129×10^{-5}	4.369	11.706	-5.554×10^{-3}	8.591	−48.232	−20.674	−22.683	−27.558
0.297	9.549×10^{-5}	4.446	11.777	-7.973×10^{-3}	8.056	−51.287	−22.766	−24.817	−28.521
0.341	2.089×10^{-4}	4.526	11.851	−0.0122	7.385	−55.116	−24.357	−25.989	−30.759
0.390	3.631×10^{-4}	4.636	11.953	−0.0168	6.914	−57.803	−26.156	−27.872	−31.647
0.446	5.754×10^{-4}	4.735	12.045	−0.0220	6.524	−60.034	−26.658	−29.128	−33.375
0.508	8.128×10^{-4}	4.839	12.142	−0.0276	6.235	−61.636	−27.872	−30.090	−33.806
0.579	1.072×10^{-3}	4.929	12.223	−0.0333	6.006	−62.988	−29.002	−31.262	−33.986
0.661	1.380×10^{-3}	5.049	12.336	−0.0398	5.799	−64.173	−29.965	−32.015	−34.208
0.756	1.738×10^{-3}	5.189	12.466	−0.0471	5.614	−65.227	−30.843	−32.810	−34.384
0.868	2.512×10^{-3}	5.344	12.610	−0.0584	5.317	−66.956	−31.722	−34.108	−35.200
0.932	3.019×10^{-3}	5.426	12.685	−0.0651	5.170	−67.759	−32.643	−34.526	−35.116
1.0	3.631×10^{-3}	5.512	12.766	−0.0715	5.023	−68.601	−33.396	−34.275	−35.204

[a] Taken from ref. 10.

The solubilities of Ph_4SbBPh_4 determined in mixed acetonitrile–water mixtures are summarized in Table 2. For calculating salt effects in each solvent mixture, activity coefficients are evaluated using the extended form of the Debye–Hückel equation (eqn. (2)). The distance parameter a in each medium is assessed by considering one solvent molecule to be between the cation and anion [15]. This was achieved by adding the radii of the two ions (Ph_4B^- and Ph_4Sb^+) to the diameter of the solvent molecule (scaled particle theory diameter σ_{SPT}). The additive radii for both ions of Ph_4SbBPh_4 was 8.5 Å, taken from ref. 16, whereas the scaled-particle-theory radii of the mixed solvents under consideration were calculated from the partial molar volume σ_o (calculated from density measurements) and by applying the following empirical equation

$$\sigma_{SPT} = 0.9275\sigma_o - 0.8465 \tag{5}$$

Considering the presence of two large spherical organic molecules with low charge density on their surfaces, it is plausible that no significant ion association may take place in solutions. In fact, strong ion–dipole interactions are found to be predominant [13]. From the solubility products of Ph_4SbBPh_4, and by applying eqn. (1), its free energies of transfer, $\Delta^s_w G^\ominus$, from water to mixed acetonitrile–water solvents were calculated and are given in Table 2. On subtracting the free energy values of Ph_4SbBPh_4 from that of Ph_4B^- cited in ref. 10, the free energies of transfer of the reference cation Ph_4Sb^+ were estimated and are also tabulated in Table 2. These values indicate that Ph_4SbBPh_4 is also an asymmetric model for single ion thermodynamics and that the free energies of Ph_4Sb^+ are greater than that of Ph_4As^+, with a difference of about 8%, due to the large size and small effective charge density of the former ion.

The single-ion free energies of transfer of Cl^-, Br^-, I^-, K^+, Rb^+, Cs^+ and Ph_4Sb^+ are presented in Fig. 1. The results in Fig. 1 indicate that alkali metal cations and halide anions are more strongly solvated by water, whereas Ph_4Sb^+ is more strongly solvated by acetonitrile. Positive $\Delta^s_w G^\ominus$ values of halide and alkali metal ions indicate that the dissolution of these ions is not favoured by addition of acetonitrile to water, due to the combined effects of the decreasing dielectric constants of the mixtures and the weak ion-solvating properties of acetonitrile. On the other hand, the ions with at least one large organic ion, i.e. Ph_4Sb^+ generally show negative $\Delta^s_w G^\ominus$ values, suggesting the stabilization of these ions by acetonitrile through dispersion and cavity forces [17]. The observed initial maxima in $\Delta^s_w G^\ominus$–composition profiles can be attributed to the water-structure-breaking ability of acetonitrile. Thus, water monomers and acetonitrile molecules together lead to the formation of intercomponent hydrogen-bonded complexes **I** and **II** [18], resulting in an increased basicity of the hydroxyl oxygen due to the presence of a lone pair of electrons on the nitrogen. The increase

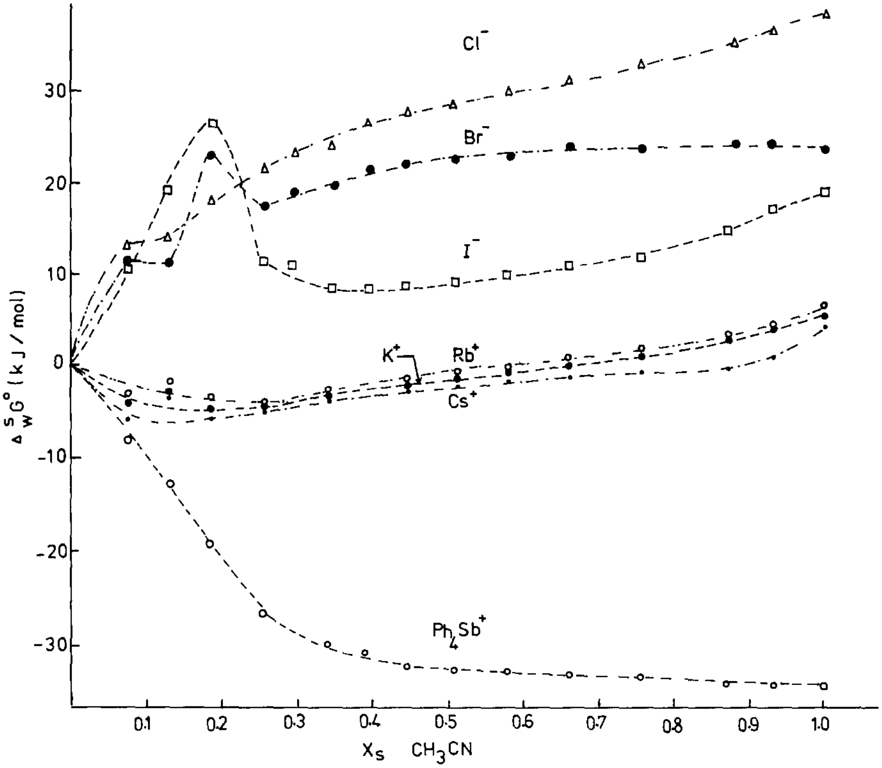
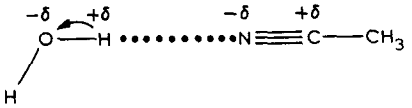


Fig. 1. Free energies of transfer for Cl^-, Br^-, I^-, K^+, Rb^+, Cs^+ and Ph_4Sb^+ from water to mixed acetonitrile–water mixtures at 25 °C.



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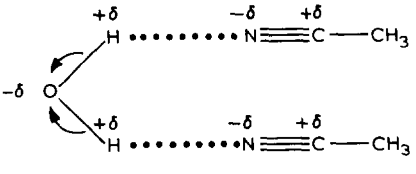
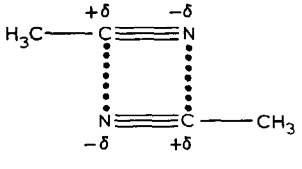


II

in the positive $\Delta^{s}_{w}G^{\ominus}$ values for halide ions at higher acetonitrile contents must be due partly to the significant Born-type electrostatic contributions and partly to the effect of the protophobicity of acetonitrile which may well arise from the possible formation of dimers (**III**), which is supported by IR studies [19,20].



III

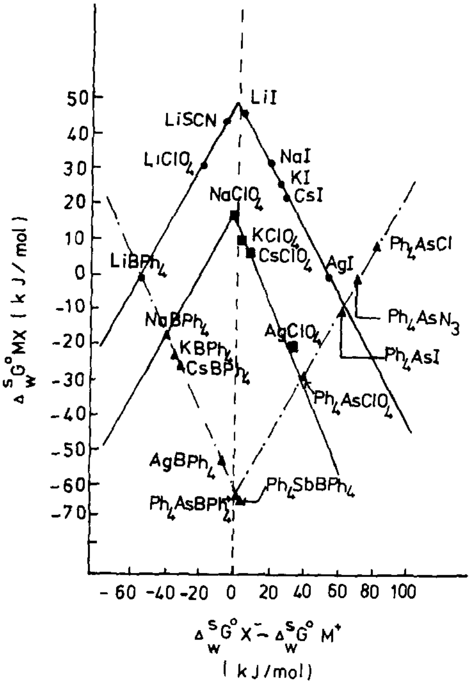


Fig. 2. Volcano–anti-volcano plots of free energies of transfer of various salts from water to acetonitrile as a function of the difference of free energies of transfer of the respective cations and anions.

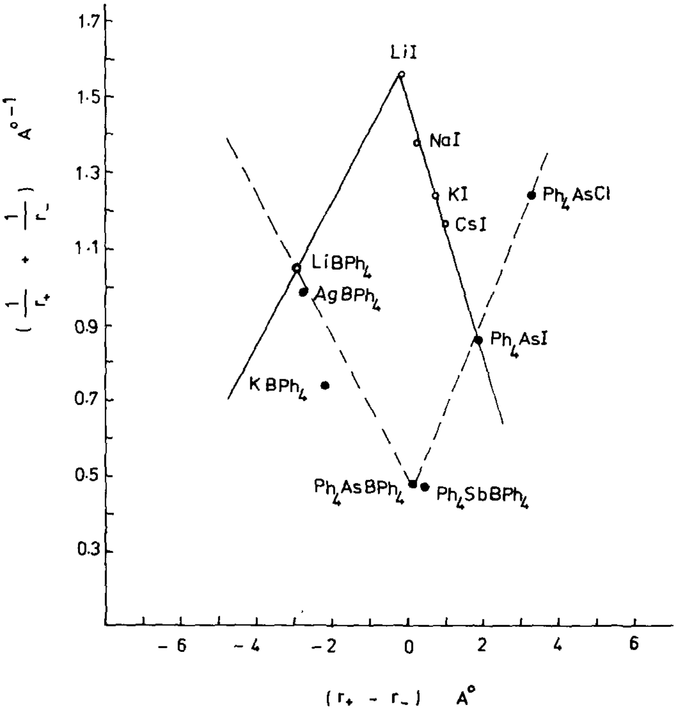


Fig. 3. Plots of the reciprocals of ionic radii (crystal radii in case of lithium salts and van der Waals radii in case of tetraphenyl derivatives) versus the difference in the ionic radii $r_+ - r_-$.

Volcano–anti-volcano-shaped relations between the transfer free energies ($\Delta_{\mathrm{w}}^{\mathrm{s}}G^{\ominus}$) of a series of salts from water to acetonitrile taken from the literature [21–23], and the difference in solvation energies of transfer of ions of the salts estimated by using the asymmetric Ph_4AsBPh_4 assumption in mixed acetonitrile–water solvents are shown in Fig. 2. This relation was first applied by Fajans [24] using hydration energies and therefore is known as Fajan's relation. The relation has a maximum when the difference of the free energy of transfer of the cation and anion approaches zero, with the exception of that of tetraphenyl derivatives which has a minimum (see Fig. 2). Figure 3 shows maxima and minima in plots of $(1/r_+ + 1/r_-)$ versus $r_+ - r_-$ as $r_+ - r_- \rightarrow 0$, which explains the maxima in the case of alkali metal salts and the minima in the case of tetraphenyl derivatives. It can be concluded that the volcano–anti-volcano relations can be readily explained as a result of the sum of two reciprocal functions of the ionic radii r_+ and r_-.

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