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Correlation of transfer enthalpies of Ph_4PCl from water to water–organic mixtures with parameters describing organic cosolvent properties

Stefania Taniewska-Osińska, Bożenna Nowicka and Anetta Pietrzak
Department of Physical Chemistry, University of Łódź, 91-416 Łódź, Pomorska 18 (Poland)

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Abstract

Heats of solution of Ph_4PCl in mixtures of water with ethanol and with acetone in the water-rich range have been measured at 25 °C. The obtained standard enthalpies of solution have been put together with $\Delta H_s^{\ominus}$ of Ph_4PCl and $NaBPh_4$ in various water–organic mixtures examined earlier by us and by other authors. The dependence of transfer enthalpies of Ph_4PCl corresponding to $\Delta H_{tr}^{\ominus}$ maxima on parameters characterizing the cosolvent features, π^* and β has been found.

INTRODUCTION

For a long time in our laboratory measurements of solution enthalpy of electrolytes in water–organic mixed solvents have been performed. The data obtained together with the literature data prove the appearance of maxima of the solution enthalpies of electrolytes containing at least one organic ion (Ph_4P^+ or Ph_4B^-) in all water–organic binary solvents. As we suppose [1] the mentioned maxima seem to have a physical sense and in the mixed solvents, whose compositions correspond to these maxima, the change of structure may occur or the maximum of hydrophobic hydration takes place.

In this work we have tried to correlate the transfer enthalpies of the chosen electrolyte $\Delta H_{tr}^{\ominus}$ from water to the mixed solvents where $\Delta H_{tr}^{\ominus}$ reach maximum values $(\Delta H_{tr}^{\ominus})^{max}$ with properties of organic components of binary solvents.

We have measured here previously unknown heats of solution of Ph_4PCl, i.e. salt with organic cation, in mixtures of water with ethanol and with acetone.

EXPERIMENTAL

Tetraphenylphosphonium chloride (Fluka, pro analysis) and the solvents, ethanol and acetone (produced by POCh Gliwice, Poland) were prepared for experiments in the way described earlier [2–4].

The measurements of heat of solution of Ph_4PCl in the mixed solvents containing from 0 to 20 mol% nonelectrolytes were performed in an "isoperibol" calorimeter [5]. Concentrations of salt did not exceed 0.003 mol kg^{-1} of solvent.

RESULTS AND DISCUSSION

Standard enthalpies of solution of Ph_4PCl in the selected two mixed solvents were determined from the experimentally obtained integral heats of solution using the Debye–Hückel limiting law [6]. The $\Delta H_s^\ominus$ values are included in Table 1 and Fig. 1 as a function of mixed solvent compositions. In the mixtures selected for the research $\Delta H_s^\ominus$ of Ph_4PCl exhibits maxima in the water-rich range corresponding to 12 mol% of ethanol and to 9 mol% of acetone.

As can be observed, positions of $\Delta H_s^\ominus$ maxima for salts with an organic cation (Ph_4P^+) are the same as the analogous ones for $NaBPh_4$, i.e. salt with an organic anion [7–9]. The maxima of $\Delta H_{tr}^\ominus$ for $NaBPh_4$ are higher than those for Ph_4PCl in all mixed solvents under consideration (Table 2). This difference may result from different interactions of ions Na^+ and Cl^- with mixed solvents. However the opposite sign of charge of Ph_4P^+ and Ph_4B^- ions may play a role, but it seems the most important reason for the difference between the solution enthalpy of the two chosen salts (with organic cation or anion) comes from unequal distribution of charges on the two organic ions discussed [10].

With the aim of finding the effect of the organic cosolvent properties on the enthalpy of transfer of Ph_4PCl $(\Delta H_{tr}^\ominus)^{max}$ from water to mixed solvent compositions corresponding to maxima, the Abraham–Kamlet–Taft equa-

TABLE 1

Standard enthalpy of solution of Ph_4PCl [a] in water–ethanol and water–acetone mixtures at 25 °C

Organic solvent (mol%)	$\Delta H_s^\ominus$ (kJ mol^{-1})	
	Water–ethanol	Water–acetone
2.5		3946
5.0	16477	10418
7.5	21707	13288
10.0	25443	13552
12.5	26255	
15.0	23548	11485
20.0	18054	9983

[a] $\Delta H_s^\ominus(Ph_4PCl)$ in water is −8.79 kJ mol^{-1} [2].

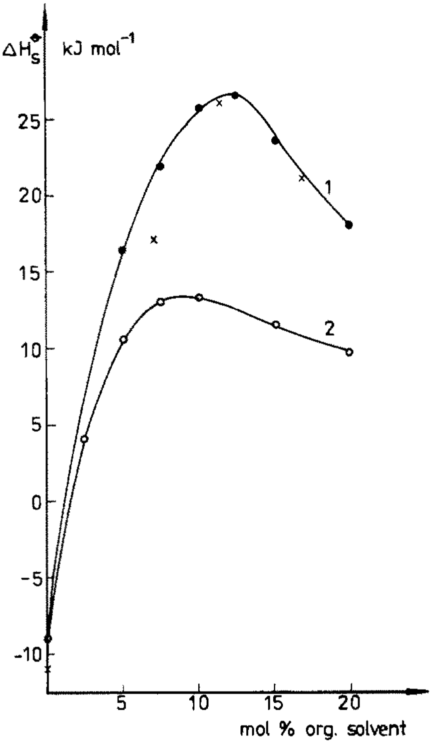

Fig. 1. Standard enthalpies of solution, $\Delta H_s^\ominus$, of Ph_4PCl in water–ethanol (1) and water–acetone (2) mixtures at 25 ° C; ×, $\Delta H_s^\ominus$ of Ph_4AsCl determined by Arnett et al. [7].

tion [18] was used. It was found that the acidity and the cohesive energy density of organic solvents do not influence the total variation of $(\Delta H_{tr}^\ominus)^{max}$.

Therefore, in the case of the transfer enthalpies of Ph_4PCl from water to

TABLE 2

Enthalpies of transfer (kJ mol^{-1}) of Ph_4PCl and $NaBPh_4$ from water to water–organic mixtures (at maximum)

Organic solvent	Ph_4PCl	$NaBPh_4$
Methanol	26.44 [11]	32.68 [11]
Ethanol	35.05	45.43 [8]
n-Propanol	38.66 [12]	52.09 [12]
i-Propanol	39.08 [13]	60.59 [13]
t-Butanol	41.58 [a] [14]	67.93 [14]
Acetone	22.34	28.03 [9]
Tetrahydrofuran	27.23 [2]	56.57 [2]
Hexamethylphosphortriamide	26.45 [15]	59.68 [15]
Sulpholane	6.07 [b] [16]	10.04 [16]
Acetonitrile	16.97 [a] [17]	19.33 [17]

[a] $(\Delta H_{tr}^\ominus)^{max}$ for Ph_4AsCl.

[b] Value calculated using the ionic contributions.

TABLE 3

Coefficients of the equation $(\Delta H_{tr}^{\ominus})_0^{max} = (\Delta H_{tr}^{\ominus})_0^{max} + s\pi^* + b\beta$ and percentage contributions of selected properties of solvents to variation of $(\Delta H_{tr}^{\ominus})^{max}$

	Ph_4PCl	$NaBPh_4$
$(\Delta H_{tr}^{\ominus max})_0$	39.67 ± 3.67	27.00 ± 16.88
s	40.34 ± 3.38	−34.69 ± 15.54
b	20.28 ± 2.56	55.00 ± 11.76
r	0.9930	0.9473
Disp.	1.7690	8.1346
n	11	11
π^*(%)	59.3	28.9
β (%)	39.3	60.8

n, Number of solvents (water and ten mixed solvents).

ten different water–organic mixtures (at maximum), the Abraham–Kamlet–Taft correlation equation could be limited to the following case:

$$\left(\Delta H_{tr}^{\ominus}\right)^{max} = \left(\Delta H_{tr}^{\ominus}\right)_0^{max} + s\pi^* + b\beta \qquad (1)$$

where π^* is a parameter designating the solvent dipolarity/polarizability and β denotes basicity parameter of the organic solvent. The obtained values of the coefficients *s* and b, the regression coefficient *r* and the relative contributions of the individual parameters to the variation of $(\Delta H_{tr}^{\ominus})^{max}$ are collected in Table 3.

From the high correlation coefficient ($r = 0.9930$) it may be inferred that eqn. (1) describes the analyzed function well. Therefore, the dominant effects in the transfer enthalpy are the basicity and the solvent dipolarity/polarizability. For the comparison we performed the same analysis for $(\Delta H_{tr}^{\ominus})^{max}$ of $NaBPh_4$, the salt with the organic anion. The application of eqn. (1) for ten mixed solvents gives the correlation with the regression coefficient $r = 0.9473$ (Table 3, third column).

As can be seen in Table 3, the relative contribution of solvent dipolarity/polarizability illustrated by π^* dominates the contribution of the solvent basicity (β) for the transfer enthalpy of Ph_4PCl. The opposite situation is true for $\Delta H_{tr}^{\ominus}$ of $NaBPh_4$. This difference may come not only from the different interactions of inorganic ions with solvents but also from the unequal distribution of the charge on the surfaces of two organic ions under discussion. Therefore the organic ion–solvent interactions are different.

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