Solubilities of Caesium and Thallium(I) Triphenylcyanoboronates and of Caesium and Mercury(II) Tetraphenylboronates in Alcohol + Water Mixtures; Transfer Chemical Potentials of the $BPh_3(CN)^-$, BPh_4^-, Tl^+, and Hg^{2+} Ions

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Solubilities (298.2 K) are reported for caesium and thallium(I) triphenylcyanoboronates in water and in methanol-, ethanol-, and t-butyl alcohol-water mixtures containing up to 40% (by volume) alcohol. Solubilities (298.2 K) are also reported for caesium tetraphenylboronate in t-butyl alcohol– and ethylene glycol–water mixtures and for mercury(II) tetraphenylboronate in t-butyl alcohol–water mixtures, again up to 40% (by volume) alcohol. From these data and published transfer chemical potentials (based on various extrathermodynamic assumptions) for appropriate ions, we have derived estimates for the transfer chemical potentials of $BPh_3(CN)^-$ *and* Tl^+ *to methanol, ethanol, and t-butyl alcohol–water mixtures, for* BPh_4^- *to t-butyl alcohol– and ethylene glycol–water mixtures, and for* Hg^{2+} *to t-butylalcohol–water mixtures.*

Introduction

The potassium, rubidium, caesium, ammonium, thallium(I), and silver(I) salts of the tetraphenylboronate anion are sparingly soluble in water and in water-rich binary aqueous mixtures [1]. They are thus suitable for the estimation of single ion transfer chemical potentials from water into such mixtures via solubility determinations. Moreover the tetraphenylboronate anion plays a central role in the extrathermodynamic assumptions of the type $Ph_4As^+ \equiv Ph_4B^-$ and $R_4N^+ \equiv Ph_4B^-$ used in some methods for obtaining single ion values [2]. However the tetraphenylboronate anion has the disadvantage of being unstable in oxidising [3] and in acidic media [4]. We and others have found that rates of decomposition are too rapid for the determination of solubilities of such salts as $Sn(BPh_4)_2$ and $Pb(BPh_4)_2$ at pHs low enough for the stability of these cations [5], and of $AgBPh_4$ in such acidic solvents as trifluoroethanol [6]. We have managed to determine solubilities of $Hg(BPh_4)_2$ in slightly acidic binary aqueous solvent mixtures by working rapidly [7].

One way of increasing the stability of tetraphenylboronates is by appropriate phenyl-substitution [8]. It is also well established that the triphenylcyanoboronate anion is considerably more robust than the tetraphenylboronate anion in acidic media [9]. It seemed to us that salts of the former anion might prove useful in estimating transfer chemical potentials (Gibbs free energies of transfer) of such ions as Sn^{2+}, Pb^{2+}, and Al^{3+}. However before tackling these ions, it is necessary to establish transfer values for the $BPh_3(CN)^-$ anion, and desirable to compare these with values for BPh_4^-. To this end we report solubilities of the potassium and caesium salts of $BPh_3(CN)^-$ in a variety of alcohol water solvent mixtures (up to 40% by volume alcohol). Thence we have derived estimates for the transfer chemical potentials $\delta_m\mu^\ominus(BPh_3(CN)^-)$, using various authors' values for transfer of alkali metal cations. We have also measured solubilities of $Tl[BPh_3(CN)]$ in some alcohol–water mixtures, thence estimating $\delta_m\mu^\ominus(Tl^+)$ using our estimates for $\delta_m\mu^\ominus(BPh_3(CN)^-)$, and of $Hg[BPh_4]_2$ in t-butyl alcohol water mixtures, thence estimating $\delta_m\mu^\ominus(Hg^{2+})$ using published data for $\delta_m\mu^\ominus(BPh_4^-)$.

Experimental

Salts were prepared by precipitation on mixing aqueous solutions containing stoichiometric amounts of sodium tetraphenylboronate (B.D.H.) or sodium

TABLE I. Transfer Chemical Potentials for Caesium Cyanotriphenylboronate and for the Cyanotriphenylboronate Anion from Water into Aqueous Alcohols; 298.2 K, Molar Scale.

Cosolvent	% v/v	x_2	$Cs[BPh_3(CN)]$		$\delta_m\mu^\ominus(Cs^+)^a$/kJ mol^{-1}				$\delta_m\mu^\ominus(BPh_3(CN)^-)^a$/kJ mol^{-1}			
			10^3 soly^b mol dm^{-3}	$\delta_m\mu^\ominus$ kJ mol^{-1}	I	II	III	IV	I	II	III	IV
Methanol	10	0.047	8.1	−1.2	−0.4	−0.4			−0.8	−0.8		
	20	0.100	9.5	−2.0	−0.1	0			−1.9	−2.0		
	30	0.160	12.8	−3.4	+0.4	+0.7			−3.8	−4.1		
	40	0.229	19.8	−5.6	+1.1	+1.2			−6.7	−6.8		
Ethanol	10	0.033	8.5	−1.4		+0.3	+0.1	+0.2		−1.7	−1.5	−1.6
	20	0.072	12.0	−3.1		+0.8	+0.1	+0.2		−3.9	−3.2	−3.3
	30	0.117	17.1	−4.9		+1.6	0	+0.1		−6.5	−4.9	−5.0
	40	0.171	25.1	−6.8		+2.6	−0.1	+0.2		−9.4	−6.7	−7.0
t-Butyl alcohol	10	0.021	8.4	−1.4	−1.1				−0.3			
	20	0.046	15.6	−4.4	−3.3				−1.1			
	30	0.076	41	−9.2	−3.9				−5.3			
	40	0.113	71	−11.9	−3.3				−8.6			

[a] Column I uses Wells's values (interpolated and converted from the mole fraction to the molar scale) from ref. [23] for methanol and from ref. [26] for t-butyl alcohol; column II uses de Ligny's values, from ref. [24]; values in column III are also derived from ref. [24], but have been recalculated on the assumption $^nBu_4N^+ \equiv BPh_4^-$; values in column IV are derived from Popovych and Dill's data on K^+ and known solubilities of KCl and CsCl. [b] Solubility in water 6.4 × 10^{-3} mol dm^{-3}.

TABLE II. Transfer Chemical Potentials for Thallium Cyanotriphenylboronate and for the Thallium(I) Cation from Water into Aqueous Alcohols: 298.2 K, Molar Scale.

Cosolvent	% v/v	$Tl[BPh_3(CN)]$		$\delta_m\mu^\ominus(BPh_3(CN)^-)^a$ kJ mol^{-1}		$\delta_m\mu^\ominus(Tl^+)^a$ kJ mol^{-1}	
		10^3 soly^b mol dm^{-3}	$\delta_m\mu^\ominus$ kJ mol^{-1}	I	II	I	II
Methanol	10	0.51	−1.8	−0.8		−1.0	
	20	0.65	−2.9	−2.0		−0.9	
	30	0.84	−4.2	−4.0		−0.2	
	40	1.26	−6.2	−6.8		+0.6	
Ethanol	10	0.47	−1.3	−1.7	−1.6	+0.4	+0.3
	20	0.58	−2.4	−3.9	−3.3	+1.5	+0.9
	30	1.07	−5.4	−6.5	−5.0	+1.1	−0.4
	40	2.17	−8.9	−9.4	−6.9	+0.5	−2.0
t-Butyl alcohol	10	0.47	−1.3	−0.3		−1.0	
	20	0.73	−3.5	−1.1		−2.4	
	30	1.92	−8.3	−5.3		−3.0	
	40	3.79	−11.7	−8.6		−3.1	

[a] Column I based on (average) Wells and de Ligny estimates and column II based on (average) large anion ≡ large cation estimates from Table I (columns I and II, III and IV respectively). [b] Solubility in water 0.36 × 10^{-3} mol dm^{-3}.

triphenylcyanoboronate (Pfaltz and Bauer) and of an appropriate caesium, potassium, thallium, or mercury(II) salt. Organic cosolvents were purified by standard procedures [10]; mixed solvents were made up by volume before mixing. Saturated solutions were generated by agitating an excess of solid with the appropriate solvent mixtures in a darkened vessel in a thermostatted water bath. Concentrations were monitored spectrophotometrically (Unicam SP800 or SP8-100 instruments), using published

TABLE III. Transfer Chemical Potentials for Caesium Tetraphenylboronate and for the Tetraphenylboronate Anion from Water into Aqueous Alcohols; 298.2 K, Molar Scale.

Cosolvent	% v/v	$Cs[BPh_4]$		$\delta_m\mu^\ominus(Cs^+)^a$ kJ mol^{-1}	$\delta_m\mu^\ominus(BPh_4^-)$ kJ mol^{-1}
		10^4 soly mol dm^{-3}	$\delta_m\mu^\ominus$ kJ mol^{-1}		
t-Butyl alcohol	10	0.61	−1.29	−1.1	−0.2
	20	1.10	−4.22	−3.3	−0.9
	30	1.92	−6.98	−3.9	−3.1
	40	3.1	−9.40	−3.3	−6.1
Ethylene glycol	10	0.51	−0.40	−0.1	−0.3
	20	0.61	−1.29	−0.1	−1.2
	30	0.77	−2.47	−0.2	−2.3
	40	1.10	−4.22	−0.3	−3.9

[a] Wells's values, interpolated and converted from the mole fraction to the molar scale, from ref. [26] for t-butyl alcohol and from refs. [35, 36] for ethylene glycol.

TABLE IV. Transfer Chemical Potentials for Mercury(II) Tetraphenylboronate and for the Mercury(II) Cation from Water into Aqueous t-butyl alcohol; 298.2 K, Molar Scale.

Cosolvent	% v/v	$Hg[BPh_4]_2$		$2\delta_m\mu^\ominus(BPh_4^-)^a$ kJ mol^{-1}	$\delta_m\mu^\ominus(Hg^{2+})$ kJ mol^{-1}
		10^5 soly mol dm^{-3}	$\delta_m\mu^\ominus$ kJ mol^{-1}		
t-Butyl alcohol	10	5.4	−0.37	−0.4	0
	20	6.9	−2.21	−1.8	−0.4
	30	10.5	−5.39	−6.2	+0.8
	40	14.6	−7.81	−12.2	+4.4

[a] From Table III.

values for the molar absorbance of the tetraphenylboronate anion [11–13]. For the triphenylcyanoboronate anion, which has absorption maxima at 258, 264, and 272 nm, we determined ϵ_{264} = 1100 by calibration using the sodium salt.

Results

Solubilities of the triphenylcyanoboronates of caesium and thallium, and of the tetraphenylboronates of caesium and mercury(II) in various binary aqueous mixtures and in water, in all cases at 298.2 K, are reported in Tables I to IV. The solubility of rubidium triphenylcyanoboronate in water at 298.2 K is 4.0×10^{-2} mol dm^{-3}.

Our value for the solubility of caesium tetraphenylboronate in water, 4.7×10^{-5} mol dm^{-3}, compares very well with Alexander and Parker's value [14] of 4.5×10^{-5} and with McClure and Rechnitz's value [15] of 5.4×10^{-5}. It also compares satisfactorily with values between 2.2 and 3.5×10^{-5} at slightly lower temperatures [16–18]. Again, our check value for potassium tetraphenylboronate, 1.75×10^{-4} mol dm^{-3}, compares very well with Rudorff and Zannier's value [19] of 1.82×10^{-4}, Pflaum and Howick's value [12] of 1.78×10^{-4}, Popovych and Friedman's value [13] of 1.78×10^{-4}, and Parker and Alexander's value [20] of 1.8×10^{-4}. It also compares satisfactorily with Siska's value [18] of 1.35×10^{-4} at 293 K and others at similar temperatures [16, 17]. However McClure and Rechnitz reported [15] a solubility of 2.3×10^{-4} (at 298 K), albeit in a THAM buffer solution rather than simply in water, Popovych and Dill values in the range 2.33 to 2.42×10^{-4} [21], and Tissier a value as high as 3.0×10^{-4} mol dm^{-3} [22].

Discussion

The triphenylcyanoboronates are significantly more soluble than the respective tetraphenylboronates, at any rate in water and in water-rich mixtures. Whether this difference can be assigned to solvation energies of the anions or to lattice energy differences (CN is much smaller than C_6H_5) cannot be decided on present information.

$\delta_m\mu^\ominus(BPh_3(CN)^-)$

We have derived estimates for transfer chemical potentials of the triphenylcyanoboronate anion, $\delta_m\mu^\ominus(BPh_3(CN)^-)$, from measured solubilities of the caesium salt (Table I). We have assumed that the ratio of the mean activity coefficients of the salt in saturated solution in pairs of solvent media is unity. For such a sparingly soluble salt of a large anion in water-rich mixtures this assumption is probably a good one, though it will break down as the proportion of organic cosolvent increases further as both increasing solubility and decreasing dielectric constant will lead to lower activity coefficients.

There are several sources of estimates for $\delta_m\mu^\ominus(Cs^+)$ for transfer into alcohol-water mixtures. For methanol-water mixtures values based on Wells's [23] and on de Ligny's [24] versions of Born-based assumptions agree closely. The same is true for ethanol-water mixtures, but here it is possible to derive two sets of $\delta_m\mu^\ominus(Cs^+)$ values from assumptions of the large cation ≡ large anion type [2]. Popovych and Dill [11] have derived values of $\delta_m\mu^\ominus(K^+)$ using the assumption $^iAm_3{}^nBuN^+ \equiv BPh_4^-$ from which we have calculated $\delta_m\mu^\ominus(Cs^+)$ by applying values of $\delta_m\mu^\ominus(Cs^+) - \delta_m\mu^\ominus(K^+)$ from Gibbs free energies of transfer of pairs of K^+ and Cs^+ salts (values of $\delta_m\mu^\ominus(Cs^+)$-$\delta_m\mu^\ominus(K^+)$ will of course not depend on single ion assumptions, though they may be affected by activity coefficient corrections). Also there are sufficient data in de Ligny's paper on transfer of ions to aqueous ethanol [25] to permit us to calculate $\delta_m\mu^\ominus(Cs^+)$ on the basis of $^nBu_4N^+ \equiv BPh_4^-$. These two sets of values agree closely, but diverge from the Born-based values as the proportion of ethanol increases (Table I). For t-butyl alcohol-water mixtures there are only $\delta_m\mu^\ominus(Cs^+)$ values from Wells [26].

Despite the uncertainties and differences introduced by the existence of various sets of values for $\delta_m\mu^\ominus(Cs^+)$, the overall picture for $\delta_m\mu^\ominus(BPh_3(CN)^-)$ is clear. Values become markedly more negative as the proportion of alcohol increases (Fig. 1), with the usual pattern of dependence on the nature of the alcohol. The $BPh_3(CN)^-$ anion is thus stabilised on transfer from water into these mixtures. Presumably solvation of the phenyl rings by the alcohols dominates over the effects of the minus charge and of the hydrophilic cyanide group [27]. Dominance of organic groups here parallels that observed [27, 28] for such cations as $Fe(phen)_3^{2+}$ and $Fe(bipy)_3^{2+}$. For these, for $BPh_3(CN)^-$, and (see below) for BPh_4^-, the periphery of the complex consists (almost) entirely of hydrophobic aromatic moieties and the small charge is at the centre of a large complex.

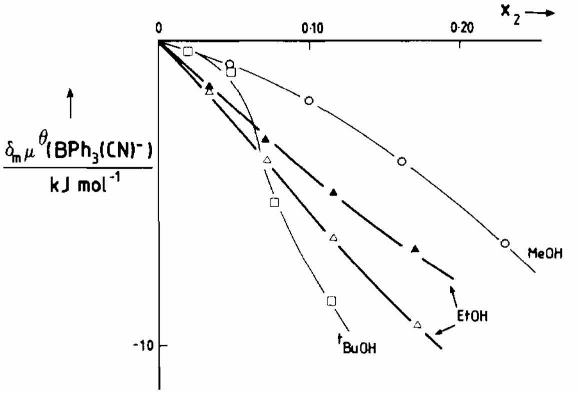

Fig. 1. Transfer chemical potentials for the $BPh_3(CN)^-$ anion from water into alcohol-water solvent mixtures (molar scale; 298.2 K). EtoH: ▲ Table I, cols. III and IV; △ Table I, col. II.

$\delta_m\mu^\ominus(Tl^+)$

Although several authors have derived values for $\delta_m\mu^\ominus(Tl^+)$ between various solvents [29–31], there is very little information relevant to transfer into aqueous mixtures. Table II shows the derivation of $\delta_m\mu^\ominus(Tl^+)$ values from measured solubilities of $TlBPh_3(CN)$. The assumption of unit ratio of activity coefficients can be used with even more confidence here, as solubilities are even lower than for the caesium salt. In view of the closeness of the Wells and de Ligny estimates for $\delta_m\mu^\ominus(BPh_3(CN)^-)$, these have been averaged for use in the "Born" column of Table II, while, for aqueous ethanol, we have averaged the two sets of $\delta_m\mu^\ominus(BPh_3(CN)^-)$ values derived from the similar large ion assumptions $^nBu_4N^+ \equiv BPh_4^-$ and $Ph_4As^+ \equiv BPh_4^-$. The main conclusion reached in Table II is that values of $\delta_m\mu^\ominus(Tl^+)$ are close to zero for transfer to all the water-rich aqueous alcohol media studied here. Trends for $\delta_m\mu^\ominus(Tl^+)$ are compared with those for K^+, Cs^+, Ag^+, and Hg^{2+} (using similar assumptions), and for $BPh_3(CN)^-$ and BPh_4^-, for methanol-water mixtures in Fig. 2. A similar pattern applied for ethanol-water mixtures. The marked similarity of plots for K^+, Cs^+, and Tl^+ is evident, with Ag^+ slightly preferred by the organic cosolvent. The doubly charged Hg^{2+} cation is markedly destabilised by the addition of methanol or ethanol. Transfer of Tl^+ from water into water-rich DMSO-water mixtures is slightly [32] or significantly [33] favourable depending whose experimental data and assumptions are used.

Although Tl^+ seems to be only slightly destabilised, or even stabilised to a small extent, on transfer from water into water-rich alcohol-water

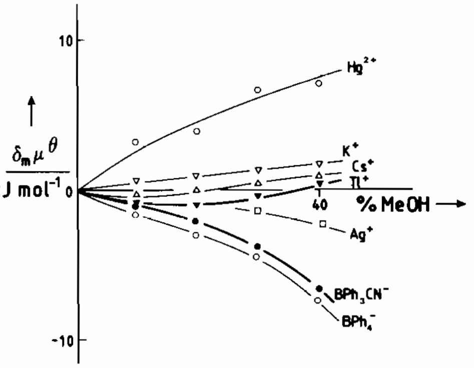

Fig. 2. Transfer chemical potentials for ions from water into methanol-water mixtures (molar scale; 298.2 K; % MeOH by volume).

mixtures, it is markedly destabilised on transfer into pure alcohols. Thus $\delta_m\mu^\ominus(Tl^+)$ = +3.5 [30] or +4.0 [31] kJ mol^{-1} for transfer into methanol, +9.2 kJ mol^{-1} for transfer into ethanol [31].

$\delta_m\mu^\ominus(BPh_4^-)$

Values of $\delta_m\mu^\ominus(BPh_4^-)$ have been estimated for transfer to a wide variety of non-aqueous solvents by many authors, but there are fewer data for transfer to binary aqueous solvent mixtures. Values have been obtained for transfer to aqueous methanol [22], aqueous ethanol [25], and aqueous ethylene glycol [34] using R_4N^+ or $Ph_4As^+ \equiv BPh_4^-$ assumptions, and for transfer to aqueous methanol and aqueous ethanol via $CsBPh_4$ solubilities and Wells's single ion assumptions. In Table III we show the derivation of transfer chemical potentials for the BPh_4^- anion from water into aqueous ethylene glycol and into aqueous t-butyl alcohol from our measurements of $CsBPh_4$ solubilities and Wells's values for transfer of Cs^+ [26, 35, 36].

Table III shows the expected stabilisation of the tetraphenylboronate anion on transfer from water into these binary aqueous alcohols. Alternative estimates for transfer into aqueous ethylene glycol based on the $Ph_4As^+ \equiv BPh_4^-$ assumption are somewhat more negative. Thus, for example, a value of −5.0 kJ mol^{-1} is given for transfer to 30% (by weight) ethylene glycol [34].

$\delta_m\mu^\ominus(Hg^{2+})$

We have previously estimated transfer chemical potentials for the Hg^{2+} cation from water into aqueous methanol and into aqueous ethanol [7]. Table IV reports solubilities of mercury(II) tetraphenylboronate in aqueous t-butyl alcohol and the derivation of $\delta_m\mu^\ominus(Hg^{2+})$ from these solubilities. At first sight it is surprising that this cation is destabilised much less on transfer from water into aqueous t-butyl alcohol than into analogous aqueous methanol or aqueous ethanol solvent mixtures. However this unexpected behaviour can be traced back to the transfer chemical potentials for Cs^+ used, for these (all based on the same assumptions) are generally positive for transfer into aqueous methanol or into aqueous ethanol, but markedly negative for transfer into aqueous t-butyl alcohol. Of course the fact that the mercury(II) cation has a 2+ charge magnifies this odd difference by a factor of two. One should seek to establish reasons for the transfer chemical potential trends for Cs^+ before worrying about those for Hg^{2+}.

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