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Enthalpies of transfer of selected ions from water to water–propan-2-ol mixtures. Some quantum chemical aspects of the ionic solvation

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Abstract

The enthalpies of solution of $NaBPh_4$ and Ph_4PCl in mixtures of water with propan-2-ol have been measured at 25°C over the whole range of compositions. The ionic enthalpies of transfer from water to this mixed solvent have been determined based on the assumption of the equality of $\Delta H^{\ominus}_{tr}(Ph_4P^+)$ and $\Delta H^{\ominus}_{tr}(BPh_4^-)$. The semi-empirical MNDO method was used for calculating the net charges after geometry optimization of the BPh_4^- and Ph_4P^+ ions. Some conclusions concerning the solvation of individual ions are presented.

INTRODUCTION

A number of methods have been proposed for the division of transfer enthalpies of electrolytes into ionic contributions [1]. Critical studies have also been carried out in order to verify the extrathermodynamic splitting criteria [2–5]. The Ph_4PPh_4B (TPTB) assumption based on the suggestion of similar interactions of the organic ions Ph_4P^+ and BPh_4^- with solvents is still the most popular because no convincing evidence countering its validity has been found. This criterion of splitting $\Delta H^{\ominus}_{tr}$(salt) was applied, for example, to electrolytic solutions in water with some alcohols and aprotic solvents [6–10]. We have used the same TPTB method for determining the unknown ionic enthalpy of transfer from water to mixtures of water with propan-2-ol. To do this, we measured the solution enthalpies of $NaBPh_4$ and Ph_4PCl in the water–propan-2-ol mixtures.

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EXPERIMENTAL

Sodium tetraphenylborate and tetraphenylphosphonium chloride (Fluka, pro analysis) were prepared for the experiments in the way described earlier [4]. The solvents, propan-2-ol (Merck, pro analysis) and water (twice distilled), were purified using standard procedures [11]. All mixtures of water with propan-2-ol were prepared by weight. The measurements of solution heat were performed in an "isoperibol" calorimeter [12]. The salt concentrations in the solutions did not exceed 3×10^{-3} mol kg^{-1} of solvent over the whole range of mixed solvent compositions.

RESULTS AND DISCUSSION

The standard enthalpies of solution obtained from the experimental values of the solution heats of $NaBPh_4$ and Ph_4PCl by means of the Debye–Hückel limiting law are presented in Table 1 and Fig. 1.

As can be seen, the standard enthalpies of $NaBPh_4$ and Ph_4PCl solution exhibit maxima corresponding to 7.5 mol.% of propan-2-ol. The maxima, as with those observed in the water–organic mixtures investigated so far [4, 6–11], are higher than those for inorganic electrolytes. These maxima are attributed to the interactions of BPh_4^- and Ph_4P^+ ions with water molecules (hydrophobic hydration effect).

The enthalpies of transfer of Ph_4PPh_4B were calculated using the obtained values of $\Delta H_S^\ominus(NaBPh_4)$ and $\Delta H_S^\ominus(Ph_4PCl)$, and the literature

TABLE 1

Standard solution enthalpies of $NaBPh_4$ and Ph_4PCl in water–propan-2-ol mixtures at 25°C

Mol.% of propan-2-ol	$\Delta H_S^\ominus$/kJ mol^{-1}	
	$NaBPh_4$	Ph_4PCl
0.0	−19.91[a]	−8.79[a]
2.5	2.01	9.59
5.0	25.15	27.99
7.5	40.68	30.29
10.0	25.64	23.51
15.0	8.00	18.91
20.0		16.77
30.0	−8.20	11.76
40.0	−10.83	8.91
60.0	−15.46	3.87
80.0	−17.70	2.45
90.0	−18.35	1.51
100.0	−18.22	1.99

[a] Values agree with the data published earlier [4].

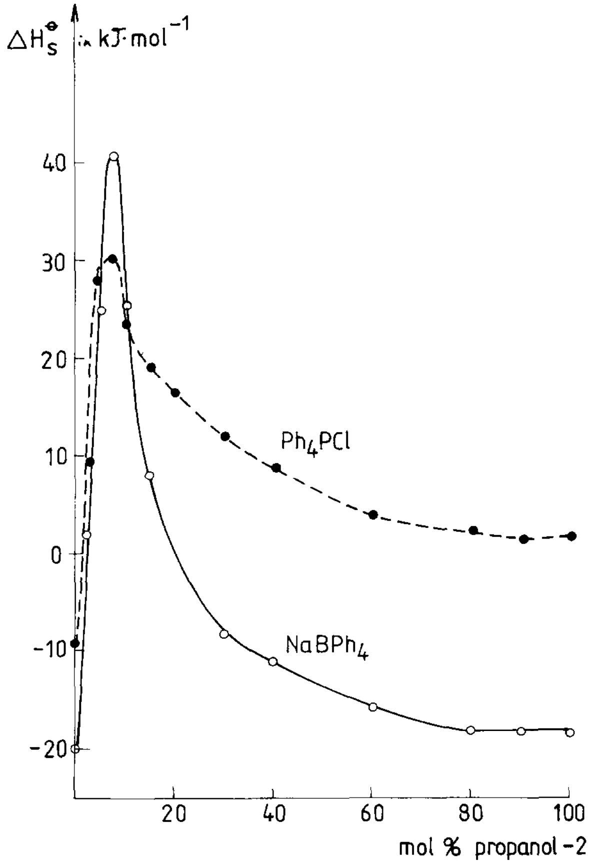

Fig. 1. Standard enthalpies of solution of $NaBPh_4$ and Ph_4PCl in water–propan-2-ol mixtures at 25°C.

data on the enthalpies of NaCl solution in water–propan-2-ol mixed solvent [13]. The ionic contributions of $\Delta H_{tr}^\ominus$ are presented in the Table 2.

TABLE 2

Ionic enthalpies of transfer from water to water–propan-2-ol mixtures at 25°C

Mol.% of propan-2-ol	$\Delta H_{tr}^\ominus$/kJ mol^{-1}			
	$BPh_4^- = Ph_4P^+$	Na^+	Cl^- [a]	I^- [a]
2.5	18.91	3.01	−0.53	−0.18
5.0	38.43	6.63	−1.65	−1.10
7.5	46.28	14.31	−7.20	−7.28
10.0	35.59	9.96	−3.28	−3.59

[a] Values calculated from $\Delta H_S^\ominus$, obtained by the interpolation of the data given by Piekarski [13, 14].

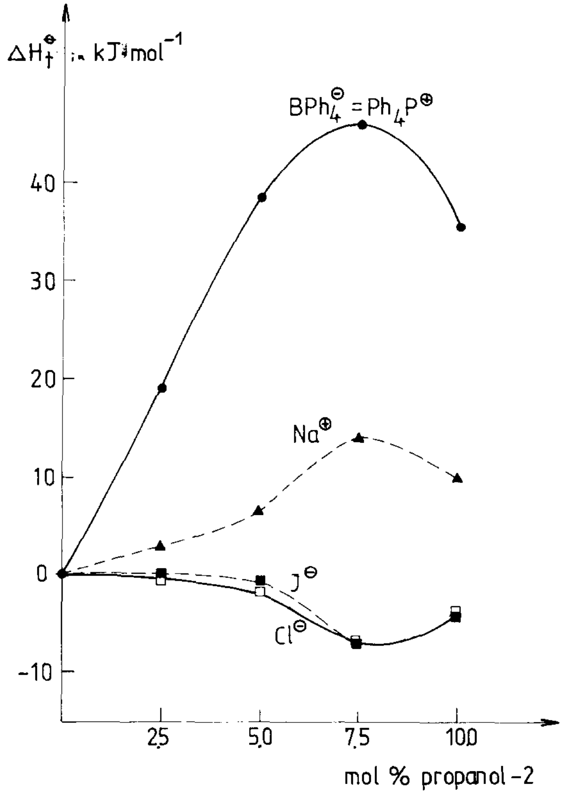

Fig. 2. Enthalpies of transfer of ions from water to water–propan-2-ol mixtures at 25°C.

The plots of $\Delta H_{tr}^{\ominus}$ for the ions (Fig. 2) indicate that the cations and anions in the investigated mixtures behave differently. Enthalpy minima for anions and maxima for cations are observed. The position of the $\Delta H_{tr}^{\ominus}$ extrema for individual ions does not depend on the nature of the ion, and it corresponds to 7.5 mol.% of propan-2-ol in the mixture.

Completely different $\Delta H_{tr}^{\ominus}$ plots for inorganic cations and anions, similar to those obtained in the system under consideration, can be observed in mixtures of water with various classes of solvents when the TPTB splitting method is used.

In our earlier works [4, 15], it was suggested that the character of the enthalpy of transfer function for organic and inorganic ions is determined by the shape of the curves of solution enthalpy for $NaBPh_4$ and Ph_4PCl.

These observations, as well as the results of investigations of aqueous and non-aqueous solutions of $NaBPh_4$ and Ph_4PCl salts by means of different experimental techniques [16–18], indicate the necessity of verifying the accuracy of the assumption concerning the similar solvation of Ph_4P^+ and BPh_4^- ions.

In order to identify an identical or different solvation ability of the organic ions mentioned above, we tried to apply a quantum-chemical approach, namely, the MNDO semi-empirical method [19, 20] which was used to calculate the electronic net charge distribution of these ions. The net charge maps allow an analysis which is at least qualitative, of the solvation mechanism of the ions, in both single and mixed water–propan-2-ol solvents.

In Fig. 3, we present the net charge distribution in each of the four benzene rings included in the BPh_4^- and Ph_4P^+ ions (Figs. 3(a) and 3(c), respectively), with respect to the single benzene molecule (Fig. 3(b)). The numbering of the carbon and hydrogen atoms is the same in all three benzene rings in Fig. 3.

As a numerical measure of the charge transfer in the benzene rings of the BPh_4^- and Ph_4P^- ions in relation to that of a normal benzene molecule, the shift of the net charge $\Delta q_i^a = q_i^a(\text{ion}) - q_i^a(\text{benzene})$, was introduced, where q_i^a is the net charge, and i is the number of the atom, as indicated in Fig. 3.

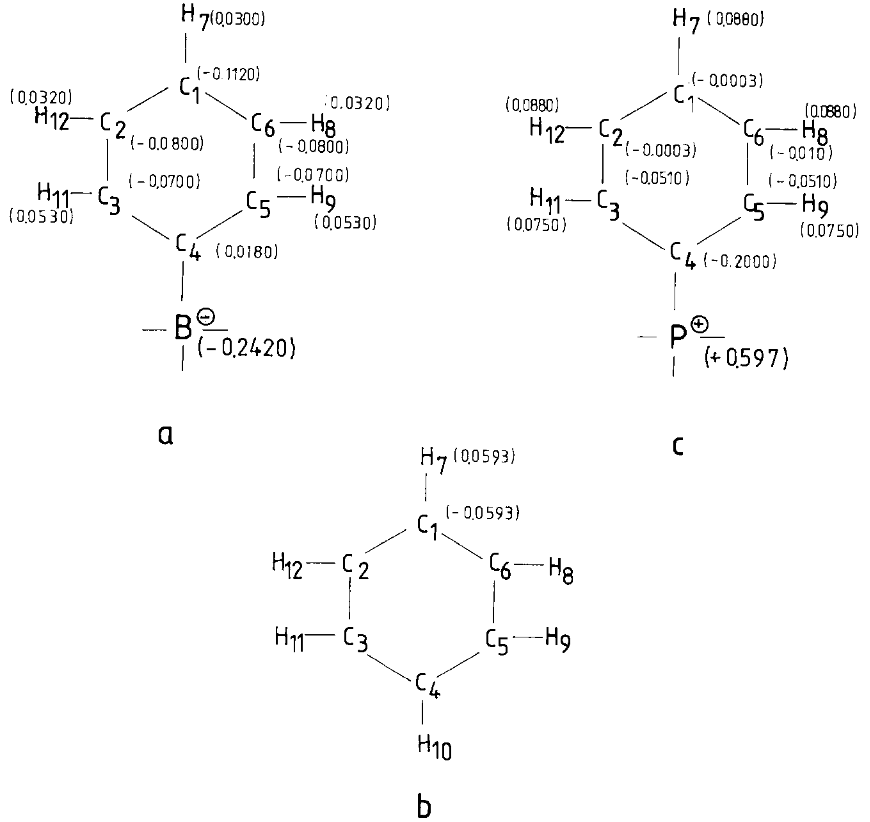

Fig. 3. Net charge distributions in the benzene rings of (a) BPh_4^- ion, (b) in a single benzene molecule, and (c) Ph_4P^+ ion. Net charges for other carbon and hydrogen atoms are the same as for C_1 and H_7, respectively.

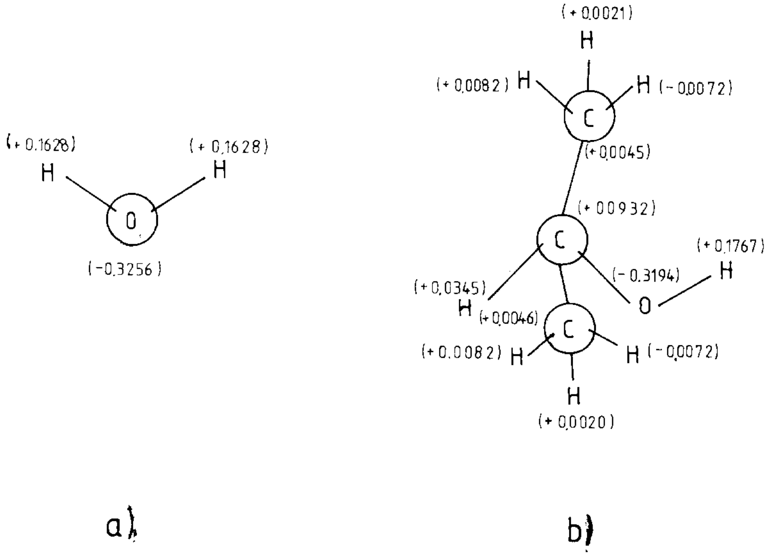

Fig. 4. Net charge distributions in (a) water and (b) propan-2-ol molecules.

The shifts of Δq_i^a in Fig. 3 are for the BPh$^-$ fragment $\Delta q_1^C = -0.0527$; $\Delta q_2^C = \Delta q_6^C = -0.0293$; $\Delta q_5^C = \Delta q_3^C = -0.0107$; $\Delta q_4^C = +0.0773$; $\Delta q_7^H = -0.0293$; $\Delta q_8^H = \Delta q_{12}^H = -0.0273$; $\Delta q_9^H = \Delta q_{11}^H = -0.0063$; and for the PhP$^+$ fragment $\Delta q_1^C = \Delta q_2^C = +0.0590$; $\Delta q_3^C = \Delta q_5^C = +0.0083$; $\Delta q_4^C = -0.1407$; $\Delta q_6^C = +0.0483$; $\Delta q_7^H = \Delta q_8^H = \Delta q_{12}^H = +0.0287$; $\Delta q_9^H = \Delta q_{11}^H = +0.0157$.

A negative sign of Δq_i^a indicates that there are more electrons on the C and H atoms in the ions than in a benzene molecule; and for positive sign of Δq_i^a, this effect is reversed.

To analyse the solvation mechanism of ions in water–propan-2-ol mixtures, it was also necessary to calculate the net charge distribution in single water and propan-2-ol molecules. The results are shown in Figs. 4(a) and 4(b).

Figures 3 and 4, together with the Δq_i^a results, lead to important conclusions concerning the solvation mechanism. It follows from the Δq_i^a analysis that a main part of the negative or positive charge carried by the B$^-$ and P$^+$ ions to the benzene ring is situated on the hydrogen atoms, not on the aromatic core. For Ph$_4$P$^+$, the shifts $\Delta q_i^H > 0$, whereas in a case of BPh$_4^-$, $\Delta q_i^H < 0$ for all hydrogen atoms in the corresponding benzene rings. This result fully confirms a conclusion derived by Krygowski and coworkers [21, 22] from Hammett's equation by ab initio analysis of mono-substituted derivatives of benzene, and has a great importance for solvation mechanisms in water–alcohol mixtures.

It is evident from the net charge maps in Figs. 3 and 4 that the solvation effect is expected to be different for BPh$_4^-$ and Ph$_4$P$^+$ ions in different solvents.

Because the net charge on –O–H bond atoms is almost the same for water and propan-2-ol molecules (Fig. 4), namely $q^{\mathrm{O}}_{\mathrm{w}} = -0.3256$; $q^{\mathrm{O}}_{\mathrm{pr}} = -0.3194$; $\Delta q^{\mathrm{H}}_{\mathrm{w}} = +0.1628$; $\Delta q^{\mathrm{H}}_{\mathrm{pr}} = +0.1767$, it seems highly probable that the Ph_4P^+ ion can be solvated to the same degree by both water and propan-2-ol in the mixed solvent. In this case the solvation mechanism consists of the penetration of the oxygen atoms from –OH groups into a space between neighbouring hydrogen atoms in the benzene rings of the Ph_4P^+ ion. The electrostatic attraction between the O atom of the water molecule and the H atoms from the ion (with average net charge $q^{\mathrm{H}}_{i} = +0.0238$) seems to be relatively strong and one can expect strong hydrogen bonds to be present. Because of spatial obstacles, solvation of ions by water molecules may be slightly preferred. Moreover, the BPh_4^- ion would prefer solvation by water. In this case, hydrogen atoms from the water –OH groups penetrate more deeply than before into the benzene ring of the ion, very close to the carbon atoms which are more negative than in the case of the Ph_4P^+ ion (Fig. 3). A special kind of C···H pseudo-hydrogen bond is created by means of a relatively strong attraction between the C and H atoms. At the same time, a repulsion between the penetrating H atom and the H atom from the benzene ring is very weak (approximately 3 times weaker than in the case of Ph_4P^+). Moreover, because of spatial obstacles, which also play an important role (as for Ph_4P^+), a penetration of hydrogen atoms from the propan-2-ol molecule so close to the carbon, as before, is practically impossible.

The above considerations suggest a different solvation aptitude for these organic ions. Thus, the TPTB assumption is not justified for the determination of ionic solvation enthalpies, nor, it seems likely, for other thermodynamic functions.

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