

# Application of calorimetric methods to investigations of interactions in solutions\*

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*Abstract:* The results of calorimetric measurements of dissolution enthalpy of electrolytes and nonelectrolytes in aqueous mixed solvents are discussed with regard to the intermolecular interactions that occur in the solution. Particular attention is given to the systems where hydrophobic hydration can play a significant role. Several ways for analysis of the hydrophobic hydration effects are presented. In the case of the dissolution enthalpies of simple inorganic electrolyte in water–organic solvent mixtures a shape of the dependence of the standard dissolution enthalpy on the mixed solvent composition can serve as a source of information about the hydrophobic properties of the organic co-solvent. A quantitative measure of the hydrophobic properties of some organic compounds can be obtained from the analysis of the organic molecule–electrolyte (used here as a probe) enthalpic pair interaction coefficients in water, determined calorimetrically. In some cases, the ‘cage model’ can be used for determination of hydrophobic hydration energetic effect. This model has been applied in our laboratory for analysis of hydrophobic properties of crown ethers. It is noteworthy, that all presented methods lead to qualitatively consistent results.

## INTRODUCTION

Molecular interactions and particularly the solute–solvent interactions influence significantly the processes and reactions that take place in a solution. For this reason they are intensively studied by means of different experimental methods. Much attention has been devoted in these studies to the aqueous solutions of organic compounds. It is well known that a special type of interactions among the apolar fragments of organic molecule and water, called ‘hydrophobic hydration’ occurs in these systems. The hydrophobic hydration influences significantly the properties and behaviour of solutions of complex organic compounds and, what is more important, biological systems. For this reason, its understanding is among the basic problems of contemporary science. The hydrophobic hydration process, no matter how it is understood, is connected with the enthalpy change. Consequently, it is possible to investigate this phenomenon by means of the solution calorimetry. However, the heat effect determined calorimetrically is a sum of different energetic effects that accompany the dissolution, dilution and mixing processes. Therefore, in order to obtain the information interesting for us from the calorimetric data, the systematic studies on selected systems and the use of appropriate model of interactions are necessary. This paper will describe the results of studies on the hydrophobic properties of different organic substances that have been carried out in our laboratory for several years. The studies have been based on the calorimetrically determined dissolution enthalpies of simple inorganic electrolytes (NaCl, NaI) and some nonelectrolytes in water–organic solvent mixtures. The details of the calorimetric measurements and the purification of solvents and solutes were given in the original works. The results refer to the temperature 298.15 K.

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## ENTHALPIES OF SOLUTION AND ENTHALPIES OF TRANSFER

As it is known, the standard dissolution enthalpy of a solid solute,  $\Delta_{\text{sol}}H^\infty$  is connected with the solvation enthalpy,  $\Delta_{\text{solv}}H$  by a simple relation:

$$\Delta_{\text{solv}}H = \Delta_{\text{sol}}H^\infty + H \text{ (crystal lattice)} \quad (1)$$

In order to compare the solvation enthalpy of a chosen solute in various solvents it is sufficient to analyse the standard dissolution enthalpy, as the enthalpy of the crystal lattice is the same in each case. For the description of solutions in binary solvents a convenient function is the enthalpy of transfer,  $\Delta_{\text{tr}}H^\infty$ , of the solute from an individual solvent (S) to the mixed solvent (M) of various compositions.

$$\Delta_{\text{tr}}H^\infty = \Delta_{\text{sol}}H^\infty(\text{M}) - \Delta_{\text{sol}}H^\infty(\text{S}) = \Delta_{\text{solv}}H^\infty(\text{M}) - \Delta_{\text{solv}}H^\infty(\text{S}) \quad (2)$$

The knowledge of the enthalpy of crystal lattice formation is not necessary here either.

The three-component systems, containing a solute and binary solvent are complicated as they are composed of three kinds of molecules interacting with one another in a different way. In ideal cases it can be expected that the  $\Delta_{\text{sol}}H^\infty$  in the binary solvent would be represented by a straight line connecting the  $\Delta_{\text{sol}}H^\infty$  values in both individual components of the mixed solvent. Such linear or almost linear courses of function  $\Delta_{\text{sol}}H^\infty$  vs. mixed solvent composition were very rarely observed, mostly in the systems containing co-solvents with similar properties and whose molecules are of a similar size, shape and structure. Usually, the mentioned above relations deviate from such a simple pattern, particularly in the case of solutions in water-organic solvent mixtures. These deviations are, to a large extent, a result of strong interactions among the molecules of both co-solvents leading to the changes of mixture structure with the change of composition.

Figure 1 presents the standard dissolution enthalpies of NaI in the mixtures of water with aliphatic alcohols as a function of the mole fraction of alcohol [1,2]. The curves representing the enthalpy of solution exhibit maxima at a low alkanol content. It is generally accepted that these maxima are related to a structure-promotion or a structure-stabilizing effect of added alkanol on water, due to the hydrophobic hydration of the alcohol alkyl group.

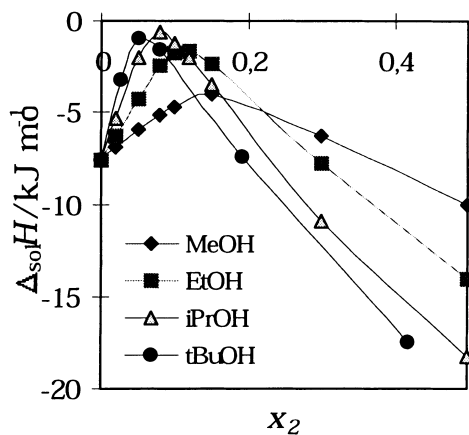
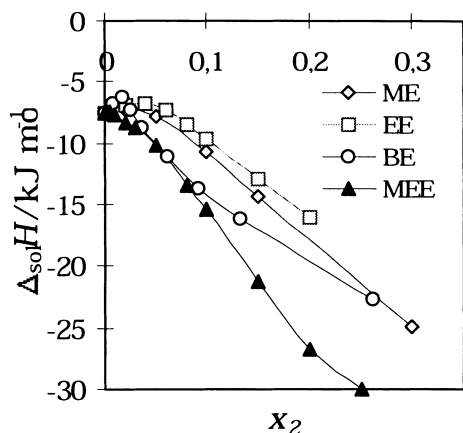


Fig. 1 Enthalpies of solution of NaI in mixtures of water with alcohols.

The position of the  $\Delta_{\text{sol}}H^\infty$  maximum and, to some extent, its height, depend on the size and the structure of apolar group of alcohol. Therefore, these parameters have been proposed as a relative measure of the hydrophobicity of the alkanol molecule. However, such a relatively simple picture concerns the solution enthalpies only in water-alcohol mixtures. It is noteworthy that the alcohol molecule includes the hydroxylic group which can be easily built in into the three-dimensional network of hydrogen bonds in water. That is why, the influence of alcohols on water depends mainly on the size and shape of the alkyl group in an alcohol molecule. In that case the effect of hydrocarbon group of alcohol seems to be almost 'pure', not disturbed by a functional group different from the OH group, which is also present in water.

The introduction of the oxygen atom to the carbon chain of the alkanol molecule changes this pattern significantly. In the mixtures of water with 2-alkoxyethanols (cellosolves) the  $\Delta_{\text{sol}}H^\infty$  maximum still appears (Fig. 2) but its height is smaller than that in the mixtures of water with the alcohol having the same number of carbon atoms in the molecule [3,4]. The presence of the highly polar ether oxygen atom in the carbon chain causes that a hydrophobic cage around the whole 2-alkoxyethanol molecule is weaker than that in the case of alkanols. The position of the maximum does not shift systematically towards a lower organic co-solvent content, when the size of the hydrocarbon group in the cellosolve molecule increases (Table 1). Moreover, in contrast to the alcohol-water mixtures, the height and the position of the maxima depend strongly on the kind of anion of the dissolved salt. The introduction of the next oxygen atom to the cellosolve molecule causes that the maximum of the  $\Delta_{\text{sol}}H^\infty$  of electrolytes in the mixtures of water with 2-(2-methoxyethoxy)ethanol does not appear [5].



**Fig. 2** Enthalpies of solution of NaI in mixtures of water with 2-alkoxyethanols (ME, EE, BE) and 2-(2-methoxyethoxy)ethanol.

**Table 1** Position,  $x_2(\text{max})^*$ , and height,  $\Delta(\Delta_{\text{sol}}H^\infty)^\dagger$ , of the  $\Delta_{\text{sol}}H^\infty$  maximum for NaI and NaCl in water–organic solvent mixtures

Solvent	$x_2(\text{max})$		$\Delta(\Delta_{\text{sol}}H^\infty)$ , kJ/mol	
	NaCl	NaI	NaCl	NaI
W-MeOH	0.170	0.150	3.55	3.55
W-EtOH	0.120	0.100	7.07	5.75
W-iPrOH	0.110	0.080	7.10	6.95
W-tBuOH	0.060	0.050	9.81	6.57
W-ME	0.055	0.020	0.97	0.23
W-EE	0.100	0.040	2.76	0.80
W-BE	0.060	0.018	3.71	1.30
W-DME	0.080	0.010	2.00	0.17
W-THF	0.250	0.025	6.48	0.48
W-HMPT	0.100	0.015	6.68	0.46

\* $x_2(\text{max})$  is the mole fraction of organic co-solvent, corresponding to the  $\Delta_{\text{sol}}H^\infty$  maximum.

$\dagger \Delta(\Delta_{\text{sol}}H^\infty) = \Delta_{\text{sol}}H^\infty(\text{MX in W-Y at } x_2(\text{max})) - \Delta_{\text{sol}}H^\infty(\text{MX in W})$ , where MX represents a salt, W, water and Y, co-solvent.

It is still more difficult to systematise the shapes of the dissolution enthalpy curves of inorganic electrolytes in the mixtures of water with organic solvents, that have a functional group other than hydroxyl one. The maxima of the  $\Delta_{\text{sol}}H^\infty$  appear (Fig. 3) in the mixtures of water with aprotic solvents, such as tetrahydrofuran (THF), hexamethylphosphotriamide (HMPT), 1,2-dimethoxyethane (DME) and

2-butanone [6–11], Similarly as in the water-cellosolve mixtures their height is smaller than in the case of alcohols, that contain the same number of carbon atoms in the molecule. (Table 1). The position of the maxima also depends strongly on the nature of the anion of the dissolved salt. In the mixtures of water with N,N-dimethylacetamide (Fig. 4), the  $\Delta_{\text{sol}}H^\infty$  of NaCl and KCl exhibit a tendency towards the appearance of the maxima, while the  $\Delta_{\text{sol}}H^\infty$  curve for NaI has no maximum [12,13], On the other hand, the dissolution enthalpies of NaI and NaCl in the mixtures of water with N,N-dimethylformamide (DMF) [14] and dimethylsulfoxide (DMSO) [15] are shown by monotonous curves within the whole range of the mixed solvent composition. (Fig. 5). The maximum of the  $\Delta_{\text{sol}}H^\infty$  of electrolytes has not been observed either in the mixtures of water with organic substances, like formamide and urea [14,16] which do not contain an apolar group in their molecules (Fig. 5).

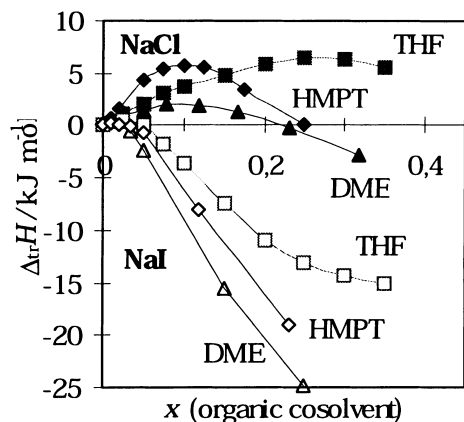


Fig. 3 Enthalpies of transfer of electrolytes from water to mixtures of water with some aprotic solvents.

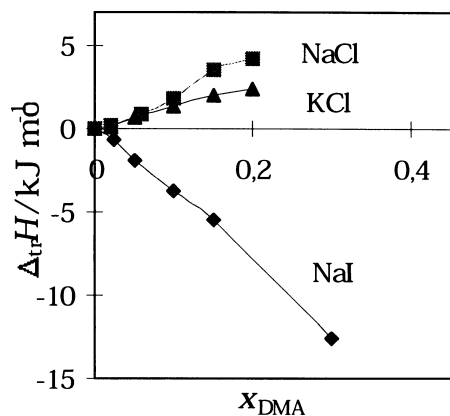


Fig. 4 Enthalpies of transfer of electrolytes from water to mixtures of water with DMA.

Undoubtedly, the observed different shape of the  $\Delta_{\text{sol}}H^\infty = f(x)$  curves reflects the different properties of the organic component of the mixed solvent. It can be supposed that also in these systems the shape depends on the hydrophobicity of the organic co-solvent molecule, at least, in the range of high water content. In this case, the hydrophobicity should be understood as a resultant of the hydrophobic effect of apolar groups and the effect of hydrophilic interactions of functional polar groups present in the molecule. These highly polar groups make it difficult to create a hydrophobic cage around the molecule, and they are able to interact strongly with the dissolved ions. As a result, the observed hydrophobic properties of the organic co-solvent molecule as a whole are weakened and the  $\Delta_{\text{sol}}H^\infty$  maximum is lower than it was expected or it even declines. The position of the  $\Delta_{\text{sol}}H^\infty$  maxima seems to be also a result of the superimposition of the above mentioned two effects. It should be added here, that in the binary solvents in

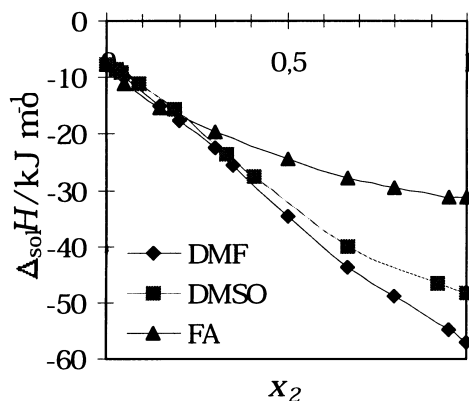


Fig. 5 Enthalpies of solution of NaI in mixtures of water with DMF, DMSO and FA.

which water has been replaced by an organic solvent, such as methanol or DMF the maxima of the  $\Delta_{\text{sol}}H^\infty$  do not appear within the composition range interesting for us.

The analysis of the shape of dissolution enthalpy curves concerning inorganic electrolytes in water–organic mixtures enables us to conclude, in many cases, about presence or absence of the hydrophobic effects in the system. Unfortunately, the quantitative evaluation of hydrophobic properties is not possible in this way. Such evaluation seems to be possible if we use for the analysis of calorimetric data the enthalpic pair interaction coefficients model, derived from the McMillan–Mayer theory [17]. The enthalpic pair interaction coefficients can be regarded as a measure of the heat effect (i.e. enthalpy of interaction) when two solute particles approach each other in dilute solutions. They can be obtained from the enthalpies of dilution (interaction between similar solutes) and the enthalpies of mixing or of dissolution, leading to three-component systems (interaction between dissimilar solutes). Essentially, the enthalpic pair interaction coefficients describe the solute–solute interactions. As these interactions are solvent mediated, it should be possible to use the above mentioned coefficients for the analysis of the solute–solvent interactions too. The enthalpic interaction coefficients,  $h_{xy}$  for a pair of particles  $X$  and  $Y$ , illustrate the sum of endothermic effects connected with a partial dehydration of molecules of both solutes, and an exothermic effect of ion-dipole (or dipole-dipole) type interaction between particles  $X$  and  $Y$ . Hence, if we consider the  $h_{xy}$  coefficients for a series of pairs consisting of one, selected solute  $X$  (in our case it is NaI) and different solutes  $Y$  in aqueous solutions, then the variations of the  $h_{xy}$  values should depend on the differences in the solvation effects of solute  $Y$  and in the effects of direct interaction between  $X$  and  $Y$ . It appears that the enthalpic pair interaction coefficients for NaI–nonelectrolyte pairs in water are linearly correlated with the molar heat capacity of hydration of the nonelectrolyte  $Y$  [18] and even better with the heat capacity of interactions,  $C_p(\text{int})$  between the nonelectrolyte  $Y$  and solvent water [10]. (Fig. 6).

The  $C_p(\text{int})$  values can be calculated from the,  $C_p(\text{hydrat})$  according to the equation:

$$C_p(\text{hydrat}) = C_p(\text{int}) + C_p(\text{cav}) = C_{p,2} - C_p^g - R[2\alpha_p T + (\delta\alpha_p/\delta T)_p T^2 - 1] \quad (3)$$

where  $C_{p,2}$  and  $C_p^g$  are the partial molar heat capacity of the dissolved solute in water and the standard molar heat capacity of the gaseous substance, respectively, and  $C_p(\text{cav})$  denotes the heat capacity of the cavity creation in water.

The presented dependence is worthy of notice as it correlates the enthalpic pair interaction coefficients with a single parameter describing some properties of components of the system and it encompasses nonelectrolytes having different properties and molecular structure. Therefore, it can be concluded that in aqueous solutions, for the pairs consisting of a given electrolyte  $X$  (NaI) and different nonelectrolytes  $Y$ , the effect of dehydration of the nonelectrolyte makes a leading contribution to the observed variation of the  $h_{xy}$  values. Other possible contributions do not influence decisively the  $h_{xy}$  variation. They remain constant or change proportionally to  $C_p(\text{int})$ . This opinion is confirmed by a similar correlation obtained when the NaI is replaced by NaCl [10] or by polar nonelectrolyte such as urea [10] (Fig. 7) or DMF [19],

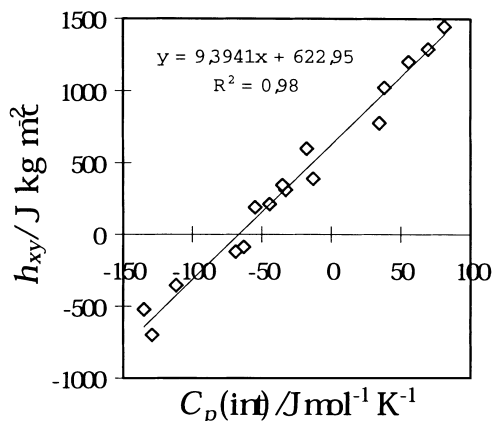


Fig. 6 Correlation between the enthalpic pair interaction coefficients,  $h_{xy}$ , for NaI-nonelectrolyte pairs in water and the  $C_p(\text{int})$  of the nonelectrolytes with solvent water.

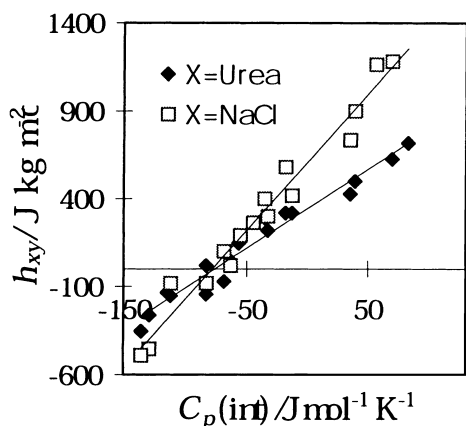
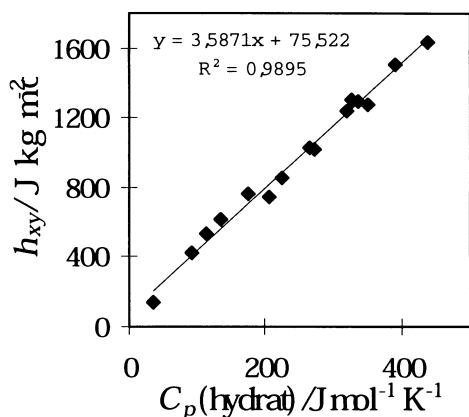


Fig. 7 Correlation between the enthalpic pair interaction coefficients,  $h_{xy}$ , for NaCl-nonelectrolyte and Urea-nonelectrolyte pairs in water and the  $C_p(\text{int})$  of the nonelectrolytes with solvent water.

although in the latter case, the  $C_p(\text{hydrat})$  better correlates the  $h_{xy}$  values. The effect of the properties of substance  $X$  (NaI, NaCl, urea, DMF), in these correlations manifests itself in a different slope of the correlating lines. The analogous dependencies have not been observed in the nonaqueous solvents investigated thus far such as DMF or methanol. It can be concluded then that the effect of hydrophobic hydration of the substance  $Y$  influences decisively the observed variation of the enthalpic pair interaction coefficients in water within that series of the pairs of substances. The substance  $X$  plays a role of a thermochemical probe in these pairs. Therefore, a set of the  $h_{xy}$  coefficients for properly selected  $X$ - $Y$  pairs can be used as a thermochemical criterion, or a thermochemical relative measure of hydrophobic properties of compounds. It makes also possible to arrange the organic substances according to their growing hydrophobicity understood as a resultant of the hydrophobic and hydrophilic properties of their molecules.

The analysed heterotactic pair interaction coefficients were calculated from the measured enthalpies of solution of the solute  $X$  in the aqueous solutions of substance  $Y$ . However, the  $h_{xy}$  values determined in this way cannot be used as a measure of hydrophobic properties of the substances when some specific interactions or chemical reactions occur in the investigated system. In this case, strong effects of the specific interactions among molecules of both solutes give a significant impact to the  $h_{xy}$  values which can even dominate over the hydration effects.

In such case it is often possible to use the 'cage model' of hydrophobic hydration proposed by Mastroianni, Pikal & Lindenbaum [20] and developed by Somsen and his group [21]. The 'cage model'



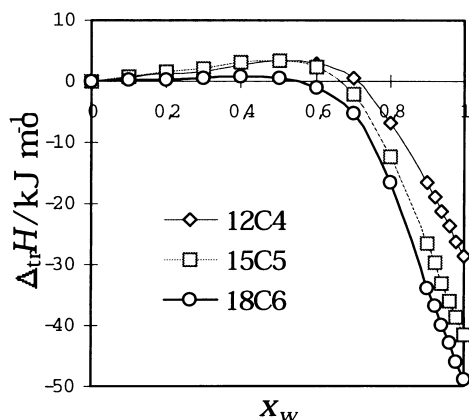
**Fig. 8.** Correlation between the enthalpic pair interaction coefficients,  $h_{xy}$ , for DMF-nonelectrolyte pairs in water and the  $C_p(\text{hydrat})$  of the nonelectrolytes with solvent water.

leads to an equation that binds the enthalpies of solution of hydrophobic compounds in water–organic solvent mixtures with those in pure solvent components, the mole fraction of water, the enthalpic contribution of hydrophobic hydration in water,  $Hb(W)$ , and the number of water molecules hydrating one alkyl group,  $n$ :

$$\Delta_{\text{sol}}H(M) = (1 - x_w)\Delta_{\text{sol}}H(S) + x_w\Delta_{\text{sol}}H(W) + (x_w^n - x_w)Hb(W) \quad (4)$$

The assumptions of the model are fulfilled in the mixtures of water with DMSO, DMF and, to a lesser extent, with DMA. This model was applied in our laboratory for the investigations of the hydrophobic properties of crown-ethers, when we studied the thermodynamic functions of crown-ether-cation complex formation and the complex hydration in aqueous solvent mixtures.

Figure 9 shows the transfer enthalpies of crown-ethers: 12-crown-4, 15-crown-5 and 18-crown-6 from water to water–DMSO mixtures [22]. The shape of the  $\Delta_{\text{tr}}H^\infty = f(x_w)$  curves is characteristic for hydrophobically hydrated substances. The calorimetric data could be described by eqn 4 very well. The  $Hb(W)$  and  $n$  values, determined by the least square analysis in terms of this equation are given in Table 2. Table 2 contains also the analogous data for 15-crown-5 and benzo-15-crown-5 [23] calculated from the results of calorimetric measurements in the mixtures of water with DMF and DMA. As it can be seen from the presented data, the effect of hydrophobic hydration becomes more exothermic when the number of  $\text{CH}_2$  groups in the crown-ether molecule grows, as it was expected. A contribution from each  $\text{CH}_2$  group in the total  $Hb(W)$  enthalpy amounts to (4.4–4.9) kJ which is a very close value to the analogous one determined by Somsen in the case of hydrophobic hydration of amines. A replacement of DMSO by DMF in the mixed solvent, practically does not change the hydrophobic hydration parameters for 15C5.

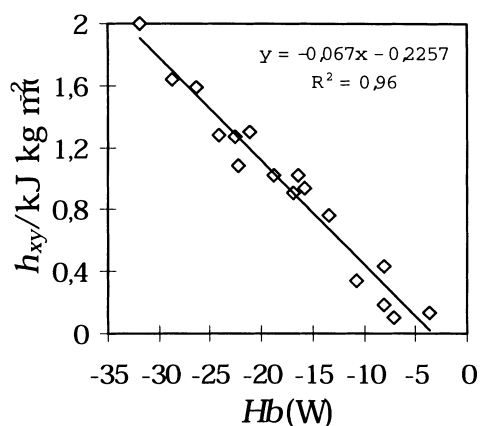


**Fig. 9** Enthalpies of transfer of crown-ethers from DMSO to DMSO–water mixtures.

**Table 2** The enthalpic effect of hydrophobic hydration in water,  $Hb(W)$ , the parameter  $n$ , at 298.15 K

Solute	co-solvent	$Hb(W)$ (kJ/mol)	$n$	solute	co-solvent	$Hb(W)$ (kJ/mol)	$n$
12C4	DMSO	-35.0	4.8				
15C5	DMSO	-48.8	4.4	B15C5	DMSO	-36.6	5.3
15C5	DMF	-49.4	4.0	B15C5	DMF	-37.8	4.7
15C5	DMA	-52.2	4.6	B15C5	DMA	-39.4	5.2
18C6	DMSO	-52.8	4.4				

A question which arises here is, to what extent the results of examinations of hydrophobic properties of substances performed by means of the 'cage model' are consistent with the results obtained from the analysis of the enthalpic pair interaction coefficients. Figure 10, which shows a correlation between the  $h_{xy}$  values for DMF-nonelectrolyte pairs and  $Hb(W)$  values for the same nonelectrolytes, indicates that both presented methods of analysis lead to analogous conclusions.

**Fig. 10** Correlation between the  $h_{xy}$  coefficients for DMF-nonelectrolyte pairs and the enthalpic effect of hydrophobic hydration of the nonelectrolyte in water.

The presented results demonstrate clearly that the solution calorimetry is an important tool in the studies of molecular interactions in a solution, and it gives a vast possibility for hydrophobic effect analysis.

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