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ENTHALPY OF TRANSFER OF IONS FROM WATER TO WATER–TETRAHYDROFURAN MIXTURES

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ABSTRACT

Integral heats of solution of $NaB\phi_4$, ϕ_4PCl and KCl in water–tetrahydrofuran mixtures from 0 to 35 mol% of THF have been measured. Additionally, enthalpies of solution of NaCl, $NaClO_4$ and NaI in the mixed solvents containing 15–35 mol% THF have been determined. Enthalpy of transfer of tetraphenylphosphonium tetraphenylboride was calculated using the obtained data and earlier data for NaCl. Ionic contributions for transfer enthalpy of several ions have been found, based on the assumption that

$$\Delta H_t^0(\phi_4P^+) = \Delta H_t^0(B\phi_4^-)$$

INTRODUCTION

In the earlier papers [1–4] the heats of solution of NaCl, $NaClO_4$, NaI and urea in water–tetrahydrofuran (THF) mixtures in the range 0–10 mol% of THF have been presented at 298.15 K.

The plots of the standard enthalpies of solution of NaI and urea versus the THF content in the mixed solvent exhibit maxima corresponding to 2.5 mol% of THF, whereas, in the system with $NaClO_4$, to 5 mol% of THF. In the case of the NaCl solutions, no maximum is observed within the range of mixed solvent compositions under investigation. To clarify the observed difference in behaviour of the electrolytes mentioned above we determined the enthalpy of transfer of individual ions from water to its mixtures with THF. The applied assumption was the equality

$$\Delta H_t^0(\phi_4P^+) = \Delta H_t^0(B\phi_4^-)$$

based on the suggestion about the similar interactions of large, spherical ions with the solvent.

Therefore, we have measured the enthalpy of solution of $NaB\phi_4$ and ϕ_4PCl in mixed solvent containing 0–35 mol% of THF. We have also extended the range of the solvent composition up to 35 mol% of THF for the enthalpies of solution of NaCl, $NaClO_4$ and NaI.

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EXPERIMENTAL

Sodium tetraphenylborate, tetraphenylphosphonium chloride (Fluka pro anal.) and potassium chloride (produced by POCh Gliwice, Poland) were dried under reduced pressure at 373.15 K. The salts, NaI, $NaClO_4$, NaCl, and the solvent, THF, were purified and dried in the way described previously [1]. The "isoperibol" calorimeter used in this work was also described earlier [1].

RESULTS AND DISCUSSION

The standard enthalpies of solution were obtained by means of the limiting Debye–Hückel law [5]. The necessary values of electrical permittivities and densities of mixed solvents were taken from the literature [6–10]. The values of D and d corresponding to the compositions of solutions investigated in this work were obtained by square interpolation. By means of polynomial approximation of functions $D(T)$ and $d(T)$ their differentials $\mathrm{d}D/\mathrm{d}T$ and $\mathrm{d}d/\mathrm{d}T$ were calculated.

The obtained standard enthalpies of solution of electrolytes in H_2O–THF mixtures are presented in Tables 1 and 2 and in Fig. 1.

Literature data concerning ΔH^0 ($NaB\phi_4$) in water are within the range -18.59 [11] to -20.79 kJ mol^{-1} [20] (Table 3), whereas our value, -19.91 kJ mol^{-1}, is in good agreement with those by Arnett [14] and Abraham [15]. The value of ΔH^0 (ϕ_4PCl), -8.79 kJ mol^{-1}, obtained by us is close to that reported by Abraham [15], -8.91 kJ mol^{-1} (Table 3). The enthalpy of

TABLE 1

Standard enthalpies of solution of $NaB\phi_4$, ϕ_4PCl and KCl in water–THF mixtures at 298.15 K

x_{THF} (mol%)	ΔH^0_{sol} (J mol^{-1})		
	$NaB\phi_4$	ϕ_4PCl	KCl
0.0	−19912	−8786	17195
2.5	7724	11196	18016
5.0	36656	18447	18857
7.5	26238	16380	19685
10.0	−536	14322	20096
15.0	−24928	10920	21235
20.0	−38878	9330	22243
25.0	−52530	8012	22895
30.0	−61245	6686	22495
35.0	−66040	5941	21022

TABLE 2

Standard enthalpies of solution of NaCl, NaI and $NaClO_4$ in water–THF mixtures at 298.15 K

X_{THF} (mol%)	ΔH^0_{sol} (J mol^{-1})		
	NaCl	NaI	$NaClO_4$
15	8690	−13703	220 [a]
20	9678	−18457	−3766
25	10268	−20625	−7820 [a]
30	10096	−21836	−11470
35	9431	−22636	−13800 [a]

[a] Values interpolated from the data included in the paper in press.

transfer of $\phi_4P\phi_4B$ was calculated using the obtained data and ΔH^0 (NaCl) from our earlier paper [1].

$$\Delta H_t^0(\phi_4P\phi_4B) = \Delta H_t^0(NaB\phi_4) + \Delta H_t^0(\phi_4PCl) - \Delta H_t^0(NaCl) \quad (1)$$

Enthalpy of transfer of ions ϕ_4P^+ and $B\phi_4^-$ was obtained according to the

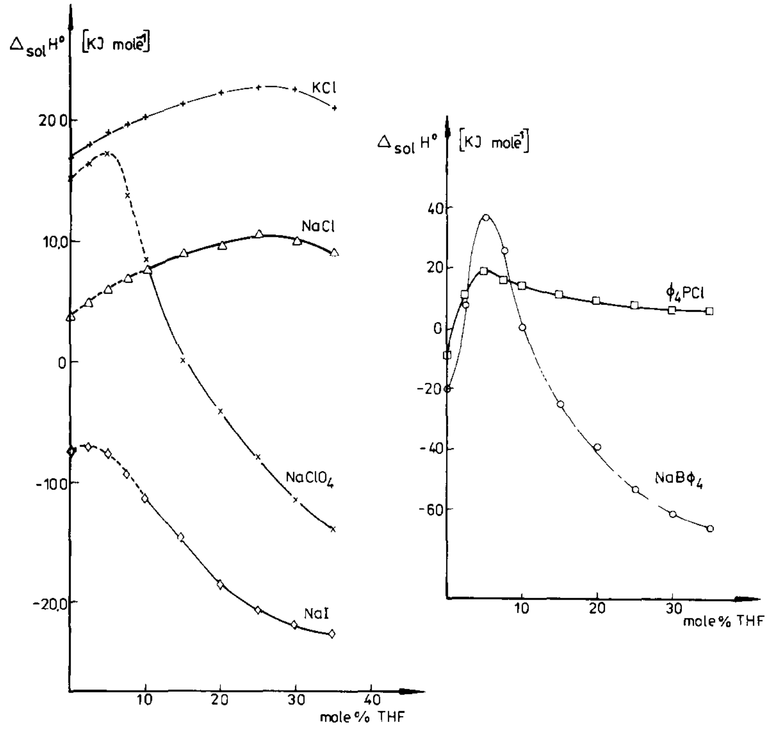

Fig. 1. Standard enthalpies of solution of some electrolytes in water–THF mixtures at 298.15 K (dashed line, earlier data [1]).

TABLE 3

Standard enthalpies of solution of $NaB\phi_4$ and ϕ_4PCl in water at 298.15 K, $\Delta H^0_{sol.}$ (kJ mol^{-1})

$NaB\phi_4$	ϕ_4PCl
−18.59 [11]	−8.91 [15]
−18.8 [12]	−9.16 [21]
−19.29 [13]	−9.18 [22]
−19.93 [14]	−8.79 Our value
−19.99 [15]	
−20.0 [16]	
−20.04 [17]	
−20.08 [18]	
−20.10 [19]	
−20.79 [20]	
−19.91 Our value	

assumption:

$$\Delta H_t^0(B\phi_4^-) = \Delta H_t^0(\phi_4P^+) = \frac{\Delta H_t^0(\phi_4P\phi_4B)}{2} \tag{2}$$

The ionic contributions of ΔH_t^0 are presented in Fig. 2 and in the Table 4. The plots of ΔH_t^0 for cations and anions are quite different in mixtures of water with THF. In the water-rich range of compositions, maxima of the endothermic enthalpy of transfer for cations and minima for anions are

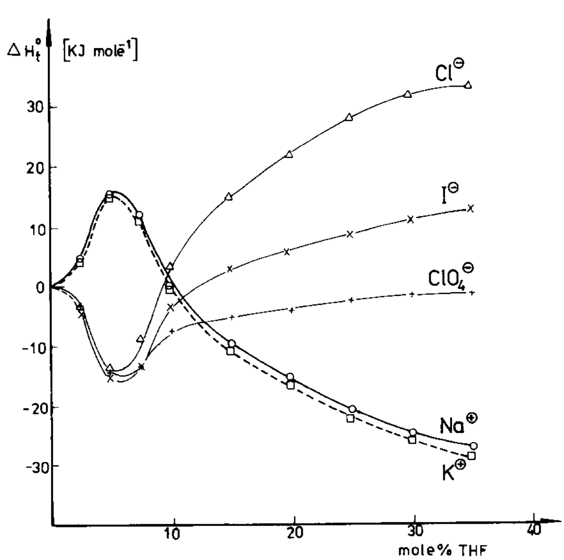

Fig. 2. Enthalpies of transfer of ion from water to water–THF mixtures.

TABLE 4

Enthalpies of transfer of ions from water to water–THF mixtures at 298.15 K, ΔH_t^0 (J mol^{-1})

X_{THF} (mol%)	$B\phi_4^- = \phi_4P^+$	Na^+	K^+	Cl^-	I^-	ClO_4^-
2.5	23254	4382	4093	−3272	−3901	−3288
5.0	40844	15724	15273	−13611	−15599	−13919
7.5	34078	12072	11401	−8911	−13914	−13826
10.0	19476	−100	−731	3632	−3542	−6782
15.0	4895	−9911	−10772	14812	3744	−5439
20.0	−3369	−15597	−16438	21486	4676	−3739
25.0	−11149	−21469	−22248	27948	8380	−1921
30.0	−16084	−25249	−26256	31556	10949	−1791
35.0	−18522	−27606	−29421	33248	12506	−1764

observed in the vicinity of 5 mol% of THF. This composition of mixture corresponds to the structure of quasi-clathrates of the second type, whose presence was suggested by several authors [23–25].

With the increase of THF content above 5 mol%, enthalpy of transfer of cations decreases and that of anions increases within the range of compositions under investigation. One can suppose that increase of exothermicity of ΔH_t^0 of cations is connected with the stronger interactions with THF than in the case of anions. This, in turn, is due to the presence of two free electron pairs in the oxygen atom. It can be seen in Fig. 2 that the courses of $\Delta H_t^0(Na^+)$ and $\Delta H_t^0(K^+)$ are very similar, suggesting an analogous effect of both cations on the properties and structure of the water–THF mixture.

The division of ΔH_t^0 into ionic contributions indicates the different behaviour of cations and anions in the investigated water–THF mixtures. It is not clear, however, why the picture is similar to the system containing electrolyte–water–*t*-butanol [11], taking into consideration the close interactions of alcohols with cations and anions.

It is noteworthy that the positions of extrema of ΔH_t^0 in the water–THF mixtures for individual ions are either the same or close, in spite of different positions of enthalpy maxima for salts. The differences in the character of the transfer enthalpy for salts and individual ions can also be observed in the other solvent mixtures. In Fig. 3 the enthalpies of transfer of Na^+ and Br^- ions from water to mixtures of water with dimethylformamide (DMF) [13], dimethylsulfoxide (DMSO) [12] and sulfolane [26] are presented. These curves exhibit extrema in the water-rich composition range, despite absence of extrema of ΔH_t^0 of salts in this range in all above-mentioned mixed solvents.

Considering the systems with $B\phi_4^-$ and ϕ_4B^+ ions, which are the basis for ionic contribution determination, one can see that the ionic enthalpies of transfer of both the above-mentioned ions in the mixtures of water with

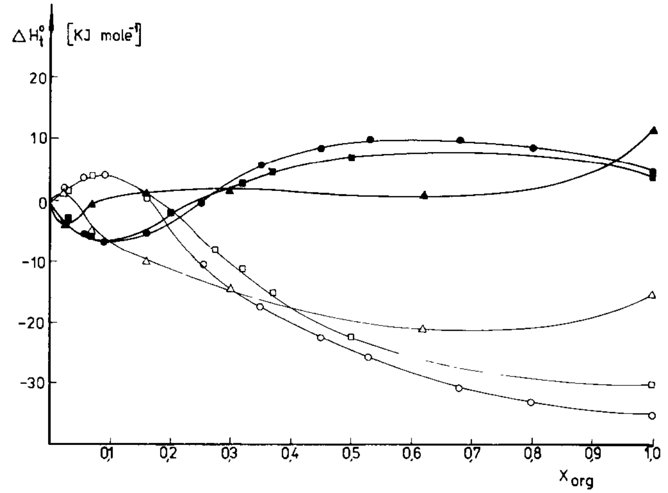

Fig. 3. Enthalpies of transfer of Na^+ and Br^- from water to water–DMF, water–DMSO and water–sulfolane mixtures (X_{org}, mole fraction of organic component): DMF, (○) Na^+, (●) Br^-; DMSO, (□) Na^+, (■) Br^-; sulfolane, (△) Na^+, (▲) Br^-.

aprotic solvents and alcohols exhibit the maxima in the water-rich region (Fig. 4). Therefore, we can assume that the main contribution in solvation of these organic ions is their interaction with water. Addition of organic solvent

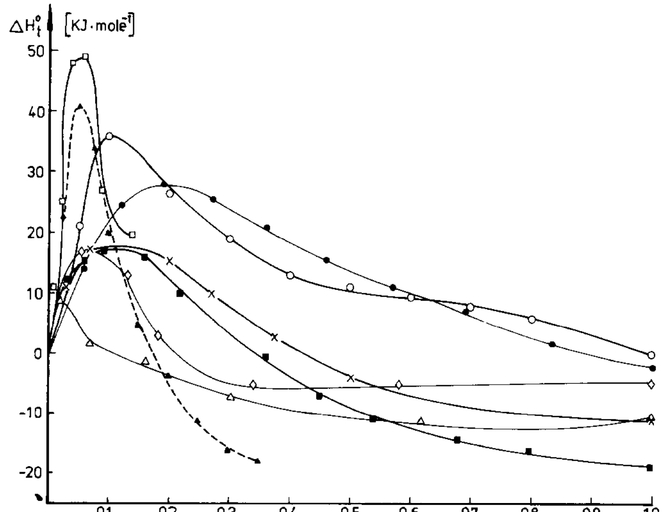

Fig. 4. Enthalpies of transfer of ϕ_4P^+ and ϕ_4B^- from water to water–organic mixtures ($X_{org.}$, mole fraction of organic component): (●) water–methanol [15]; (○) water–ethanol [20]; (□) water–*t*-butanol [11]; (■) water–DMF [13]; (△) water–sulfolane [26]; (×) water–DMSO [12]; (◇) water–acetonitrile (values of ionic enthalpies of transfer were calculated from experimental data) [18]; (▲) water–THF.

diminishes hydrophobic hydration or causes quasi-clathrate formation, resulting in the appearance of maxima on the curves of the enthalpy of transfer in a similar range of compositions in different classes of solvents. It can be supposed that the character of these curves determines the shape of the same functions for inorganic ions. It seems that the method used for splitting enthalpy of transfer of electrolytes into ionic contributions is not suitable for solutions in binary solvents. Somsen [13] examined the system salt–water–DMF and came to a similar conclusion.

It could be mentioned that partition of solvation enthalpies into ionic contributions, based on $\Delta H_t^0(\phi_4P^+) = \Delta H_t^0(B\phi_4^-)$, points at a quite opposite behaviour of cations and anions. The data concerning ionic Walden product [27] do not confirm, however, such opposite behaviour, indicating only some dissimilarities in it. It seems that the splitting method based on the inorganic ions would be more convenient for our purpose because of the same mechanism of solvation of ions.

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