

SINGLE-ION TRANSFER ENTHALPIES FOR $\text{Ph}_4\text{P}^+ = \text{BPh}_4^-$, Na^+ AND I^- IONS IN METHANOL–*N,N*-DIMETHYLFORMAMIDE MIXTURES

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ABSTRACT

Enthalpies of solution of Ph_4PI and NaBPh_4 in methanol–*N,N*-dimethylformamide (DMF) mixtures have been measured within the whole range of the mixed solvent composition. The ionic contribution to the transfer enthalpy from methanol to methanol–DMF mixtures based on the assumption that $\Delta H_t^\ominus(\text{BPh}_4^-) = \Delta H_t^\ominus(\text{Ph}_4\text{P}^+)$, has been calculated using the data obtained and earlier data for NaI solution. The single-ion transfer enthalpies change monotonically with the mixture's composition, without any extrema typical of the systems containing water as a component of the mixed solvent.

INTRODUCTION

Systematic investigations of the dissolution enthalpy of electrolytes in water–organic and organic–organic mixtures have been carried out at our laboratory for many years. Recently our studies have been extended to single-ion solvation enthalpies in the mixed solvent. The method, based on the assumption about the equality of the transfer enthalpies of Ph_4P^+ and BPh_4^- ions, has been used for the partition of the electrolyte transfer enthalpies into an ionic contribution. We have discussed in detail the behaviour of single ions in water–tetrahydrofuran [1] and water–HMPA [2] mixtures. In the course of the discussion there arose doubts as to whether the assumption mentioned above is true for mixed solvents containing water as one of the components. Therefore, we decided to determine the single-ion transfer enthalpies in mixed organic–organic solvent. This was to enable us to compare the shape of $\Delta H_t^\ominus = f(x)$ curves for the ions in the mixtures containing and not containing water. The methanol–*N,N*-dimethylformamide (DMF) mixture has been chosen for these studies. The NaI –methanol–DMF system has already been investigated calorimetrically in our laboratory [3]. Now we present the measured dissolution enthalpies of sodium tetraphenylborate (NaBPh_4) and tetraphenylphosphonium iodide (Ph_4PI) in the above-mentioned mixture and enthalpies of transfer of Na^+ ,

I^- , Ph_4P^+ and BPh_4^- ions from methanol to methanol–DMF mixtures determined from the obtained data.

EXPERIMENTAL

$NaBPh_4$ (Merck, pro analysi) and Ph_4PI (Aldrich Chemical) were dried for several days under vacuum at a temperature of about 310 K.

The solvents methanol (POCh-Gliwice, Poland), and *N,N*-dimethylformamide (Merck) were purified and dried by means of the methods described in the earlier paper [3]. The mixtures of methanol and DMF were prepared by weight in a dry box from freshly distilled solvents.

Measurements of dissolution enthalpies were performed using a calorimetric system described in our recent paper [3]. Six to eight dissolution experiments were carried out for each mixed solvent composition in the range of electrolyte concentrations from 2×10^{-3} to 2×10^{-2} mol kg^{-1} . The uncertainties in the measured enthalpies did not exceed $\pm 0.5\%$ of the measured value. All measurements were performed at 298.15 K.

RESULTS AND DISCUSSION

The enthalpies of solution of Ph_4PI and $NaBPh_4$ in methanol, DMF and methanol–DMF mixtures at 298.15 K were extrapolated to infinite dilution using the method proposed by Criss and Cobble [4] in order to determine the standard dissolution enthalpies ΔH_s^\ominus of the salts. Owing to the relatively high electric permittivities of both components of the mixed solvent no adjustment for ionic association was introduced into the extrapolation method. The values of ΔH_s^\ominus for $NaBPh_4$ and Ph_4PI are presented in Table 1. The standard enthalpies of solution of $NaBPh_4$ in pure methanol (ΔH_s^\ominus

TABLE 1

Standard dissolution enthalpies for Ph_4PI and $NaBPh_4$ in methanol–*N,N*-dimethylformamide mixtures at 298.15 K

DMF (mol%)	ΔH_s^\ominus (kJ mol $^{-1}$)	
	Ph_4PI	$NaBPh_4$
0	32.22 ± 0.20	-41.10 ± 0.30
2	29.62 ± 0.23	-46.20 ± 0.35
5	26.10 ± 0.18	-51.25 ± 0.20
10	23.65 ± 0.20	-56.20 ± 0.20
15	21.25 ± 0.15	-60.35 ± 0.20
20	19.90 ± 0.20	-62.90 ± 0.30
30	17.50 ± 0.15	-65.60 ± 0.25
40	15.10 ± 0.15	-67.25 ± 0.25
60	10.90 ± 0.15	-69.50 ± 0.30
80	6.50 ± 0.12	-71.30 ± 0.20
100	2.45 ± 0.07	-72.35 ± 0.20

= $-41.10 \pm 0.30 \text{ kJ mol}^{-1}$) and in pure DMF ($\Delta H_s^\ominus = -72.35 \pm 0.25 \text{ kJ mol}^{-1}$) determined in this paper are in good agreement with the literature data ($-42.09 \text{ kJ mol}^{-1}$ [5] and $-41.78 \text{ kJ mol}^{-1}$ [6] in methanol and $-72.38 \text{ kJ mol}^{-1}$ [5] in DMF). The standard solution enthalpies of Ph_4PI in methanol and in DMF are not reported in the literature. However, taking into account the known values of the transfer enthalpy for Ph_4P^+ and I^- ions from water to methanol [6] as well as the dissolution enthalpy of Ph_4PI in water [7], the value of ΔH_s^\ominus for Ph_4PI in methanol can be obtained.

Since

$$\Delta H_t^\ominus(\text{Ph}_4\text{PI})(\text{H}_2\text{O} \rightarrow \text{MeOH}) = \Delta H_t^\ominus(\text{Ph}_4\text{P}^+)(\text{H}_2\text{O} \rightarrow \text{MeOH}) + \Delta H_t^\ominus(\text{I}^-)(\text{H}_2\text{O} \rightarrow \text{MeOH}) \quad (1)$$

and

$$\Delta H_t^\ominus(\text{Ph}_4\text{PI})(\text{H}_2\text{O} \rightarrow \text{MeOH}) = \Delta H_s^\ominus(\text{Ph}_4\text{PI})(\text{MeOH}) - \Delta H_s^\ominus(\text{Ph}_4\text{PI})(\text{H}_2\text{O}) \quad (2)$$

where ΔH_s^\ominus denotes the standard dissolution enthalpy and ΔH_t^\ominus is the enthalpy of transfer, therefore

$$\begin{aligned} \Delta H_s^\ominus(\text{Ph}_4\text{PI})(\text{MeOH}) &= \Delta H_s^\ominus(\text{Ph}_4\text{PI})(\text{H}_2\text{O}) + \Delta H_t^\ominus(\text{Ph}_4\text{P}^+)(\text{H}_2\text{O} \rightarrow \text{MeOH}) \\ &\quad + \Delta H_t^\ominus(\text{I}^-)(\text{H}_2\text{O} \rightarrow \text{MeOH}) \end{aligned} \quad (3)$$

Using the data for $\Delta H_t^\ominus(\text{Ph}_4\text{P}^+)$ and $\Delta H_t^\ominus(\text{I}^-)$ from water to methanol and the $\Delta H_s^\ominus(\text{Ph}_4\text{PI})$ value in water from the literature [5–7] in eqn. (3) we obtain

$$\Delta H_s^\ominus(\text{Ph}_4\text{PI})(\text{MeOH}) = 35.48 - 1.42 - 2.01 = 32.05 \text{ kJ mol}^{-1}$$

The standard dissolution enthalpy of Ph_4PI in methanol calculated as above is in very good agreement with the value $\Delta H_s^\ominus(\text{Ph}_4\text{PI}) = 32.22 \pm 0.20 \text{ kJ mol}^{-1}$ determined in this work.

The dependence of the transfer enthalpy of the examined salts from methanol to methanol–DMF mixtures, i.e.

$$\Delta H_t^\ominus(\text{MeOH} \rightarrow \text{mixt}) = \Delta H_s^\ominus(\text{mixt}) - \Delta H_s^\ominus(\text{MeOH}) \quad (4)$$

on the mixed solvent composition is presented in Fig. 1. The analogous function concerning the NaI solutions, investigated earlier [3], is also plotted in the same graph for comparison.

As can be seen from the presented data, the ΔH_t^\ominus function for all electrolytes under examination decreases monotonically with increasing DMF content in the mixture; this drop is the sharpest for high methanol contents in the mixture. It is possible that small amounts of DMF introduced into pure methanol disturb its initial structure, which makes the salt's dissolution more exothermic. The steepest decrease in the ΔH_t^\ominus function is

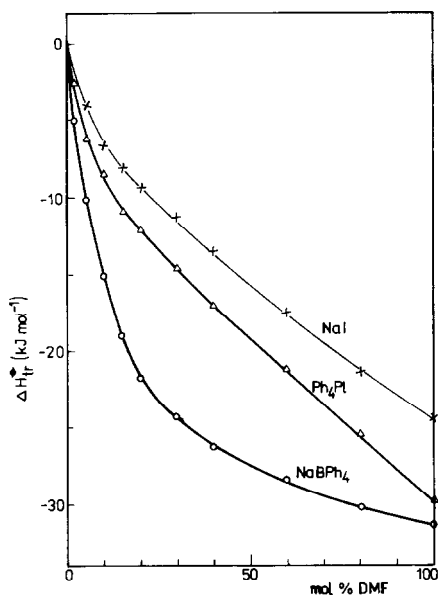


Fig. 1. Enthalpies of transfer of NaBPh_4 , Ph_4PI and NaI [5] from methanol to methanol-DMF mixtures at 298.15 K.

observed in NaBPh_4 solutions, while for both investigated iodides the slopes of the discussed functions are much smaller. This indicates a different influence of the mixed solvent composition on the solvation of the corresponding ions.

In order to analyse the observed phenomenon in more detail we divided the transfer enthalpies of the examined salts into ionic contributions, accepting the extrathermodynamic assumption about equality of the transfer enthalpies of Ph_4P^+ and BPh_4^- ions [8], i.e. $\Delta H_t^\ominus(\text{Ph}_4\text{P}^+) = \Delta H_t^\ominus(\text{BPh}_4^-)$:

$$\begin{aligned} \frac{1}{2} [\Delta H_t^\ominus(\text{NaBPh}_4) + \Delta H_t^\ominus(\text{Ph}_4\text{PI}) - \Delta H_t^\ominus(\text{NaI})] &= \Delta H_t^\ominus(\text{Ph}_4\text{P}^+) \\ &= \Delta H_t^\ominus(\text{BPh}_4^-) \end{aligned} \quad (5)$$

and

$$\Delta H_t^\ominus(\text{C}^+\text{A}^-) = \Delta H_t^\ominus(\text{C}^+) + \Delta H_t^\ominus(\text{A}^-) \quad (6)$$

The ionic enthalpies of transfer from pure methanol to methanol-DMF mixtures for Ph_4P^+ (equal to that of BPh_4^-), Na^+ and I^- ions, calculated in this way are presented in Table 2 and in Fig. 2 as a function of the mixed solvent composition.

The single-ion enthalpies of transfer from pure methanol to pure DMF determined in this work, i.e. $-18.2 \text{ kJ mol}^{-1}$ for BPh_4^- , $-12.9 \text{ kJ mol}^{-1}$ for Na^+ and $-11.6 \text{ kJ mol}^{-1}$ for I^- , are in very good agreement with the appropriate values calculated from the literature data [5,6] which amount to

TABLE 2

Single-ion transfer enthalpies from methanol to methanol–*N,N*-dimethylformamide mixtures at 298.15 K

DMF (mol%)	ΔH_t^\ominus (kJ mol ⁻¹)		
	Ph ₄ P ⁺ (or BPh ₄ ⁻)	Na ⁺	I ⁻
0	0	0	0
2	-2.6	-2.5	0
5	-6.0	-4.1	-0.1
10	-8.5	-6.5	-0.1
15	-11.1	-8.2	+0.1
20	-12.4	-9.3	+0.1
30	-13.9	-10.6	-0.8
40	-14.9	-11.3	-2.2
60	-16.1	-12.4	-5.2
80	-17.3	-12.9	-8.5
100	-18.2	-12.9	-11.6

–17.9 kJ mol⁻¹, –12.5 kJ mol⁻¹ and –11.8 kJ mol⁻¹ respectively. Because of the unavailability of appropriate experimental data we were not able to use more ΔH_s^\ominus values for calculating the single-ion transfer enthalpies. Therefore, the uncertainty of the results presented in Table 2 could be approximated only on the basis of experimental errors in the determination

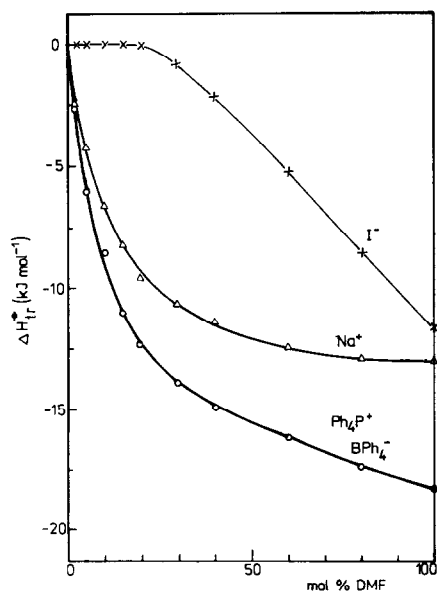


Fig. 2. Enthalpy of transfer of single ions from methanol to methanol–DMF mixtures at 298.15 K.

of the ΔH_s^\ominus values for the investigated salts. The uncertainty in question is assumed to be equal to ca. $\pm 0.5 \text{ kJ mol}^{-1}$.

As can be seen from the presented data, the single-ion transfer enthalpies for Na^+ , I^- and Ph_4P^+ (or BPh_4^-) ions change monotonically within the whole range of the mixed solvent composition. Any extrema of the ΔH_t^\ominus function typical of systems containing water as a component of the mixed solvent [1,2,6,9–12] are not observed in DMF–methanol mixtures.

The sharp decrease in ΔH_t^\ominus for low DMF contents observed for the organic ions as well as for the Na^+ cation (Fig. 2) suggests that the solvation shells of these ions change rapidly from those typical for methanolic solution to those typical for DMF solution in this range of the mixed solvent composition. Therefore, the Na^+ , Ph_4P^+ and BPh_4^- ions seem to be preferentially solvated by DMF molecules in systems containing more than 20 mol% of DMF. The relatively high dipole moment of the DMF molecule and its stronger basicity in comparison with the methanol molecules are probably the main reasons of the observed behaviour of the discussed system.

The enthalpy of transfer of iodide ion in the mixtures containing less than 20 mol% of DMF is almost independent (within the error limits) of the mixed solvent composition. This suggests that I^- anions are preferentially solvated by methanol in these mixtures. Possibly, the interactions between two Lewis bases (I^- and DMF) in a solvent with a relatively high electric permittivity ($\epsilon = 32.6$) are too weak to destroy the methanolic solvation shell of iodide ions in the mixtures with high methanol content. An additional argument supporting the above opinion is the possibility of hydrogen bond formation between the iodide anion and a methanol molecule suggested in several papers [13]. A further increase in the DMF content in the mixture from 20 to 100 mol% causes an almost linear decrease of the iodide anion transfer enthalpy. It is possible that in this range of the mixed solvent composition the solvation cosphere of the I^- anions changes its structure gradually to that typical for solutions in pure DMF.

The monotonic course of the transfer enthalpies for the investigated salts as well as for single ions at low DMF contents in the methanol–DMF solvent suggests that in the examined system there are no phenomena analogous to the hydrophobic hydration typical for water–organic solvent mixtures.

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