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THERMOCHEMISTRY OF SOLVATION OF NON-ELECTROLYTES IN MONO- AND POLYATOMIC ALCOHOLS AND THEIR MIXTURES WITH WATER *

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ABSTRACT

Thermochemical data on the enthalpies of solvation of non-polar and polar non-electrolytes in solvents of different natures are discussed. Contributions from universal and specific solvation of polar molecules are distinguished. The rules of universal solvation of substances are considered using the solvation of alkanes as an example. The enthalpies of the specific solvation are discussed taking into account the specific interaction of the solvent with electron-donating and electron-accepting atoms of a polar molecule, special attention being paid to the solutions in associated liquids using water, alcohols and water–alcohol mixtures as examples.

INTRODUCTION

Peculiarities of the solvation processes are manifested in their thermodynamic characteristics. These characteristics reflect a complex character of solvation and hence they present certain difficulties for interpretation. In this connection, their details are distinguished by means of different contributions.

$$\Delta H^0_{\text{solv}}(\text{AB}) = \Delta H^{\text{sp}}_{\text{solv}}(\text{AB}) + \Delta H^{\text{univ}}_{\text{solv}}(\text{AB}) \qquad (1)$$

where $\Delta H^{\text{sp}}_{\text{solv}}$ and $\Delta H^{\text{univ}}_{\text{solv}}$ are the enthalpies of specific and universal solvation of the polar substance AB, respectively.

$$\Delta H^{\text{sp}}_{\text{solv}}(\text{AB}) = \Delta H^0_{\text{tr},\text{S}_\text{R}\to\text{S}}(\text{AB}) - \Delta H^0_{\text{tr},\text{S}_\text{R}\to\text{S}}(\text{M}) \qquad (2)$$

where $\Delta H^0_{\text{tr},\text{S}_\text{R}\to\text{S}}$ is the enthalpy of transfer of the substance and its model compound (M) from a reference (S_R) solvent to the solvent under investigation (S) [1,2].

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For the solvents without hydrogen bonds

$$\Delta H_{\text{solv}}^{\text{sp}}(\text{AB}) = -\Delta H_{\text{int}}^{\text{sp}} \tag{3}$$

$$\Delta H_{\text{int}}^{\text{sp}} = \Delta H_{\text{S}\rightarrow\text{S}_\text{R}}^{0}(\text{AB}) - \Delta H_{\text{S}\rightarrow\text{S}_\text{R}}(\text{M})$$

where $\Delta H_{\text{int}}^{\text{sp}}$ is the enthalpy of the donor–acceptor interaction between solute and solvent.

For the solvents with H-bonds

$$\Delta H_{\text{solv}}^{\text{sp}} = -\Delta H_{\text{int}}^{\text{sp}} + \Delta H_{\text{str}}^{\text{sp}}$$

The magnitude of $\Delta H_{\text{str}}^{\text{sp}}$ is determined by the changes in the energies of the hydrogen bonds in the solvent due to the specific solvent–solute interactions.

EXPERIMENTAL

Substances

We used alcohols of chemically pure classification, and nitromethane, formamide and 1,4-dioxane of pure for analysis classification which were further purified according to techniques described elsewhere [3]. Hexamethylphosphoric triamide of "pure" classification was purified according to the technique described in ref. 4. The water content determined according to Fischer's method in alkanol was less than 0.04 wt.%; in the remaining substances it was less than 0.01 wt.%. The water was doubly distilled ($\kappa = 1$ μSm sm^{-1}).

METHOD

The thermal effects of the dissolution of substances were measured using a microcalorimeter described elsewhere [5]. The technique of extrapolation of the thermal effects at infinite dilution is described in ref. 6.

RESULTS AND DISCUSSION

The standard enthalpies of solution of non-electrolytes in the solvents investigated are given in Tables 1 and 2. The enthalpies of the specific solvation of substances were calculated from eqn. (2). The necessary data on the solution enthalpies of *n*-alkanes in the solvents studied are taken from refs. 12–15.

The use of alkanes as model substances is determined by the amphiprotic character of the solvents studied and substantiated by the fact that the

TABLE 1

Enthalpies of solution of hexamethylphosphoric triamide, 1,4-dioxane nitromethane and formamide in alcohols and carbon tetrachloride (kJ mol^{-1})

Solvent	Abbreviation	Solute			
		HMPA	DO	NM	FA
Water	H_2O	-49.52+0.16	-9.59+0.04	3.32+0.08	1.80+0.01
Methanol	MeOH	-15.86+0.05	4.08+0.02	4.36+0.01	2.07+0.01
Ethanol	EtOH	-11.11+0.04	6.47+0.08	6.29+0.01	3.79+0.02
1-Propanol	1PrOH	-10.43+0.05	7.85+0.03	8.65+0.01	5.61+0.04
2-Propanol	2PrOH	-8.08+0.04	9.12+0.02	11.35+0.03	6.02+0.06
1-Butanol	BuOH	-8.95+0.05		9.45+0.03	
1,2-Ethanediol	$Et(OH)_2$	-12.80+0.04		3.90+0.04	
1,2,3-Propantriol	$Pr(OH)_3$	-13.20+0.24		-	
Carbon tetrachloride	CCl_4	-7.04 [a]	0.67 [b]	8.78+0.05	24.1 [c]

The errors of ΔH^0_{soln} values were calculated from the formula

$$\sigma = \left(\frac{\sum (\Delta y_i)^2}{n-m} \right)^{1/2}$$

where n is the number of points and m is the degree of the approximating polynomial.

[a] Ref. 7.

[b] Ref. 8.

[c] Ref. 9.

TABLE 2

Enthalpies of solution of hexamethylphosphoric triamide and nitromethane in some organic solvents (kJ mol^{-1})

Solvent	Abbreviation	Solute	
		$[(CH_3)_2N]_3PO$	CH_3NO_2
n-Heptane	Hep	7.44 [a]	13.90+0.09 [b]
Benzene	B	-5.23 [a]	3.29+0.04
1,2-Dichlorethane	DCE	-14.11 [c]	
Chloroform	ChF		0.68+0.02
Formamide	FA	-17.42+0.1 [d]	3.09+0.06 [d]
N,*N*-Dimethylformamide	DMFA	-1.48 [c]	-1.42+0.01 [d]
Propylene carbonate	PC	-2.65+0.05 [d]	-0.34+0.04 [b]
Acetonitrile	AN	-4.08+0.02 [d]	0 [d]
1,4-Dioxane	DO		-0.36+0.01 [b]
Acetone	AO	-2.06 [c]	
Dimethylsulfoxide	DMSO	0.57 [c]	-0.66+0.01 [d]
Hexamethylphosphoric triamide	HMPA	0	-5.26+0.01 [d]

[a] Ref. 7.

[b] Ref. 10.

[c] Ref. 11.

[d] Ref. 12.

universal solvation of a polar molecule in solvents of different natures is mainly determined by the dispersion interaction [16]. It is established [17] that the induction forces are not considerable upon solvation of ketones in various solvents. A *n*-alkane with a molar volume equal to that of a polar substance is taken as the model of a polar* substance.

It is noteworthy that since molar volume is included in the expressions for the calculation of the enthalpy of cavity formation and the enthalpies of interactions, it is a factor in favour of the choice of this parameter [18]

$$\Delta H_{\text{cav}} = V_2\delta_1^2$$

$$\Delta H_{\text{interac}} = 2V_2\delta_1\delta_2$$

where $\delta = [(\Delta H_{\text{evap}} - RT)/V]^{1/2}$.

The model compound must satisfy the condition that the sum of the enthalpies of cavity formation and of universal interactions for the polar molecule is equal to the sum of the corresponding contributions for the model substance.

Universal solvation

The influence of the nature of the solvent on alkane solvation is demonstrated in Fig. 1. Solvation of alkane in non-aqueous solvents becomes

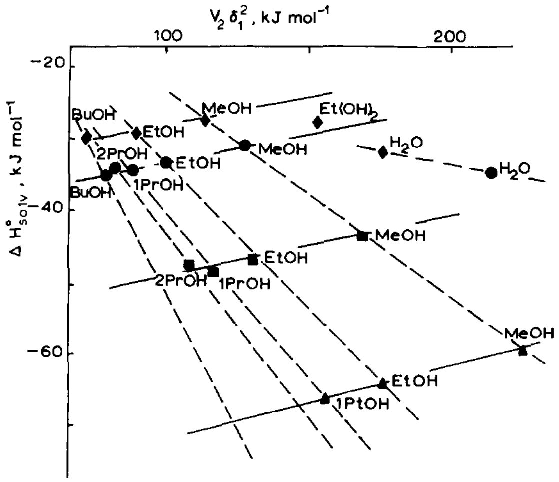

Fig. 1. Enthalpies of solvation of hexane (◆), heptane (●), decane (■) and tetradecane (▲) in alcohols and water vs. $V_2\delta_1^2$ values. In all the figures $T = 298.15$ K; Subscript 1 denotes the solvent and 2 the solute.

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* We understand polarity as the ability of a particle to participate in donor–acceptor interactions.

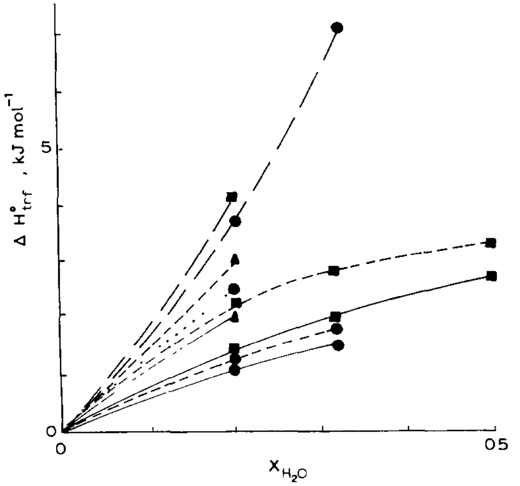

Fig. 2. Enthalpies of transfer of heptane (●), decane (■), tetradecane (▲) from methanol (·—·—·), ethanol (······), 1-propanol (— — —), and 2-propanol (———) into mixtures of alcohols with water.

weaker with increase in $V_2\delta_1^2$ values. The dependence considered confirms the conclusion concerning the weakening of self-association in alcohols with increasing size of the hydrocarbon radical due to the effects of weight increase [19].

The enthalpies of solvation of alkanes in a solvent become more exothermic with the increase in size of their molecules (Fig. 1). Strengthening of solute–solvent interaction here prevails over the increase in endothermicity of the enthalpy of cavity formation.

The addition of water to alcohols reduces the solvation of alkanes (Fig. 2). According to Mikhailov and Grigoryeva [20] and Krestov et al. [21] water molecules "suture" the alcohol associates to form mixed complexes. At constant composition of a mixed solvent, the observed action of water becomes stronger with a decrease in the molecular mass of the alcohol. As expected, the strengthening of the association in water–alcohol solvent in comparison with anhydrous alcohol mainly affects the solvation of these alkanes which have large molecules.

Specific solvation

Specific 1–2 interactions include contributions from the interactions of electron-donating (ED) and electron-accepting (EA) atoms (orbitals) of a dissolved molecule with the corresponding atoms (orbitals) of solvent molecules. Evaluation of these contributions is generally the most complicated (and unresolved) problem. A simple variant of interactions: strong electron donor–weak electron acceptor, strong electron acceptor (H-donor)–weak

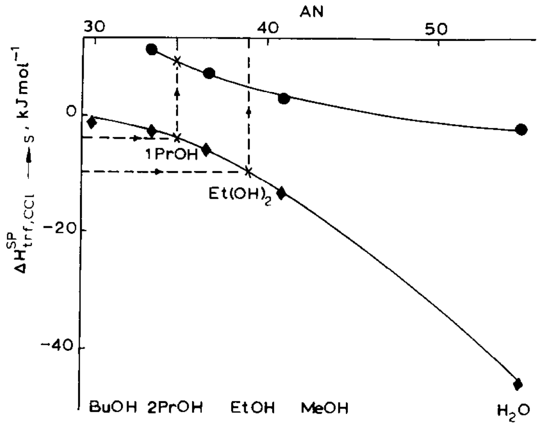

Fig. 3. Enthalpies of specific solvation of 1,4-dioxane (●) and hexamethylphosphoric triamide (◆) in alcohols and water vs. acceptor numbers [22] of solvents.

electron donor, is not realized in practice since strong H-donors (compounds with H-bonds) are also strong electron donors. For this reason the enthalpy of hydrogen bonding of a solute H-donor with a solvent which is a strong electron donor, determined by the pure base method, also includes a contribution from the interaction in which the solute acts as an electron donor.

The situation becomes much more complicated when the H-donor compound is a solvent; this is connected with the processes of self-association in such liquids.

Figures 3 and 4 show the enthalpies of the specific solvation of non-electrolytes in hydroxyl-containing solvents.

The specific solvation of 1,4-dioxane and hexamethylphosphoric triamide (HMPA) becomes stronger with increasing electron acceptability of solvents,

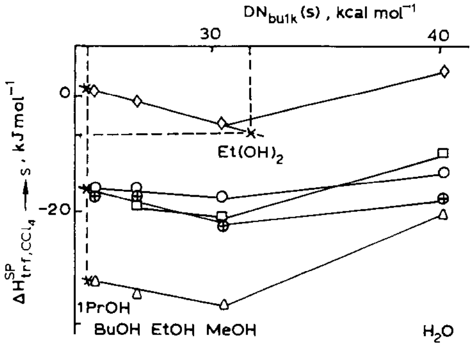

Fig. 4. Enthalpies of specific solvation of nitromethane (◇), formamide (□), methanol (○), ethanol (⊕), water (△) in alcohols and water vs. donor numbers [26] of solvents. Data for calculation of ΔH^{sp}_{solv} of water, methanol, ethanol are taken from refs. 14 and 23–25. *n*-Heptane is used as a reference solvent for water.

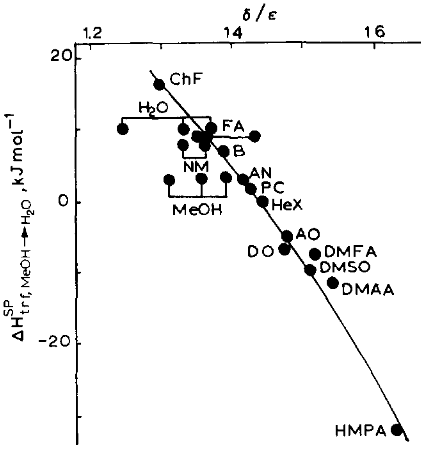

Fig. 5. Specific enthalpies of transfer of non-electrolytes from methanol to water vs. reduced donor number of solvent σ/ϵ [27]. $\sigma = 0.04336\mathrm{DN} + 8.83$, eV; $\epsilon = 0.029\mathrm{AN} + 6.125$, eV [28]. The following DN values were used to calculate σ/ϵ: for water (18, 33, 40.3), methanol (19, 25.7, 31.3), formamide (24, 24.7, 36.8), nitromethane (2.7, 7.6) [26].

water included (Fig. 3). The contribution from solute–solvent interaction through EA atoms of these solutes does not break the general rule here, but determines the somewhat different character of the dependences for 1,4-dioxane and HMPA. The existence of the correlations allows the determination of the acceptor numbers of 1-propanol and ethylene glycol which equal ~ 35.0 and ~ 39.0 units of acceptability, respectively, from the thermochemical data.

The specific solvation of nitromethane and H-donating non-electrolytes strengthens with the increase in electron-donating ability of the alcohol (Fig. 4). However, the role of the contribution from solute–solvent interactions in which solvent acts as H-donor remains vague. The fact is that, over a series of alcohols, their electron-accepting ability changes in the same direction as does the electron-donating ability. From the thermochemical data, the donor numbers of 1-propanol and ethylene glycol over the scale used are equal to ~ 26.1 and ~ 31.5 kcal mol^{-1}, respectively. Endothermic deviations for the non-electrolytes considered in water can be explained by the structural endo-contribution.

It follows from Figs. 3 and 4 that the solvation of polar molecules differs substantially in such solvents as water and alcohols in the dependence on their EDA ability. The data in Fig. 5 show that the difference between the enthalpies of the specific solvation of non-electrolytes in water and methanol becomes more exothermic with increasing σ/ϵ values of non-electrolyte [27]. The correlation includes *n*-hexane and benzene; this points to the donor–acceptor nature of the interactions of these substances with water and methanol. All substances shown in Fig. 5 can be subdivided into two groups: (1) $\sigma/\epsilon > 1.44$, $\Delta H^{\mathrm{sp}}_{\mathrm{tr,CH_3OH \rightarrow H_2O}} < 0$ and (2) $\sigma/\epsilon < 1.44$,

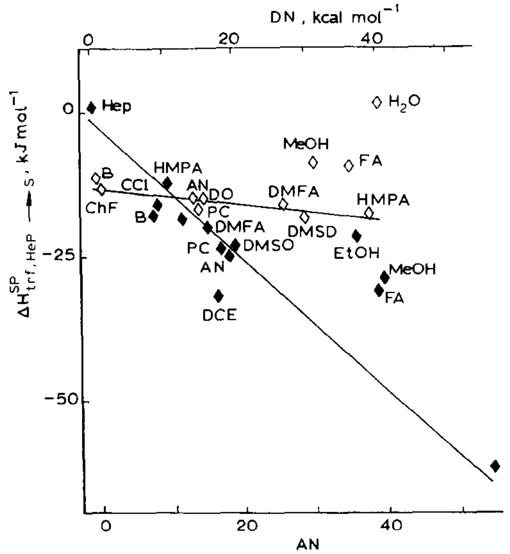

Fig. 6. Enthalpies of specific solvation of hexamethylphosphoric triamide (◆) vs. acceptor numbers of solvents and of nitromethane (◇) vs. donor numbers of solvents.

$\Delta H^{\mathrm{sp}}_{\mathrm{tr,CH_3OH \rightarrow H_2O}} > 0$. The existence of these groups of substances is proved by investigations on their solvation in other alcohols; this will be demonstrated below.

Increase in the electron-accepting ability (ϵ) of a solute weakens the exothermicity of $\Delta H^{\mathrm{sp}}_{\mathrm{tr,CH_3OH \rightarrow H_2O}}$ values, which can be explained by the structural endo-contribution upon hydration of electron-accepting atoms [27].

The peculiarities of the solvation of non-electrolytes are apparent on consideration of a wide series of solvents (Fig. 6). The specific solvation of HMPA becomes stronger over the series *n*-heptane, aprotic polar solvents, water, in conformity with increasing solvent electron-accepting ability (Fig. 6). HMPA in chlorinated hydrocarbons and benzene shows exo-deviation, and in alcohols and formamide endo-deviation relative to the line including the solvents noted.

The specific solvation of nitromethane increases with increasing solvent electron-donating ability (Fig. 7). The deviations which exist are explained first of all by the structural endo-contribution to the enthalpy of the specific solvation of nitromethane. The electron-donating ability must also be taken into account.

So far we have generalized the data on the enthalpies of solution of substances in water and alcohols and made an attempt to overcome the apparent difficulties by the introduction of the $\sigma_1\epsilon_2 + \sigma_2\epsilon_1$ parameter which reflects the total effect of the specific interactions (Fig. 7). The existence of two groups of solutes allows us to refer to them as "predominantly" electron

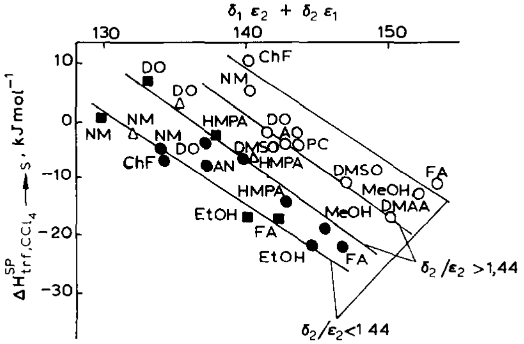

Fig. 7. Enthalpies of specific solvation of non-electrolytes in water (○), methanol (●), ethanol (△) and 1-propanol (■) vs. $\sigma_1\epsilon_2 + \sigma_2\epsilon_1$ values. Data for ΔH^{sp}_{solv} calculations are taken from refs. 6, 25 and 29–31.

donors or to "predominantly" electron acceptors on the basis of their quantitative thermochemical characteristics. The fact that the substances of the first group ($\sigma_2/\epsilon_2 > 1.44$) in alcohols, and of the second group ($\sigma_2/\epsilon_2 < 1.44$) in water are displaced into the endo-region is very interesting and confirms what has been said above.

It follows from the data of Tables 1 and 3 that the increase in the number of hydroxyl groups in alcohol molecules causes the strengthening of both electron-accepting and electron-donating properties. The strengthening of the specific solvation of the predominantly electron donating hexamethylphosphoric triamide and of predominantly electron accepting nitromethane testifies to this. We should note that the increase in the number of methyl groups in an alcohol molecules acts oppositely.

A comparison between the dependences shown in Fig. 8 allows us to speak about a symbatic change in the enthalpic characteristics of 1,4-dioxane and HMPA and the acceptor numbers of mixed solvents. The character of the dependences does not contradict the spectroscopic investigations [33] according to which in the region rich in alcohol there are water molecules that are bonded to the surrounding alcohol by two H-bonds

TABLE 3

Enthalpies of specific solvation of nitromethane and hexamethylphosphoric triamide in alcohols (kJ mol^{-1})

Solvent	Solute	
	CH_3NO_2	$[(CH_3)_2N]_3PO$
Methanol	−4.91	−13.44
Ethanol	−1.41	−5.6
1,2-Ethanediol	−6.0	−9.5
1-Propanol	1.7	−3.6

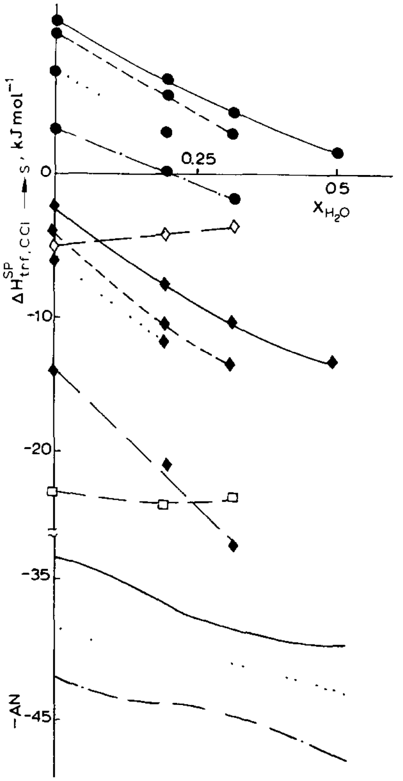

Fig. 8. Enthalpies of specific solvation of 1,4-dioxane (●), hexamethylphosphoric triamide (◆), nitromethane (◇), formamide (□) in methanol (·—·—·), ethanol (······), 1-propanol (— — —), and 2-propanol (———), and their mixtures with water and acceptor numbers [32] of solvents. Data for ΔH^{sp}_{solv} calculations are taken from refs. 13 and 15.

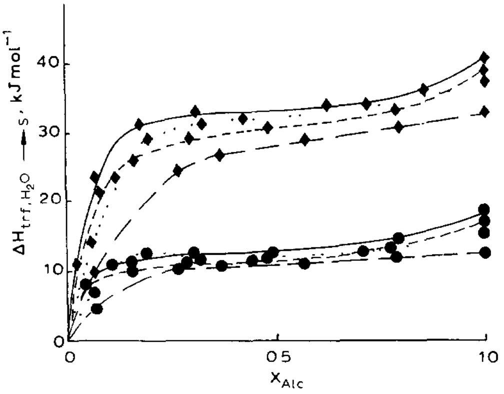

Fig. 9. Enthalpies of transfer of hexamethylphosphoric triamide (◆) and 1,4-dioxane (●) from water to its mixtures with methanol (·—·—·), ethanol (······), 1-propanol (— — —), and 2-propanol (———).

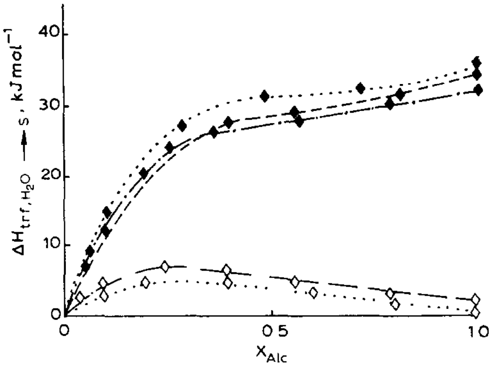

Fig. 10. Enthalpies of transfer of hexamethylphosphoric triamide (◆) and nitromethane (◇) from water to its mixtures with methanol (·—·—·), 1,2-ethanediol (······), and 1,2,3-propanetriol (— — —).

through hydrogen and oxygen atoms. The non-bonded hydrogen of water can be responsible for the increase in the electron-accepting ability of the mixture and the strengthening of the solvation of 1,4-dioxane and HMPA upon the addition of water to alcohol.

The specific solvation of formamide remains practically unchanged and that of nitromethane becomes somewhat weaker upon the addition of water to methanol. Taking into account the electron-donating ability to formamide (water additions to alcohol strengthen the specific solvation of the electron-donating atoms of formamide), one can evidently speak about a certain weakening of the electron-donating ability of the solvent on addition of water to methanol.

Comparison of the data on the enthalpies of the universal and specific solvation on non-electrolytes in mixed solvents (Figs. 2 and 8) and the data in Fig. 9 shows that the specific solute–solvent interactions make a determining contribution to the enthalpy of solvation of non-electrolytes in the solvents investigated. It follows from Fig. 10 that the closest character of $\Delta H^0_{tr} = f(x)$ isotherms is observed for the mixtures of water with methanol, ethylene glycol and glycerine. This can be connected with a similar structure of water–alcohol mixtures for those alcohols having the same number of methyl and hydroxyl groups.

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