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Enthalpies of transfer of several ions from water to water–*n*-propanol mixtures at 298.15 K

Małgorzata Jóźwiak, Bożenna Nowicka and Stefania Taniewska-Osińska
Department of Physical Chemistry, University of Łódź, ul Nowotki 18, 91-416 Łódź (Poland)

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Abstract

Measurements were made of the dissolution heats of $NaBPh_4$ and Ph_4PCl in water–*n*-propanol mixtures over the whole range of compositions. Assuming the equality of $\Delta H_{tr}^{\ominus}(Ph_4P^+)$ and $\Delta H_{tr}^{\ominus}(BPh_4^-)$, the transfer enthalpies of several ions from water to water–*n*-propanol mixtures at 298 15 K were calculated

INTRODUCTION

The interactions of ions with solvents can be better understood when we know the ionic contributions of the considered thermodynamic function. So far, the ionic enthalpies of transfer are known in water–methanol [1], water–ethanol [2] and water–*tert*-butanol [3], but not in mixtures with other alcohols.

In this paper we describe the behaviour of ions in aqueous solutions of *n*-propanol on the basis of the dependence of the ionic transfer enthalpies on the composition of the mixed solvent. It is difficult to choose an extra-thermodynamic division criterion that would not be criticised by other authors. The most popular one is based on an equality of the transfer enthalpy or other functions of BPh_4^- and Ph_4P^+ ions [4–9]. In order to employ this criterion, we measured the enthalpy of solution of $NaBPh_4$ and Ph_4PCl in water–*n*-propanol mixtures.

EXPERIMENTAL

Sodium tetraphenylborate and tetraphenylphosphonium chloride (Fluka, pro analysi) were prepared for the investigations as described earlier [10]. The solvents used were *n*-propanol (Merck, pro analysi) and water (twice distilled).

Mixtures of water with *n*-propanol were pretreated by weight. The heat of solution measurements were carried out using the "isoperibol" calorimeter [11]. The salt concentrations in solutions did not exceed 3×10^{-3} mol kg^{-1} of solvent over the whole range of mixed solvent compositions.

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TABLE 1

Standard enthalpies of solution of $NaBPh_4$ and Ph_4PCl in water–n-propanol mixtures at 298.15 K

n-Propanol (mol %)	$\Delta H_s^{\ominus}$ (kJ mol^{-1})	
	$NaBPh_4$	Ph_4PCl
0.0	−20.00	−8.37
1.5	−10.21	
2.5	−1.84	13.05
3.5	8.74	23.74
5.0	27.45	28.74
6.0	32.09	30.29
7.5	23.18	26.99
10.0	7.74	23.30
20.0	−9.08	17.87
40.0	−15.31	11.80
60.0	−20.79	8.49
80.0	−25.56	5.15
100.0	−29.58	3.31
	−33.01 ± 0.8 [a]	1.05 [b]

[a] Value obtained experimentally by Abraham et al. [13].

[b] Value calculated from the ionic contributions given by Abraham et al. [13].

RESULTS AND DISCUSSION

The standard enthalpies of solution were calculated from the experimental values of the heats of solution of $NaBPh_4$ and Ph_4PCl by means of the

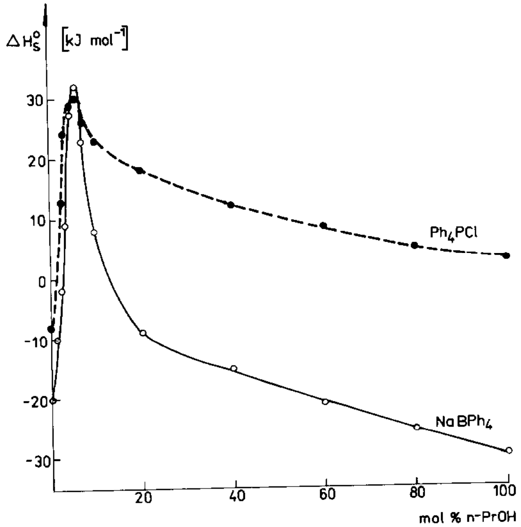

Fig. 1. Standard enthalpies of solution of $NaBPh_4$ and Ph_4PCl in water–n-propanol mixtures at 298.15 K as a function of mol.% n-propanol.

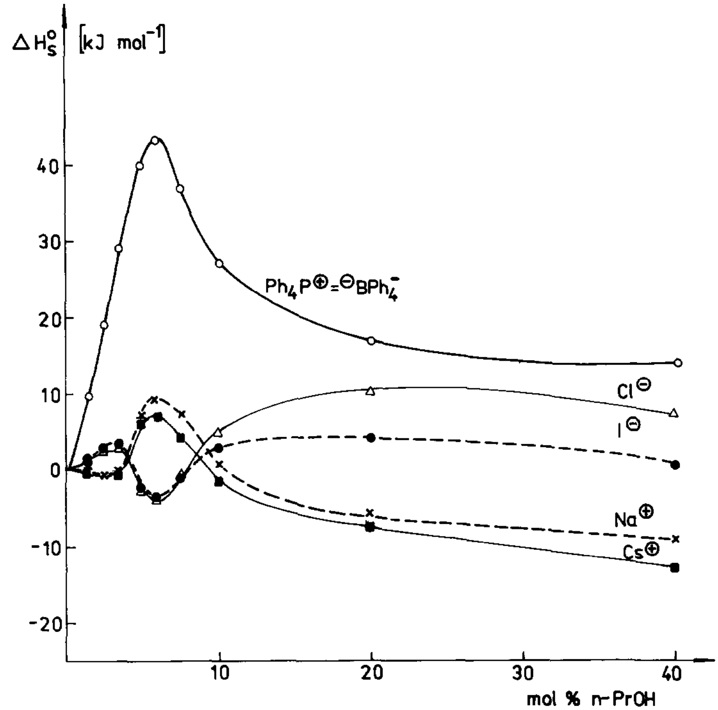

Fig. 2. Ionic enthalpies of transfer from water to water–*n*-propanol mixtures at 298.15 K as a function of mol.% *n*-propanol.

Debye–Hückel limiting law [12] (Table 1, Fig. 1). The $\Delta H_s^{\ominus}$ values obtained for both salts in water agree well with the data published earlier [10,14] but those corresponding to pure *n*-propanol were more endothermic than the

TABLE 2

Ionic enthalpies of transfer from water to water–*n*-propanol mixtures at 298.15 K

n-Propanol (mol.%)	$\Delta H_{tr}^{\ominus}$ (kJ mol^{-1})				
	$BPh_4^- = Ph_4^+$	Na^+	Cs^+	Cl^-	I^-
1.5	9.71 [a]	0.08	0	0.96	1.26 [a]
2.5	19.08	−0.92	−1.21	2.76	3.10 [a]
3.5	29.16	−0.42	−0.96	3.10	3.43 [a]
5.0	40.46	6.99	6.11	−2.72	−2.72
6.0	43.10	9.00	7.11	−4.02	−3.85
7.5	36.40	6.78	4.44	−0.59	−1.67 [a]
10.0	27.24	0.50	−1.72	4.90	3.10
20.0	16.82	−5.90	−7.57	9.87	4.39 [a]
40.0	13.89	−9.20	−13.31	6.69	0.42 [a]

[a] Values calculated from $\Delta H_s^{\ominus}$, obtained by the interpolation of the data included in this work and in ref. 19

$\Delta H_s^\ominus$ values reported by Abraham et al. [13]. As can be seen in Fig. 1, the standard enthalpies of solution of $NaBPh_4$ and Ph_4PCl exhibit maxima corresponding to 6 mol.% of *n*-propanol. These maxima are much higher and sharper than those shown by inorganic salts. They were also observed for other water–organic mixtures [1,3,10,14–17] and have been attributed to the hydrophobic hydration effect [10,14].

The transfer enthalpies of tetraphenylphosphonium tetraphenylborate, $\Delta H_{tr}^\ominus(Ph_4PPh_4B)$, were obtained from the values of $\Delta H_s^\ominus(NaBPh_4)$ and $\Delta H_s^\ominus(Ph_4PCl)$, as well as from the $\Delta H_s^\ominus(NaCl)$ values obtained from previous work published from our laboratory [18]. The standard enthalpies of solution for NaI [19] and CsI [20] needed for the determination of the ionic enthalpies, were found in the literature.

The transfer enthalpies of $BPh_4^- = Ph_4P^+$ and of some inorganic ions from water to mixtures of water with *n*-propanol, are presented in Fig. 2 and Table 2. As can be seen in Fig. 2, the $\Delta H_{tr}^\ominus$ plots for cations are different from those for anions. The endothermic maxima of the transfer enthalpies of cations and the minima of the anions correspond to contents of 6 mol.% of *n*-propanol in the mixture. Therefore the positions of the extrema of $\Delta H_{tr}^\ominus$ for individual ions do not depend on the nature of the ions present, but reflect a feature of the mixtures.

The similar composition of the water–*n*-propanol mixture corresponds to a minimum of the heat of mixing (5 mol.% of *n*-propanol, according to Lama and Lu [21] or 10 mol.%, according to Marongiu et al. [22]); this probably indicates the greatest hydrophobic hydration of alcohol by water.

The same criterion of sharing enthalpy for ions was apparent in water with methanol [1] and with *tert*-butanol [3], as well as in other organic solvents, i.e. totally different $\Delta H_{tr}^\ominus$ plots for cations and anions, similar to those observed in the system under consideration. These functions in the range of extrema resemble the mirror reflections for transfer enthalpies of positive and negative ions. Taking into account the absence of this strange phenomenon in the case of organic–organic binary solvents [23], it can be concluded that water is responsible for the strong extrema.

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