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THERMOCHEMICAL CHARACTERISTICS OF SOLVATION OF IONS IN MIXTURES OF WATER WITH FORMAMIDE, DIMETHYLSULFOXIDE AND HEXAMETHYLPHOSPHORIC TRIAMIDE *

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ABSTRACT

The enthalpies of solution of *n*-C_7H_{16}, *n*-$C_{10}H_{22}$, *n*-$C_{14}H_{30}$, and *n*-$C_{18}H_{38}$ in hexamethylphosphoric triamide (HMPA), acetonitrile and also of $LiNO_3$, $NaNO_3$, KNO_3, $CsNO_3$, NH_4NO_3, and $NaBPh_4$ in formamide (FA), dimethylsulfoxide (DMSO), HMPA and their mixtures with water at 298.15 K are measured by the calorimetric method. The enthalpic characteristics of transfer of individual ions are calculated. The approach based on the quantitative evaluation of separate contributions to the enthalpy of ion transfer is used for this purpose. The equations testifying to the donor–acceptor nature of ion–solvent interactions are revealed. On these bases the results of the thermochemical investigations on solutions of electrolytes in mixed water–organic solvents are discussed.

INTRODUCTION

Understanding of the nature of ionic solvation requires the determination of the physico-chemical and thermodynamic characteristics of an individual ion. Here, it is not only of great importance to obtain reliable data on the values of the enthalpies of solution at infinite dilution, but also the choice of the physically substantiated method of the division of ΣH^0_{solv} into its ionic constituents. The existing methods for obtaining the enthalpic characteristics of ions [1–4] have a common disadvantage in the absence of a quantitative account of the different contributions to the enthalpy of the solvation of an ion by the solvent. The problem seems to be more complicated for mixed solvents. That is why the authors of [5,6] discuss the thermodynamic characteristics of solvation of a stoichiometric mixture of ions. It should be noted that the question of the applicability of this or that method or

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combination of methods to the determination of the characteristics of an individual ion in various composition ranges of the mixed solvent has been insufficiently studied. There is an attempt at such an investigation in refs. 7 and 8.

The present work is devoted to revealing the details of the influence of the nature of components and the composition of mixed solvents on the enthalpic characteristics of the solvation of ions. The results are interpreted taking into account the conclusions obtained earlier [9–11] and based on the results of thermochemical investigations on nitromethane (NM) and HMPA in the solvents considered.

EXPERIMENTAL

Technique and equipment

We used *n*-alkanes of "chemically pure" classification. The characteristics of salts and their purification are described elsewhere [8,12,13]. The values of the enthalpies of solution were determined at electrolyte concentrations below 0.02–0.06 mol kg^{-1} of solvent. Non-aqueous solvents were purified according to known techniques [14,15]. Purity control was conducted by conductometric and chromatographic methods; the enthalpies of solution of substances were measured on a hermetic calorimeter [16]. Here we used a set of calorimetric vessels with volumes of 35, 50 and 70 cm^3.

The standard enthalpies of solution of alkanes (Table 1) were calculated as an average of 5 or 6 experimental points, since no dependence of the enthalpy of solution on solute concentration [which did not exceed 0.3 mol (55.51 mol of solvent)$^{-1}$] was found.

The values of the standard enthalpies of solution of 1 : 1 electrolytes were calculated according to the Debye–Hückel equation in the second approximation. The values of the temperature derivatives of the density and dielectric permeability which are necessary for the calculations are taken from refs. 17–20. A part of the data obtained is shown in Table 2.

TABLE 1

Standard enthalpies of solution of *n*-alkanes in polar solvents (kJ mol^{-1})

Solvent	Solute			
	n-C_7H_{16}	*n*-$C_{10}H_{22}$	*n*-$C_{14}H_{30}$	*n*-$C_{18}H_{38}$
Acetonitrile	11.6 [a]		22.5 ± 0.3	
HMPA	4.80 ± 0.02	6.1 ± 0.2	9.7 ± 0.4	63.0 ± 0.6

[a] Ref. 25.

TABLE 2

Standard enthalpies of solution (kJ mol^{-1}) of 1:1 electrolytes in mixtures of water with dimethylsulfoxide, hexamethylphosphoric triamide, formamide at 298.15 K
X is the molar fraction of the non-aqueous component.

X_{DMSO}	$\Delta_{soln}H^0$	X_{HMPA}	$\Delta_{soln}H^0$	X_{FA}	$\Delta_{soln}H^0$
$LiNO_3$		$CsNO_3$		$NaNO_3$	
0.000	−2.51±0.02	0.000	39.60±0.10	0.000	20.19 ±0.05
0.005	−2.79±0.02	0.045	40.26±0.20	0.099	14.87 ±0.00
0.008	−2.97±0.08	0.097	28.29±0.12	0.221	11.01 ±0.05
0.012	−2.98±0.02	0.214	14.54±0.05	0.277	9.26 ±0.03
0.025	−3.45±0.02	0.300	11.55±0.10	0.499	5.05 ±0.05
0.050	−4.59±0.01	CsF		0.687	2.47 ±0.01
0.107	−6.31±0.01	0.000	−36.54±0.01	0.851	0.835±0.005
0.253	−13.82±0.01	0.047	−27.22±0.02	1.000	0.359±0.001
0.449	−24.69±0.01	0.109	−21.10±0.01	$CsNO_3$	
0.609	−29.44±0.02	0.270	−10.51±0.17	0.097	33.45 ±0.16
0.847	−31.34±0.12	0.412	−16.04±0.01	0.302	27.66 ±0.04
1.000	−30.77±0.12	0.501	−14.02±0.01	0.485	24.46 ±0.07
NH_4NO_3		0.675	−13.81±0.03	0.711	21.17 ±0.05
0.000	25.69±0.02	0.755	−13.05±0.08	0.869	19.38 ±0.13
0.005	25.39±0.03	$NaB(C_6H_5)_4$		1.000	17.88 ±0.09
0.008	25.30±0.01	0.000	−19.36±0.04	$NaB(C_6H_5)_4$	
0.051	24.38±0.03	0.016	24.93±0.10	0.072	−14.08 ±0.08
0.091	23.19±0.05	0.020	40.23±0.40	0.122	−13.87 ±0.03
0.211	18.23±0.08	0.025	38.00±0.30	0.187	−18.45 ±0.05
0.253	15.37±0.02	0.044	16.23±0.07	0.240	−21.16 ±0.06
0.346	8.97±0.02	0.103	−41.45±0.02	0.446	−28.34 ±0.07
0.601	−4.66±0.02	0.208	−74.82±0.08	0.682	−31.38 ±0.02
0.798	−9.21±0.03	0.521	−87.56±0.20	0.855	−33.32 ±0.13
1.000	−12.76±0.04	0.813	−94.90±0.13	1.000	−35.02 ±0.02
		1.000	−99.31±0.68		

RESULTS AND DISCUSSION

We have proposed an approach [21] for the evaluation of the enthalpic characteristics of individual ions based on the following preconditions. The enthalpy of transfer of an ion (i) from solvent S_1 into solvent S_2 $[\Delta_{trf}H_{S_1 \rightarrow S_2}(i)]$ is represented as a sum of two constituents (contributions)

$$\Delta_{trf}H_{S_1 \rightarrow S_2}(i) = \Delta_{trf}H^{univ}_{S_1 \rightarrow S_2}(i) + \Delta_{trf}H^{char}_{S_1 \rightarrow S_2}(i) \qquad (1)$$

The universal constituent $[\Delta_{trf}H^{univ}_{S_1 \rightarrow S_2}(i)]$ of the enthalpy of transfer of an ion is assumed to equal the enthalpy of transfer of a non-polar particle having a size close to that of an ion. In the case of small ions we used the data on the enthalpies of solution of noble gases. The data on water and methanol were taken from refs. 22 and 23. Extrapolated data were used for the solvents for which no data were available and the dependences similar to those shown in

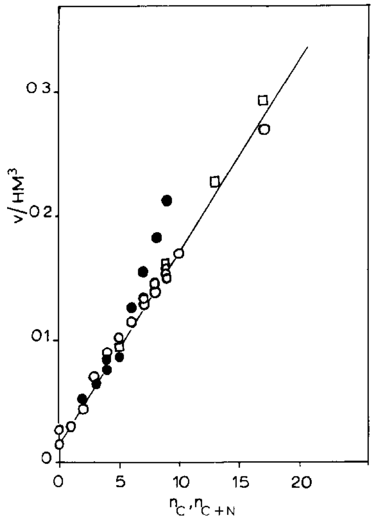

Fig. 1. Dependence of the volumes of *n*-alkane molecules and tetraalkylammonium ions ($V = (4/3)\pi r^3$) on the number of carbon atoms in them. The radii of particles are taken from refs. 23 and 27. ○, ●, C_nH_{2n+2}; □, $(C_nH_{2n+1})_4N^+$.

Fig. 2 were used for this purpose. *n*-Alkanes were used for tetraalkylammonium (TAA) ions. The dependence shown in Fig. 1 confirms the use of *n*-alkanes as model substances. The enthalpies of transfer of *n*-alkanes from methanol to HMPA and acetonitrile (Fig. 2) were calculated using the literature [24,25] and our (Table 1) data on the enthalpies of their solution in non-aqueous solvents. We failed to determine experimentally the enthalpy of solution of *n*-$C_{18}H_{38}$ in methanol due to its low solubility. Since the enthalpy of transfer is equal to the difference between the enthalpies of solvation, i.e.

$$\Delta_{\mathrm{trf}}H^0_{\mathrm{MeOH}\rightarrow\mathrm{HMPA}}(C_{18}H_{38}) = \Delta_{\mathrm{solv}}H^0_{\mathrm{HMPA}}(C_{18}H_{38}) - \Delta_{\mathrm{solv}}H^0_{\mathrm{MeOH}}(C_{18}H_{38}) \tag{2}$$

the enthalpy of solvation of octadecane in methanol was found by linear

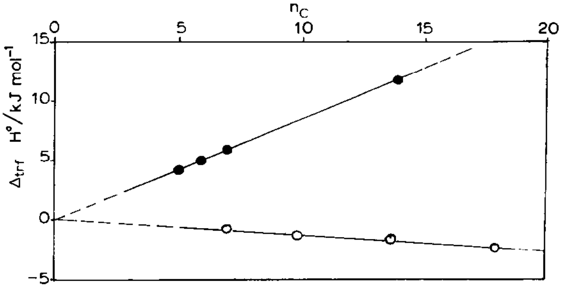

Fig. 2. Enthalpies of transfer of *n*-alkanes from methanol to acetonitrile (●) and HMPA (○) vs. the number of carbon atoms in the alkane molecule.

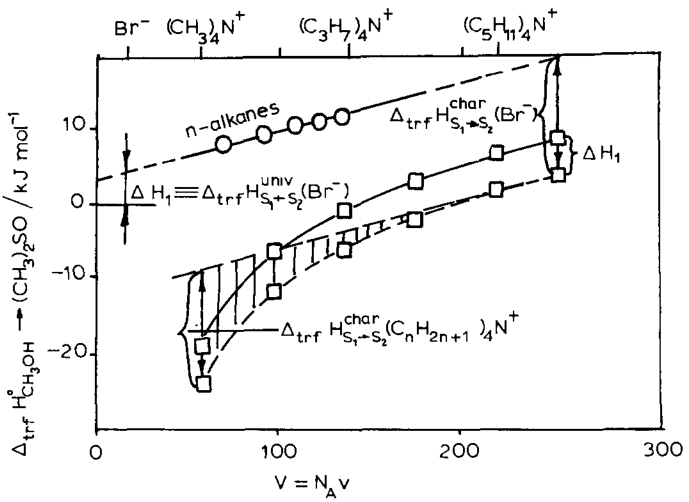

Fig. 3. Dependence of the enthalpy of transfer of *n*-alkanes and tetraalkylammonium bromides from methanol to dimethylsulfoxide vs. particle volume (cm^3 mol^{-1}).

extrapolation of the literature data [24] on the enthalpies of solvation of *n*-alkanes C_7–C_{16}. The value of the enthalpy of solvation of octadecane in HMPA was found from the equation

$$\Delta_{\mathrm{solv}} H^0_{\mathrm{HMPA}}(C_{18}H_{38}) = \Delta_{\mathrm{soln}} H^0_{\mathrm{HMPA}}(C_{18}H_{38}) - \Delta_{\mathrm{subl}} H(C_{18}H_{38}) \qquad (3)$$

where $\Delta_{\mathrm{subl}}H$ is the enthalpy of sublimation of alkane. The value of $\Delta_{\mathrm{subl}}H$ of octadecane was found from eqn. (3) proceeding from the extrapolated values of the enthalpies of solvation of $C_{18}H_{38}$ according to the data of Stephenson and Fuchs [24] and from experimentally obtained $\Delta_{\mathrm{soln}}H^{\circ}$ values of this alkane in five solvents (benzene, CCl_4, toluene, 1,2-DCE, and heptane). It was found to be 146.1 ± 0.2 kJ mol^{-1}.

The other constituent $[\Delta_{\mathrm{trf}} H^{\mathrm{char}}_{S_1 \to S_2}(\mathrm{i})]$ of eqn. (1) includes all the types of interactions between the atomic–molecular particles in solution that are determined by the ionic charge.

Figure 3 shows the constituents of the enthalpy of transfer of ions from methanol into DMSO vs. The volume of particles ($V = N_A v$). With the increase in TAA ion size, the value of $\Delta_{\mathrm{trf}} H^{\mathrm{char}}_{S_1 \to S_2} \Sigma (C_nH_{2n+1})_4N^+Br^-$ approaches some limiting value corresponding to $\Delta_{\mathrm{trf}} H^{\mathrm{char}}_{S_1 \to S_2}(Br^-)$. We believe that over a series of TAA ions with a general formula $(C_nH_{2n+1})_4N^+$ their charge constituent approaches zero with increasing size of the hydrocarbon radical. The physical reason for this comes from the increasing screening of the positive charge located on the nitrogen atom by the alkyl groups of the organic cation [26].

Using literature data [23,25,27–31] and our own data on the enthalpies of solution of substances, we calculated the values of the charge constituents of

TABLE 3

Coefficients of the linear equations $\Delta_{trf}H^{char}_{PC\rightarrow S}(i) = a + b\mathrm{DN}_{SbCl_5}$ and $\Delta_{trf}H^{char}_{PC\rightarrow S}(i) = a + b\mathrm{AN}$ [a]

	Li^+	Na^+	K^+	Cs^+	$(CH_3)_4N^+$	$(C_4H_9)_4N^+$	Cl^-	Br^-	I^-
a	33	29	16	16	8	0.1	41	25	12
b	−2.5	−2.0	−1.2	−1.0	−0.5	0	−2.5	−1.7	−0.9
AN_i	2.5	2.0	1.2	1.0	0.5	0			
DN_i							2.5	1.7	0.9

[a] S = nitromethane, acetonitrile, dimethylsulfoxide, hexamethylphosphoric triamide.

the enthalpies of transfer of ions from propylene carbonate into non-aqueous solvents.

We discovered that there is a linear dependence between the charge constituent of the transfer of ions and the donor (DN_{SbCl_5}) and acceptor (AN) numbers of a series of polar aprotic solvents. The existence of such correlations testifies to the fact that the cation interacts predominantly with the electron-donating atom of the solvent molecules, and the anion with the electron accepting atom. The coefficients of the linear equations of the dependences are given in Table 3.

The magnitude of coefficient b is a measure of the electron accepting (AN_i is the acceptor number) or electron donating (DN_i is the donor number) ability of ions. These numbers increase regularly from $(C_4H_9)_4N^+$ to Li^+ and from I^- to Cl^-. The positive deviations from the straight line $\Delta_{trf}H^{char}_{S_1\rightarrow S_2}(i)$ of ions occur in the solvents associated by H-bonds (water, methanol, formamide). We relate this fact to the structural endo-contribution upon solvation of ions in the solvents used.

The above facts allow us to explain the dependences in Figs. 4 and 5 proceeding from the donor–acceptor nature of ion–solvent and solvent–solvent interactions. Here, the non-electrolytes (HMPA and nitromethane) served as "probes" to evaluate the relative donor–acceptor properties of mixed solvents.

The observed increase in exothermicity of the enthalpies of transfer of $[(CH_3)_2N]_3PO$ molecules from formamide into its mixtures with water (Fig. 3) testifies to the strengthening of the electron-accepting ability of the mixed solvent with increasing in water content. An insignificant change in $\Delta_{trf}H^0$ values for nitromethane in the mixed solvent considered can be explained by small changes in the electron-donating ability of the mixture relative to formamide.

According to the above conclusions, the endothermicity of the enthalpies of transfer of electrolytes from formamide into its mixtures with water is conditioned by weakening solvation of cations. The increase in exothermicity of transfer of electrolytes on transition from iodides to chlorides can be explained by the strengthening electron-accepting ability of formamide–

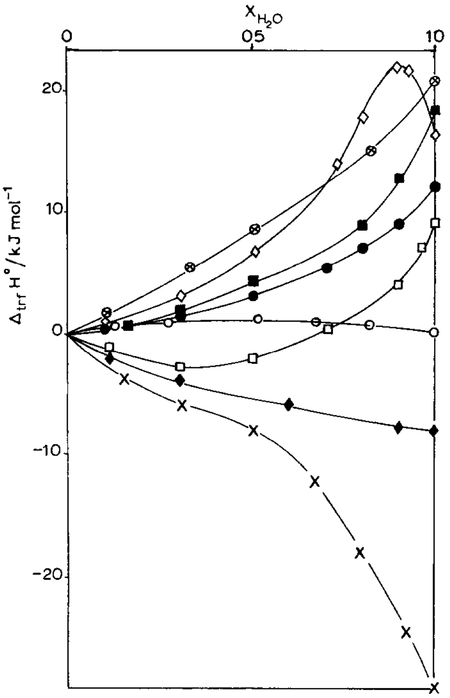

Fig. 4. Standard enthalpies of transfer of substances form formamide to its mixtures with water. ◇, $NaB(C_6H_5)_4$; ⊗, NaI; ■, NH_4NO_3; ●, NaCl; □, $LiNO_3$; ○, CH_3NO_2; ◆, NaF; ×, $[(CH_3)_2N]_3$ PO.

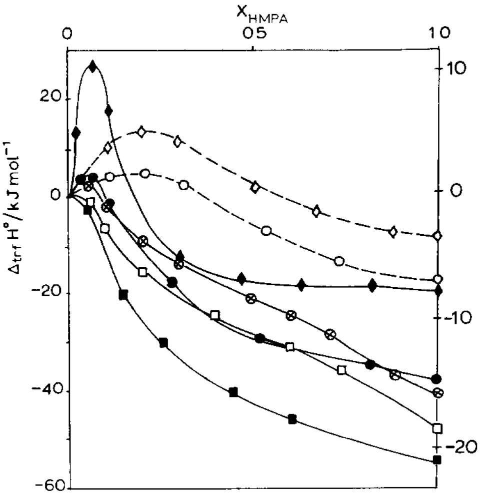

Fig. 5. Standard enthalpies of transfer of substances from water to its mixtures with dimethylsulfoxide (broken lines) and hexamethylphosphoric triamide. ◆, ◇, CH_3NO_2; ●, ○, $HCONH_2$; ⊗, $NaNO_3$; □, $LiNO_3$; ■, NH_4NO_3. The right-hand scale is for the non-electrolytes (◇, ◆, ○, ●).

water mixtures and increasing electron-donating ability of the anions (Table 3). A decrease in endothermicity of the enthalpies of transfer of electrolytes on addition of formamide to water agrees with the literature concepts of the destruction of water structure by formamide which results in a decrease of the endo-contribution from the destruction of intermolecular bonds in a mixed solvent compared with water [9].

The character of the dependences shown in Fig. 5 at $X_{\mathrm{HMPA}} > 0.1$ m.f. can be explained by the strengthening electron-donating ability of mixtures compared with water. Here, the solvency of the mixed solvent is expressed to a greater extent relative to formamide, the electron-accepting ability of which is higher than that of nitromethane. A similar picture is observed in water–dimethylsulfoxide mixtures.

Taking into account what has been stated above, it seems logical that the exothermicity of the enthalpies of transfer of electrolytes with the anion from water into its mixtures with HMPA increases over the series: K^+, Na^+, Li^+, NH_4^+. The greatest increase in exothermicity of transfer for the ammonium salt confirms the donor–acceptor nature of cation–solvent interaction.

For electrolytes with the same cation, the exothermicity of the enthalpies of transfer from water into water–HMPA mixtures increases over the series: Cl^-, Br^-, NO_3^-, I^-, which is a result of a weakening electron-accepting ability of the mixture and decreasing electron-donating ability of the anion. Such explanations are also correct for water–DMSO mixtures.

Solvation of cations and electron acceptors grows with increasing donor number of the non-aqueous component of mixtures over the series: water–FA, water–DMSO, water–HMPA.

The existence of the endothermicity maximum (relative to water) in $\Delta H^0_{\mathrm{soln}} = \mathrm{f}(X)$ functions is characteristic of the majority of the systems considered. It is concluded [32] that the increase in endothermicity of the enthalpies of solution (transfer) upon addition of the non-aqueous component to water is conditioned by various contributions (change in the enthalpy of cavity formation, in electron-donating ability, electron-accepting ability, by structural effects and perhaps by other factors). In this connection, the endothermicity maximum upon solution of $NaB(C_6H_5)_4$ in water–formamide mixtures is explained by the prevailing contribution from the enthalpy of cavity formation upon transition of the $B(C_6H_5)_4$ ion from water into the mixed solvent together with the exo-contribution from solvation of the Na^+ ion. As for nitromethane, the contribution from the effect of cavity formation upon transfer of $NaB(C_6H_5)_4$ from a mixture of water with non-aqueous additives decreases over a series of cosolvents: HMPA, DMSO, FA.

The linear dependence of the height of the endothermicity maximum on the magnitude of the DN_{SbCl_5}/AN ratio discovered by us (Fig. 6) can be explained by the fact that the nature of the maximum is connected with the

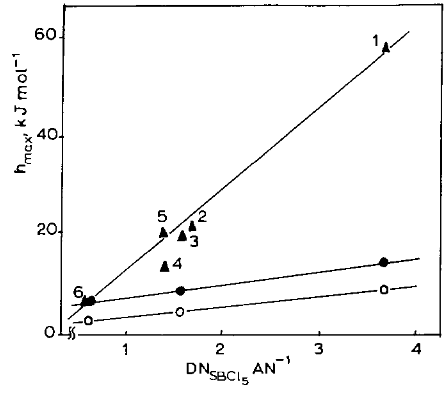

Fig. 6. Dependence of the height of the endothermicity maxima in $\Delta_{solvn}H^0 = f(X)$ functions on reduced donor number of the non-aqueous additive of the mixed solvent: 1, HMPA; 2, DMFA; 3, DMSO; 4, dioxane; 5, acetonitrile; 6, formamide; ▲, $NaB(C_6H_5)_4$; ●, n-$C_3'H_7OH$; o, CH_3NO_2.

differences in the specific interactions between the components of the mixed solvent that are determined by the donor–acceptor properties of cosolvents.

It can be seen from the data in Fig. 7 that the influence of small additions of the non-aqueous component on water structure which is related to the strengthening of the specific interactions between the mixed solvent components, manifests itself in the position of the endothermicity maximum over the composition axis and is determined by the value of the DN_{SbCl_5}/AN ratio.

The results of the thermochemical investigations on solutions of the electrolytes in water–HMPA mixtures ($X_{HMPA} = 0–0.20$) testifies to the fact that the magnitude and position of the endothermicity maxima in the

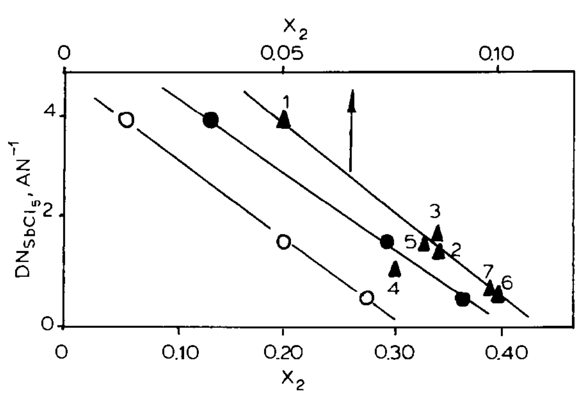

Fig. 7. Dependence of the positions of the endothermicity maxima over composition axis on reduced donor number of non-aqueous additive of the mixed solvent. 1-6, ▲, ●, o, as in Fig. 6; 7, ethanol.

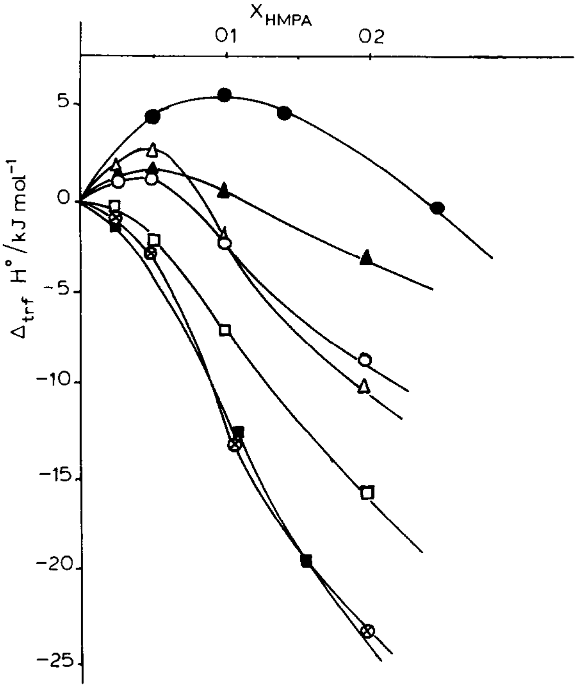

Fig. 8. Standard enthalpies of transfer of 1:1 electrolytes from water to water–HMPA mixtures. ●, NaCl; ▲ NaBr; ○, $NaNO_3$; △, KNO_3; □, $LiNO_3$; ■, NH_4NO_3; ⊗, NaI.

composition functions (Fig. 8) depend not only on the type of anion, as considered in the literature [33], but on the cation and on the peculiarities of ion–solvent interaction.

Thus, this paper reveals the regularities of the influence of the nature of the components and of the composition of mixed solvents on the universal and specific solvation of particles vs. their donor–acceptor properties, size and also the donor–acceptor ability of solvent. It is established that

(a) the specific solvation of anions becomes weaker, and of cations stronger upon the addition of aprotic polar solvents to water;

(b) in the mixed solvent relative to water the universal solvation of a substance becomes weaker with increasing size of the solvated particle and in the electron-donating ability of the non-aqueous component;

(c) when interpreting the extremal character of the $\Delta H_{soln} = f(X)$ dependence, one should take into account the donor–acceptor nature of the interparticle interactions in solution; this determines the existence of the contributions from the enthalpy of cavity formation, structural effects in the solvent and specific ion–solvent, solvent–solvent interactions;

(d) the solvency of mixed water–organic solvents relative to cations increases with the donor number of the non-aqueous component of the mixture.

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