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Some remarks on the interactions of $NaBPh_4$ and Ph_4PX with solvents

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Abstract

The enthalpies of solution of $NaBPh_4$ in mixtures of water and methanol, *sec*-butanol or dimethyl sulphoxide, and those of Ph_4AsCl in mixtures of water and *sec*-butanol or acetonitrile, as well the density of *sec*-butanol–water mixed solvent, have been measured at a temperature of 298.15 K.

Enthalpic pair interaction coefficients of the organic salt–cosolvent have been calculated (h_{xy}). The relationships $h_{xy} = f(v_{\Phi_{22}})$ for the salts under investigation have been plotted and discussed. It has been confirmed that the interactions of both salts with the mixed solvent, and particularly with water, are different.

INTRODUCTION

In our previous paper [1], we proposed the parameter $v_{\Phi_{22}}$ as a measure of the hydrophobicity of organic solvents. It has been shown that the solvent hydrophobicity is connected with the maximum value of $\Delta H_s^{\ominus}$ ($NaBPh_4$). The standard enthalpy of transfer of $NaBPh_4$ and Ph_4PX or Ph_4AsX (where X is Cl^-, Br^-, I^-) from water to a mixed solvent is often used to calculate ionic contributions of this function [2]. The ionic enthalpies of transfer from water to the mixed solvent [3–19] obtained in this way show strange and, in our opinion, not very probable shapes [3–5] of the relationship $\Delta H_{tr}^{\ominus}(\text{ion}) = f(\text{mol\% organic solvent in water})$. These relationships show minima for anions and maxima for cations which are almost mirror images, and they have been accepted as correct in Abraham et al.'s [15] and Juillard's [14] papers. It seems to us that such extrema for ions result from the method of dividing the enthalpy into ionic fractions, because both organic ions probably affect the solvent in different ways [20].

In the present paper, we have attempted to express the differences in the behaviour of the two organic ions, comparing the interaction coefficients of pairs h_{xy} of these salts and organic solvent in water at 298.15 K.

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EXPERIMENTAL

The enthalpies of solution of $NaBPh_4$ in mixtures of water and methanol (MeOH), *sec*-butanol (*sec*-BuOH) or dimethylosulphoxide (DMSO), and those of Ph_4AsCl in mixtures of water and *sec*-BuOH or acetonitrile (ACN) were measured.

Sodium tetraphenylborate (Fluka pro analysi) was prepared for the investigations as described earlier [4]. Tetraphenylarsonium chloride (Fluka pro analysi) was dried at 373 K under vacuum. The dimethylsulphoxide (pro analysi, REACHIM, USSR), methanol (pro analysi POCH Gliwice, Poland) and *sec*-butanol (pro analysi POCH Gliwice, Poland) used in the study were purified by standard methods [21]. Acetonitrile (pro analysi, PCK, DDR) was purified and dried by means of the method described in the literature [22].

Measurements of the enthalpies of solution of $NaBPh_4$ and Ph_4AsCl were performed using an isoperibol calorimeter [23] at 298.15 ± 0.005 K.

Enthalpies of solution of the electrolyte were measured in the molality (m) range 0.0015–0.0086 mol kg^{-1} of mixed solvent and the content of organic solvent in the mixtures ranged from 1.0 to 4.0 mol% for MeOH and DMSO, from 0.5 to 3.5 mol% for *sec*-BuOH, and from 1.0 to 7.0 mol% for ACN. The estimated experimental error was 0.5%.

The density of the mixed solvent (*sec*-BuOH–water) was measured at 298.15 K in order to calculate the apparent molar volume. Density measurements were carried out using a magnetic densimeter [24]. The measurement

TABLE 1

Molar enthalpies of solution of $NaBPh_4$ in water–methanol mixtures at 298.15 K

$m/(\mathrm{mol\ kg^{-1}})$	$\Delta H_s/(\mathrm{kJ\ mol^{-1}})$	$m/(\mathrm{mol\ kg^{-1}})$	$\Delta H_s/(\mathrm{kJ\ mol^{-1}})$
$x = 1.0$ [a]		$x = 3.0$ [a]	
0.0025	−17.89	0.0028	−13.13
0.0029	−17.86	0.0030	−13.10
0.0033	−17.82	0.0032	−13.09
0.0059	−17.80	0.0062	−13.03
0.0065	−17.76	0.0068	−13.05
0.0069	−17.78	0.0069	−12.90
$x = 2.0$ [a]		$x = 4.0$ [a]	
0.0030	−16.53	0.0032	−10.71
0.0031	−16.51	0.0034	−10.65
0.0033	−16.51	0.0044	−10.62
0.0059	−16.45	0.0063	−10.58
0.0063	−16.44	0.0069	−10.57
0.0066	−16.41	0.0086	−10.55

[a] Mol% of methanol in mixed solvent.

error was $\pm 0.00002\ \text{g cm}^{-3}$. The densimeter was embedded in a thermostat (maintaining the required temperature to within 5×10^{-4} K). The content of *sec*-BuOH in the mixtures ranged from 0.50 to 3.97 mol%.

TABLE 2

Molar enthalpies of solution of $NaBPh_4$ in water–*sec*-butanol mixtures at 298.15 K

$m/(\text{mol kg}^{-1})$	$\Delta H_s/(\text{kJ mol}^{-1})$	$m/(\text{mol kg}^{-1})$	$\Delta H_s/(\text{kJ mol}^{-1})$	$m/(\text{mol kg}^{-1})$	$\Delta H_s/(\text{kJ mol}^{-1})$
$x = 0.5$ [a]		$x = 1.5$ [a]		$x = 3.5$ [a]	
0.0031	−15.89	0.0039	−4.47	0.0039	52.18
0.0037	−15.95	0.0043	−4.41	0.0041	52.23
0.0048	−15.84	0.0043	−4.42	0.0046	52.21
0.0050	−15.78	0.0051	−4.44	0.0047	52.15
0.0051	−15.77	0.0053	−4.43	0.0057	52.36
0.0052	−15.75	0.0063	−4.39	0.0062	52.39
0.0056	−15.78	$x = 2.5$ [a]			
0.0057	−15.81	0.0036	15.51		
$x = 1.0$ [a]		0.0041	15.53		
0.0037	−10.73	0.0042	15.58		
0.0041	−10.70	0.0043	15.60		
0.0045	−10.67	0.0045	15.62		
0.0046	−10.66	0.0050	15.69		
0.0050	−10.63				
0.0056	−10.64				

[a] Mol% of *sec*-butanol in mixed solvent.

TABLE 3

Molar enthalpies of solution of $NaBPh_4$ in water–dimethylsulphoxide mixtures at 298.15 K

$m/(\text{mol kg}^{-1})$	$\Delta H_s/(\text{kJ mol}^{-1})$	$m/(\text{mol kg}^{-1})$	$\Delta H_s/(\text{kJ mol}^{-1})$
$x = 1.0$ [a]		$x = 3.0$ [a]	
0.0024	−15.45	0.0024	−8.98
0.0024	−15.43	0.0026	−8.93
0.0038	−15.42	0.0031	−8.89
0.0049	−15.38	0.0049	−8.92
0.0051	−15.38	0.0052	−8.85
0.0064	−15.32	0.0071	−8.87
$x = 2.0$ [a]		$x = 4.0$ [a]	
0.0030	−12.06	0.0035	−6.18
0.0032	−12.04	0.0039	−6.22
0.0032	−12.04	0.0042	−6.19
0.0056	−11.99	0.0072	−6.16
0.0063	−11.96	0.0073	−6.07
0.0064	−11.96	0.0075	−6.10

[a] Mol% of dimethylsulphoxide in mixed solvent.

TABLE 4

Molar enthalpies of solution of Ph_4AsCl in water–*sec*-butanol mixtures at 298.15 K

$m/(\mathrm{mol\ kg^{-1}})$	$\Delta H_s/(\mathrm{kJ\ mol^{-1}})$	$m/(\mathrm{mol\ kg^{-1}})$	$\Delta H_s/(\mathrm{kJ\ mol^{-1}})$
$x = 0.0$ [a]		$x = 2.5$ [a]	
0.0027	−10.85	0.0022	20.08
0.0027	−10.79	0.0023	20.11
0.0036	−10.75	0.0027	20.16
0.0038	−10.74	0.0031	20.17
0.0039	−10.74	0.0035	20.22
		0.0038	20.19
$x = 1.5$ [a]		$x = 3.5$ [a]	
0.0030	6.85	0.0020	28.58
0.0034	6.91	0.0025	28.62
0.0039	6.99	0.0030	28.69
0.0048	7.05	0.0033	28.68
0.0057	7.09	0.0034	28.79
0.0072	7.17	0.0039	28.72

[a] Mol% of *sec*-butanol in mixed solvent.

TABLE 5

Molar enthalpies of solution of Ph_4AsCl in water–acetonitrile mixtures at 298.15 K

$m/(\mathrm{mol\ kg^{-1}})$	$\Delta H_s/(\mathrm{kJ\ mol^{-1}})$	$m/(\mathrm{mol\ kg^{-1}})$	$\Delta H_s/(\mathrm{kJ\ mol^{-1}})$	$m/(\mathrm{mol\ kg^{-1}})$	$\Delta H_s/(\mathrm{kJ\ mol^{-1}})$
$x = 1.0$ [a]		$x = 4.0$ [a]		$x = 6.0$ [a]	
0.0029	−5.73	0.0016	4.60	0.0011	6.27
0.0030	−5.75	0.0021	4.65	0.0013	6.33
0.0033	−5.70	0.0031	4.62	0.0018	6.31
0.0045	−5.68	0.0044	4.76	0.0029	6.37
0.0049	−5.56	0.0059	4.79	0.0034	6.42
0.0051	−5.49	0.0061	4.78	0.0050	6.47
$x = 2.0$ [a]		$x = 5.0$ [a]		$x = 7.0$ [a]	
0.0015	−1.93	0.0024	5.92	0.0023	5.62
0.0028	−1.95	0.0029	5.97	0.0032	5.67
0.0032	−2.00	0.0031	5.95	0.0037	5.73
0.0034	−1.89	0.0039	5.99	0.0042	5.70
0.0047	−1.64	0.0045	6.05	0.0051	5.76
0.0059	−1.79	0.0053	6.02	0.0060	5.74
$x = 3.0$ [a]					
0.0019	1.88				
0.0025	1.91				
0.0030	1.88				
0.0037	1.94				
0.0049	1.97				
0.0060	1.99				

[a] Mol% of acetonitrile in mixed solvent.

RESULTS AND DISCUSSION

In the literature, we have found values for the standard enthalpies of solution of salts with the organic ions BPh_4^- and Ph_4As^+ or Ph_4P^+ in the mixed solvents MeOH–H_2O [15], DMSO–H_2O [16] and ACN–H_2O [8–10]. There are, however, no $\Delta H_s^\ominus$ data available within the water-rich range necessary to calculate the pair interaction coefficients h_{xy}. Therefore, we have measured the enthalpies of solutions of $NaBPh_4$ in MeOH–H_2O, *sec*-BuOH–H_2O and DMSO–H_2O mixtures (Tables 1–3) and the molar enthalpies of solution of Ph_4AsCl in *sec*-BuOH–H_2O and ACN–H_2O mixtures (Table 4, 5).

The standard enthalpies of solution were calculated from the experimental values of the heats of solution of $NaBPh_4$ and Ph_4AsCl by means of the Debye–Hückel limiting law [25] (Table 6, Fig. 1). The value of $\Delta H_s^\ominus$ of Ph_4AsCl in water, 11.07 kJ mol^{-1}, obtained in this study is in satisfactory agreement with literature data, 10.88 kJ mol^{-1} [11]. The value of the standard enthalpy of solution of $NaBPh_4$ in water has been reported in our previous paper [4] to be 20.02 kJ mol^{-1}.

The pair interaction coefficients h_{xy} were calculated by the method proposed by Perron et al. [26]. Analogous coefficients for the salts under consideration in other aqueous–organic solvents were calculated using literature data for $\Delta H_s^\ominus$ (Table 7).

TABLE 6

Standard enthalpies of solution $\Delta H_s^\ominus$/kJ mol^{-1} of $NaBPh_4$ and Ph_4AsCl in water–organic solvent mixtures and enthalpic pair interaction coefficients h_{xy}/kJ kg mol^{-2} for $NaBPh_4$–non-electrolyte and Ph_4AsCl–non-electrolyte interactions in water at 298.15 K

x [a]	$NaBPh_4$			Ph_4AsCl	
	MeOH	*sec*-BuOH	DMSO	*sec*-BuOH	ACN
0.0	–	–	–	−11.07	–
0.5	–	−16.19	–	–	–
1.0	−18.01	−10.99	−15.59	–	−6.09
1.5	–	−4.60	–	6.61	–
2.0	−16.69	–	−12.21	–	−2.14
2.5	–	14.93	–	19.89	–
3.0	−13.29	–	−9.05	–	1.76
3.5	–	51.80	–	28.35	–
4.0	−10.83	–	−6.37	–	4.47
5.0	–	–	–	–	5.78
6.0	–	–	–	–	6.19
7.0	–	–	–	–	5.49
h_{xy}/(kJ kg mol^{-2})	1.74	4.46	4.18	11.04	4.72

[a] Mol% of organic solvent in mixed solvent.

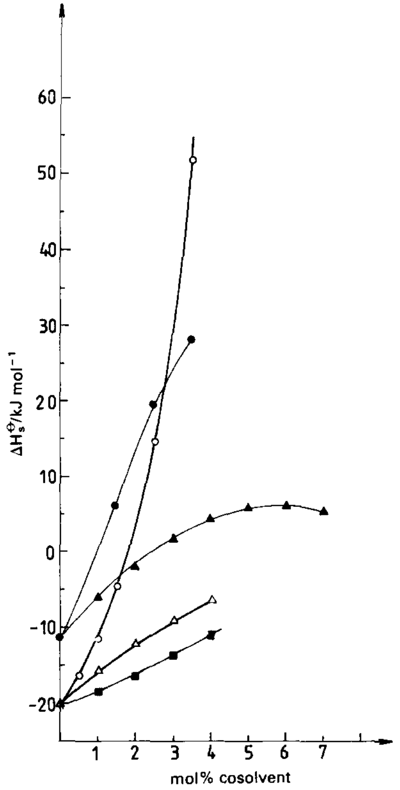

Fig. 1. Standard enthalpies of solution of $NaBPh_4$ in mixtures: ■, $MeOH-H_2O$; △, $DMSO-H_2O$; ○, *sec*-BuOH; and of Ph_4AsCl in mixtures: ●, *sec*-$BuOH-H_2O$; ▲, $ACN-H_2O$ at 298.15 K.

In addition, the density of the mixed solvent *sec*-$BuOH-H_2O$ was measured in order to calculate the molar apparent volume (V_Φ) and $v_{\Phi_{22}}$ of this solvent in water (Table 8).

Using the calculated h_{xy} values for both salts and the $v_{\Phi_{22}}$ value previously reported by us [1], the relationships $h_{xy}(NaBPh_4) = f(v_{\Phi_{22}})$ (Fig. 2) and $h_{xy}(Ph_4PX$ or $Ph_4AsX) = f(v_{\Phi_{22}})$ (Fig. 3) were plotted. Figure 2 shows two straight lines. One of them illustrates the coefficients h_{xy} of the solutions containing alcohols and in this case no dependence of h_{xy} on the alcohol hydrophobicity is observed; the other, representing the coefficients h_{xy} of the solutions containing aprotic solvents, shows a very strong dependence of h_{xy} on the solvent hydrophobicity. Thus, the coefficients h_{xy} for $NaBPh_4$ clearly differentiate the protic and aprotic solvents. In the case of the analogous relationship for Ph_4PX or Ph_4AsX, a common straight line for all the considered systems is observed (Fig. 3). The same figure also shows h_{xy}-(NaI) [28] vs. $v_{\Phi_{22}}$. As can be seen these coefficients are considerably lower than those of the salts containing organic ions. Therefore, we believe that

TABLE 7

Enthalpic pair interaction coefficients h_{xy}/kJ kg mol^{-2} for $NaBPh_4$ and Ph_4PX or Ph_4AsX (where X is Cl^-, Br^-, I^-)–non-electrolyte pairs in water solution at 298.15 K

Solvent	$NaBPh_4$	Ref.	Ph_4AsX or Ph_4PX	Ref.
MeOH	1.74 [a]		3.62	15
EtOH	5.06	12	4.52	12
1-PrOH	4.80	5	5.24	5
2-PrOH	4.26	7	8.80	7
t-BuOH	4.60	14	9.36	14
sec-BuOH	4.46 [a]		11.04 [a]	
THF	10.58	3	7.42	3
Glycerol (G)	2.32	1	–	
F	0.68	27	–	
DMF	3.40	18	4.98	18
DMA	5.68	19	9.62	19
HMPA	30.20	4	13.00	4
DMSO	4.18 [a]		4.38	16
ACN	5.54	1	4.71 [a]	

[a] This work.

TABLE 8

Densities d of *sec*-butanol–water mixtures and apparent molar volumes V_Φ of *sec*-butanol in *sec*-butanol–water mixtures at 298.15 K

x [a]	m/mol kg^{-1}	d/g cm^{-3}	V_Φ/cm^3 mol^{-1}
0.0000	0.00000	0.99707	86.12
0.00496	0.27654	0.99405	85.62
0.01006	0.56433	0.99125	85.27
0.01537	0.86655	0.98838	84.98
0.02022	1.14582	0.98629	84.81
0.02512	1.43031	0.98400	84.74
0.03009	1.72183	0.98135	84.78
0.03513	2.02122	0.97884	84.96
0.03972	2.29609	0.97626	85.25

[a] Mol% of *sec*-butanol in mixed solvent; $v_{\Phi_{22}} = -1.91$ cm^3 kg mol^{-2} was calculated by us or the basis of data given in this table.

the inorganic ions have virtually no effect on the behaviour of the salts containing the organic ions under consideration. Hence, it may be concluded that the reason for the different behaviour of the salts results from the diverse ways that these organic ions interact with solvent. EPR investigations can distinguish clearly between Ph_4As^+ and BPh_4^- in aqueous solution [29, 30]. It seems likely that the charge is distributed more in BPh_4^- than in Ph_4As^+ [20]. Thus, the electrostatic interactions are weaker in the case of BPh_4^-, and

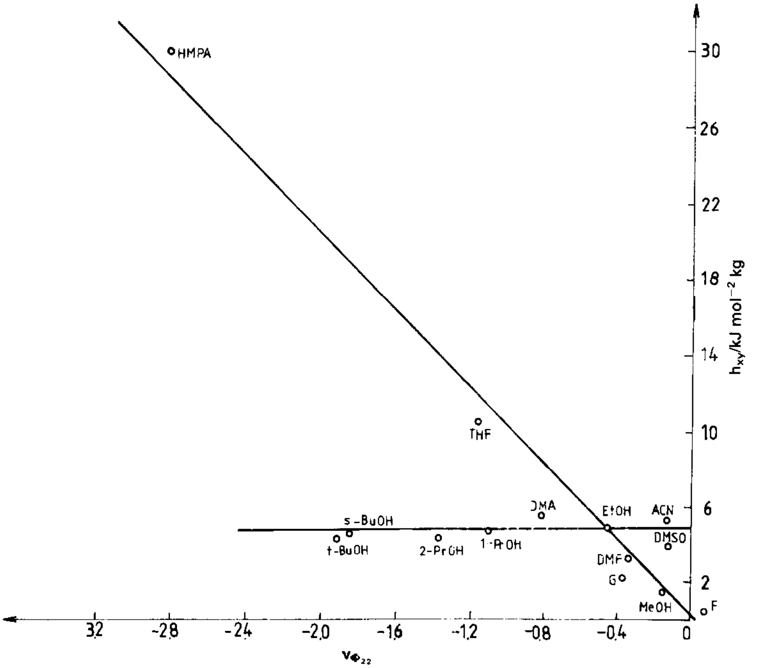

Fig. 2. Enthalpic pair interaction coefficients of $NaBPh_4$–cosolvent vs. appropriate values of $v_{\Phi_{22}}$ for organic solvents in water at 298.15 K.

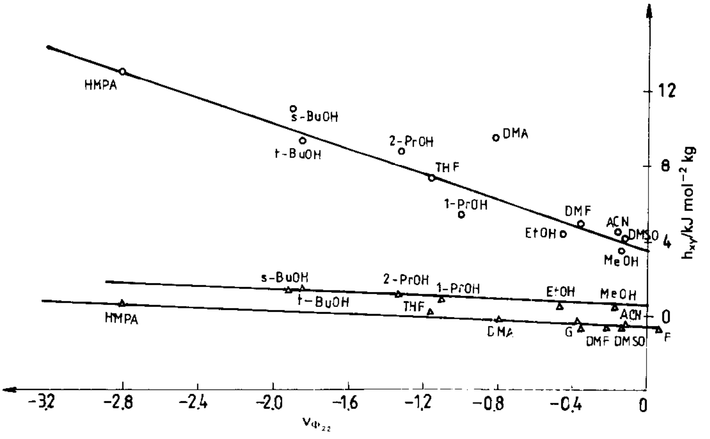

Fig. 3. Enthalpic pair interaction coefficients of Ph_4AsX or Ph_4PX–cosolvent (○) and NaI–cosolvent (Δ) vs. appropriate values of $v_{\Phi_{22}}$ for organic solvents in water at 298.15 K.

therefore the hydrophobic interactions should be more visible than in the case of Ph_4As^+. This conclusion is confirmed by the high maxima of the $\Delta H_s^\ominus$ for $NaBPh_4$ within the water-rich range, which in the case of aprotic solvents are higher than the analogous maxima for Ph_4PX or Ph_4AsX [3, 4, 16, 18, 19].

The IR studies [31, 32] show the quite different behaviours of BPh_4^- and Ph_4P^+ in their interaction with water, notwithstanding their similarity. Both ions show a specific behaviour which is reflected in the heat of transfer of these ions between protic and aprotic solvents [33]. There are many data [20] which show that, in solutions, the solvent molecules near Ph_4As^+ are spectroscopically distinguishable from those molecules near BPh_4^-. Coetzee and Sharp have shown [32, 34] that the molar shift observed in NMR spectra is different for BPh_4^- as compared with other ions.

The difference in behaviour of these ions is likely to result from their different charge distributions. The conclusion concerning the different interactions of the ions BPh_4^- and Ph_4As^+ or Ph_4P^+ with solvent seems very probable. This is another demonstration that the TPTB method should not be used to divide the standard enthalpy of transfer into ionic fractions, particularly in water–organic solvent mixtures.

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