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Single-ion transfer enthalpies in methanol–acetonitrile mixtures at 298.15 K based on the $Ph_4P^+ = BPh_4^-$ assumption

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Abstract

The enthalpies of solution of KI, $NaBPh_4$ and Ph_4PI in methanol–acetonitrile mixtures were measured at 298.15 K. From these data, together with those for NaI taken from our earlier work, and with literature data that refer to $(n\text{-Bu})_4NBr$, $(n\text{-Bu})_4NI$ and $(n\text{-Bu})_4ClO_4$, the enthalpies of transfer of the individual ions Ph_4P^+, BPh_4^-, Na^+, K^+, Br^-, I^-, ClO_4^- and $(n\text{-Bu})_4N^+$ from methanol to acetonitrile–methanol mixtures were calculated employing the assumption $\Delta H_t^\ominus(Ph_4P^+) = \Delta H_t^\ominus(BPh_4^-)$.

INTRODUCTION

A knowledge of the properties of individual ions in solution is necessary when studying the influence of the structure and properties of a solvent on the behaviour of ionic solutions. Numerous papers devoted to the analysis of single-ion transfer enthalpies in mixed solvents have already been published; most of them have been concerned with water–organic solvent mixtures. However, so far only a few investigations have been carried out in binary organic mixtures [1–6]. In one of our earlier works, the thermochemical properties of the NaI–methanol–acetonitrile system were studied [7]. Continuing these investigations, we have decided to find out which ion is responsible for the observed complex shape of the NaI dissolution enthalpy function in methanol–acetonitrile mixtures.

As is known, several methods of partitioning the electrolyte solvation or transfer enthalpies into ionic contributions have been proposed thus far, see, for example, ref. 8. Among them, despite many reservations [9], the method based on the assumption about the equality of the transfer enthalpies of tetraphenylboride and tetraphenylphosphonium or tetraphenylarsenium ions for every solvent (the TATB or TPTB method [10]) has acquired most significance. Therefore, we have measured the dissolution enthalpies of $NaBPh_4$ and Ph_4PI in the above-mentioned mixtures over the whole range of compositions. These data, together with those for NaI taken from our earlier work [7], make it possible to calculate the transfer enthalpies of the individual ions Ph_4P^+, BPh_4^-, Na^+ and I^- from methanol to acetonitrile–methanol mixtures. Moreover, in order to observe the influence of the cation size on the $\Delta H_t^{\ominus}$ function shape, we have also measured the dissolution enthalpy of KI in the same mixtures.

The single-ion transfer enthalpies, $\Delta H_t^{\ominus}$, in the methanol–acetonitrile binary solvent have already been published in the literature. Kondo et al. determined the single-ion quantities for Br^-, I^-, ClO_4^- and $B(n\text{-}Bu)_4^-$ anions, but they assumed the equality of the transfer enthalpies of tetra-*n*-butyl-ammonium and tetra-*n*-butylborate ions (TBATBB method) [3]. Thus, it is possible to compare the results obtained using the different methods for the transfer enthalpy partition.

EXPERIMENTAL

The salts $NaBPh_4$ (p.a., Aldrich Chemical), Ph_4PI (Aldrich Chemical) and KI (p.a., Merck) were dried for several days under vacuum at about 330 K (the organic salts) and about 370 K (KI).

The solvents acetonitrile (Fluka p.a.) and methanol (POCh-Gliwice, Poland) were purified and dried following the methods described in the literature [11,12]. The mixtures of acetonitrile with methanol were prepared by weight in a dry box.

The dissolution enthalpies were measured using the calorimeter described in our earlier report [13]. Six to eight dissolution experiments were made for each mixed solvent composition in the range of electrolyte concentration 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.

RESULTS AND DISCUSSION

The enthalpies of solution of $NaBPh_4$, Ph_4PI and KI in methanol, acetonitrile and methanol–acetonitrile mixtures at 298.15 K were extrapolated to an infinite dilution by the method proposed by Criss and Cobble [14] in order to determine the standard dissolution enthalpies, $\Delta H_s^{\ominus}$, of the salts. Owing to the relatively high electric permittivity of the mixed solvent, no correction for ionic association was introduced into the extrapolation method.

The standard enthalpies of solution of $NaBPh_4$ and KI in pure methanol and pure acetonitrile determined here are in good agreement with the literature data: for $NaBPh_4$ in methanol $\Delta H_s^{\ominus} = -41.10$ kJ mol^{-1} (-41.78 kJ mol^{-1} [15] and -42.09 kJ mol^{-1} [16]); for $NaBPh_4$ in acetonitrile, $\Delta H_s^{\ominus} = -43.42$ kJ mol^{-1} (-43.51 kJ mol^{-1} [17]); for KI in methanol,

$\Delta H_s^{\ominus} = -0.68$ kJ mol^{-1} (-0.63 kJ mol^{-1} [16]); and for KI in acetonitrile $\Delta H_s^{\ominus} = -10.09$ kJ mol^{-1} (-9.75 kJ mol^{-1} [18] and -10.40 kJ mol^{-1} [19]).

The standard enthalpy of Ph_4PI solution in methanol ($+32.22$ kJ mol^{-1}) and in acetonitrile ($+15.69$ kJ mol^{-1}) could not be compared with the literature values due to the lack of appropriate literature data. However, taking into account the data concerning the transfer enthalpies for Ph_4P^+ and I^- ions from water to methanol [15], in addition to the dissolution enthalpy of Ph_4PI in water [20], the $\Delta H_s^{\ominus}$ of Ph_4PI in methanol can be calculated because

$$\begin{aligned}\Delta H_t^{\ominus}(\mathrm{Ph_4PI})[\mathrm{H_2O} \rightarrow \mathrm{MeOH}] &= \Delta H_t^{\ominus}(\mathrm{Ph_4P^+})[\mathrm{H_2O} \rightarrow \mathrm{MeOH}] \\ &\quad + \Delta H_t^{\ominus}(\mathrm{I^-})[\mathrm{H_2O} \rightarrow \mathrm{MeOH}] \qquad (1)\end{aligned}$$

and

$$\begin{aligned}\Delta H_t^{\ominus}(\mathrm{Ph_4PI})[\mathrm{H_2O} \rightarrow \mathrm{MeOH}] &= \Delta H_s^{\ominus}(\mathrm{Ph_4PI})[\mathrm{MeOH}] \\ &\quad - \Delta H_s^{\ominus}(\mathrm{Ph_4PI})[\mathrm{H_2O}] \qquad (2)\end{aligned}$$

where $\Delta H_t^{\ominus}$ denotes the standard enthalpy of transfer. Therefore

$$\begin{aligned}\Delta H_s^{\ominus}(\mathrm{Ph_4PI})[\mathrm{MeOH}] &= \Delta H_s^{\ominus}(\mathrm{Ph_4PI})[\mathrm{H_2O}] + \Delta H_t^{\ominus}(\mathrm{Ph_4P^+}) \\ &\quad \times [\mathrm{H_2O} \rightarrow \mathrm{MeOH}] + \Delta H_t^{\ominus}(\mathrm{I^-})[\mathrm{H_2O} \rightarrow \mathrm{MeOH}] \qquad (3)\end{aligned}$$

Using the corresponding literature data in eqn. (3), we obtain $\Delta H_s^{\ominus}(\mathrm{Ph_4PI})[\mathrm{MeOH}] = 35.48 - 1.42 - 2.01 = 32.05$ kJ mol^{-1}.

The standard dissolution enthalpy of Ph_4PI in methanol calculated above is in very good agreement with the value $\Delta H_s^{\ominus}(\mathrm{Ph_4PI}) = 32.22$ kJ mol^{-1} determined in this work, as mentioned above. The standard transfer enthalpies $\Delta H_t^{\ominus}$ of the salts from methanol to methanol–acetonitrile mixtures were calculated according to

$$\Delta H_t^{\ominus}[\mathrm{MeOH} \rightarrow \mathrm{MeOH + AN}] = \Delta H_s^{\ominus}[\mathrm{MeOH + AN}] - \Delta H_s^{\ominus}[\mathrm{MeOH}] \qquad (4)$$

where $\Delta H_s^{\ominus}[\mathrm{MeOH + AN}]$ and $\Delta H_s^{\ominus}[\mathrm{MeOH}]$ denote the standard solution enthalpies in the mixed solvent at a given composition and in pure methanol, respectively. The calculated values of $\Delta H_t^{\ominus}$ for $NaBPh_4$, Ph_4PI and KI are presented in Table 1. The analogous data concerning the NaI salt determined on the basis of the dissolution enthalpies published earlier [7] are also given in Table 1. The dependences of the standard transfer enthalpy of the investigated salts on the molal composition of the methanol–acetonitrile mixtures are shown in Fig. 1.

As can be seen from the data, the $\Delta H_t^{\ominus}$ function for all the electrolytes under examination exhibits a sharp decrease in the methanol-rich composition range and a minimum in the high acetonitrile composition range. The

TABLE 1

Molar enthalpy of transfer of electrolytes $\Delta H_t^{\ominus}$ (kJ mol^{-1}) from methanol to methanol–acetonitrile mixtures at 298.15 K

mol.% AN	$NaBPh_4$	Ph_4PI	NaI [a]	KI
5	−4.90	−3.22	−1.80	−2.09
10	−7.85	−5.86	−3.06	−3.64
30	−11.45	−9.83	−4.98	−8.16
40	−11.90	−11.30	−5.90	−9.41
50	−12.69	−12.88	−7.99	−11.30
60	−12.90	–	–	–
70	−13.57	−16.07	−11.01	−14.43
80	−12.53	−18.07	−10.80	−15.48
85	−11.85	–	−10.38	–
90	−9.72	−19.25	−9.08	−14.85
95	−6.71	–	−5.12	–
100	−2.32	−16.53	+3.04	−9.41

[a] Ref. 10.

position of this extremum depends on the cation present. For sodium salts ($NaBPh_4$, NaI), it corresponds to around 70 mol.% of acetonitrile; for potassium iodide (KI), to around 80 mol.% of AN; and for Ph_4PI, to around 90 mol.% of acetonitrile. The sharpest minimum is observed in Ph_4PI and KI solutions, whereas for $NaBPh_4$ it is flat and wide.

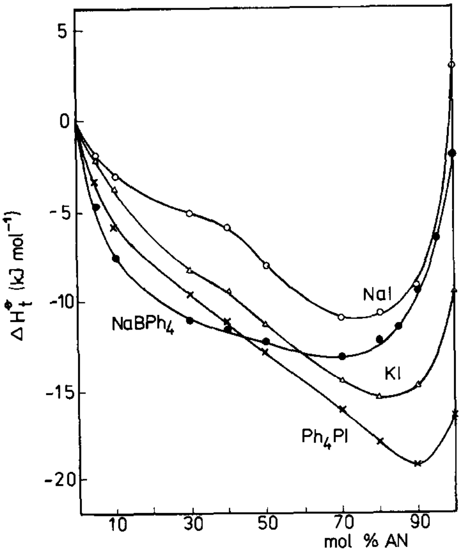

Fig. 1. Enthalpy of transfer of electrolytes from methanol to methanol–acetonitrile mixtures at 298.15 K.

TABLE 2

Enthalpy of transfer $\Delta H_t^{\ominus}$ (kJ mol^{-1}) of single ions from methanol to methanol–acetonitrile mixtures at 298.15 K

mol.% AN	Ph_4P^+ BPh_4^-	Na^+	K^+	I^-	Br^- [a]	ClO_4^- [a]	$(n\text{-}Bu)_4N^+$
5	−3.16	−1.74	−2.03	−0.06	–	–	–
10	−5.33	−2.52	−3.11	−0.53	−0.32	−2.33	−2.86
25	–	–	–	−1.55	−1.27	−4.35	−4.73
30	−8.15	−3.30	−6.48	−1.68	–	–	–
40	−8.65	−3.25	−6.76	−2.65	–	–	–
50	−8.79	−3.90	−7.21	−4.09	−3.92	−7.77	−5.20
70	−9.32	−4.25	−7.68	−6.75	–	–	–
75	–	–	–	−7.33	−6.91	−11.10	−4.97
80	−9.90	−2.63	−7.31	−8.17	–	–	–
90	−9.95	+0.23	−5.55	−9.30	−8.33	−13.99	−3.42
100	−10.95	+8.63	−3.82	−5.59	+2.40	−14.50	−3.11
Lit.	−10.4	+8.4	−3.9	−5.1	+3.5	−14.7	−2.9

[a] Calculated from the transfer enthalpies of $(n\text{-}Bu)_4NBr$, $(n\text{-}Bu)_4NI$ and $(n\text{-}Bu)_4NClO_4$ published in ref. 3, using TPTB method.

Accepting the assumption concerning the equality of the transfer enthalpies of Ph_4P^+ and BPh_4^- ions [10], we divided the transfer enthalpies of the examined salts into ionic contributions using the equation

$$\tfrac{1}{2}\left[\Delta H_t^{\ominus}(NaBPh_4) + \Delta H_t^{\ominus}(Ph_4PI) - \Delta H_t^{\ominus}(NaI)\right]$$
$$= \Delta H_t^{\ominus}(Ph_4P^+) = \Delta H_t^{\ominus}(BPh_4^-) \quad (5)$$

The ionic enthalpies of transfer from pure methanol to methanol–acetonitrile mixtures calculated in this way are presented in Table 2 and are shown in Fig. 2 as a function of the mixed solvent composition. The uncertainty of the results presented in Table 2 approximated on the basis of the experimental errors in determining the $\Delta H_s^{\ominus}$ values for the investigated salts is assumed to be equal to around 0.5 kJ mol^{-1}.

Taking into account the data of Kondo et al. [3] mentioned above concerning the transfer enthalpies for $(n\text{-}Bu)_4NBr$, $(n\text{-}Bu)_4NI$ and $(n\text{-}Bu)_4NClO_4$, and combining them with our enthalpies, we also calculated the ionic transfer enthalpies for $(n\text{-}Bu)_4N^+$, Br^- and ClO_4^- ions. The values obtained are also given in Table 2.

The ionic enthalpies of transfer from pure methanol to pure acetonitrile determined in this work, −10.95 kJ mol^{-1} for BPh_4^-, +8.63 kJ mol^{-1} for Na^+, −3.82 kJ mol^{-1} for K^+ and −5.59 kJ mol^{-1} for I^-, are in very good agreement with the corresponding literature data or with the values calculated from the literature [21], which are −10.4 kJ mol^{-1}, +8.4 kJ mol^{-1}, −3.9 kJ mol^{-1} and −5.1 kJ mol^{-1}, respectively. The same can be said of the $\Delta H_t^{\ominus}$ values for Br^-, ClO_4^- and $(n\text{-}Bu)_4N^+$ ions calculated from the

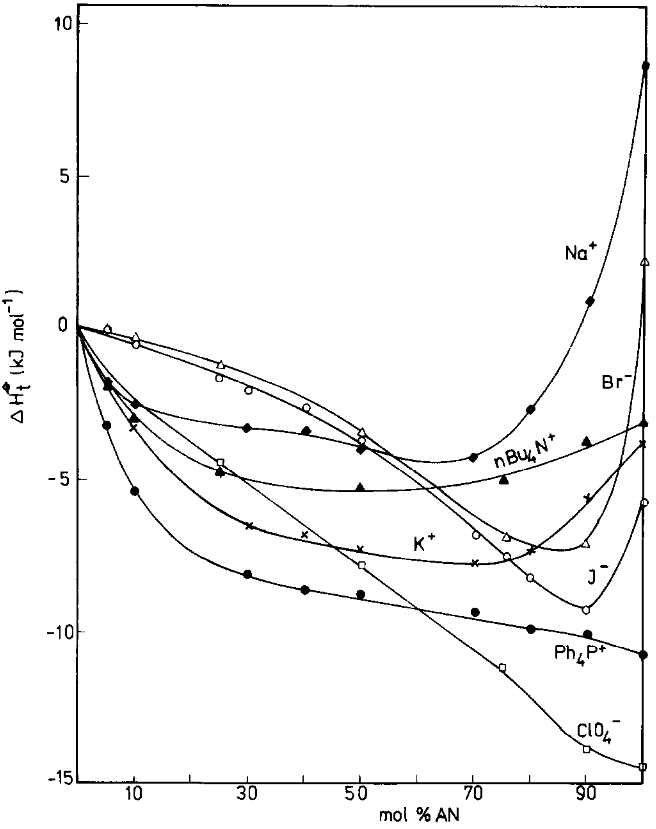

Fig. 2. Single-ion transfer enthalpies in methanol–acetonitrile mixtures.

salt transfer enthalpies given in the paper of Kondo et al. and split into ionic contributions using the TPTB method (see Table 2).

As can be seen from these data, the enthalpies of solvation curves for Na^+ and K^+ ions show a decrease within the methanol-rich region, then they exhibit a large, flat minimum and a sharp increase in the acetonitrile-rich region. It seems that both the addition of acetonitrile to the methanolic salt solution and of methanol to the solution of electrolyte in acetonitrile, involve meaningful changes in the solvation of the inorganic cations. The observed effect in the acetonitrile-rich region is greater the higher the cation charge density, and seems to be connected with a preferential solvation of the small cations by the methanol molecules in mixtures rich in acetonitrile. The solvation enthalpies of the large organic cations Ph_4P^+ and $(n\text{-Bu})_4N^+$, also fall rapidly in the range 0–40 mol.% AN, but unlike the inorganic cations, the organic cations react to only a small extent to the addition of methanol to the acetonitrile solution. The $\Delta H_t^{\ominus}$ values for the inorganic anions, except for ClO_4^- ion, exhibit only a small decrease in the methanol-rich region. They decrease significantly in the intermediate region and reach their minima at 80–90 mol.% AN; then they increase rapidly in the acetonitrile-rich region. It can be assumed that within the region of high methanol content the halide anions are preferentially solvated by the methanol [3], and that the acetonitrile molecules do not disturb, to any significant extent, the methanolic solvation shells of the anions.

Some investigations of the methanol–acetonitrile binary system suggest a specific behaviour of mixtures containing a small amount of methanol. Among others, the partial molar volume and the partial molar heat capacity of methanol exhibit extrema (a minimum and a maximum respectively) corresponding to around 90 mol.% of acetonitrile [22]. Therefore, it can be assumed that the $\Delta H_t^{\ominus}$ curves for Br^- and I^- probably reflect changes in the mixed solvent structure or properties in the low-methanol content range. The above conclusion agrees with an opinion presented in the literature that the halide ions, unlike alkali cations, appear to be particularly sensitive to the structural conditions of the solvent [23]. The transfer enthalpy of the large perchlorate ion decreases steadily with increasing AN content over the whole range of the mixture composition, irrespective of the properties of the mixed solvent.

The transfer enthalpies for iodide anions from pure methanol to methanol–acetonitrile mixtures obtained by means of TPTB [this work] and TBATBB [3] methods are compared in Fig. 3. Although the values of both functions are different, the shapes of the curves are essentially the same.

It should also be noted that the ionic transfer enthalpy plots within the high-acetonitrile range of the methanol–acetonitrile mixtures are similar to those in the water–acetonitrile system [24,25]. However, with low acetoni-

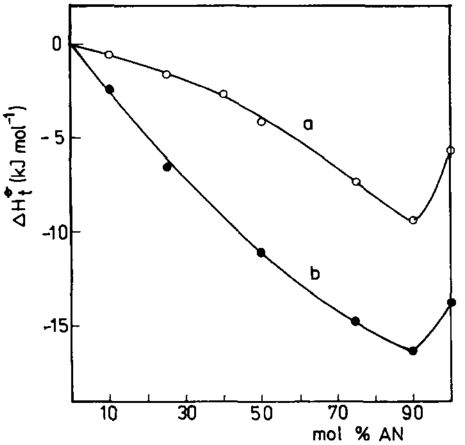

Fig. 3. A comparison of the transfer enthalpies of I^- ion from methanol to methanol–acetonitrile mixtures, calculated by the use of (a) TPTB method and (b) TBATBB method.

trile contents, the extrema of the $\Delta H_t^{\ominus}$ function observed in water–acetonitrile mixtures do not appear when water is replaced by methanol.

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