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Solution calorimetry of organic nonelectrolytes as a tool for investigation of intermolecular interactions

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The paper is mainly the review and generalization of the previous publications of the authors. It demonstrates that solution calorimetry method gives the opportunities of more detailed understanding of various aspects of intermolecular interactions in solution. We are assured that prerequisite to such an understanding is the successive analysis of various solute–solvent systems from the simplest ones which include alkanes as a solute or as a solvent to the most complex systems with solvent self-association via hydrogen bonding. Particular findings discussed in this paper are (i) an inconspicuous contribution of electrostatic solute–solvent interaction to the solvation enthalpy and, accordingly, the dominating contribution of dispersion interactions for nonspecifically solvated solutes; (ii) new, very general method for the extraction of specific interaction enthalpy from the enthalpy of solvation; (iii) new method of determination of self-association enthalpies for the solvents associated via hydrogen bonding; (iv) new method for determination of cooperative hydrogen bonding enthalpies of proton acceptors with associated species of alcohols; (v) the unique method of experimental determination of the hydrophobic effect enthalpy. Copyright © 2007 John Wiley & Sons, Ltd.

Keywords: solution calorimetry; intermolecular interactions; hydrogen bonds; aliphatic alcohols; enthalpy of solution; cooperativity effect; linear solvation–energy relationships

INTRODUCTION

One of the main tasks of investigations in the field of solvation thermodynamics of nonelectrolytes is the more deep insight into the nature of intermolecular interactions in condensed media and the application of this knowledge to other fields of physical organic chemistry such as the solvent effects on chemical equilibria and kinetics, spectral properties, etc. Another task is the quantitative description of solvent effects on various physico-chemical parameters (including the solvation thermodynamic parameters itself) based on some molecular characteristics of solutes and solvents. These two tasks seem to be closely interrelated. The complexity of liquid systems leads to the fact that more rigorous ‘physical’ approaches often give rather modest results for quantitative description of solvent effects. On the other hand, a range of empirical and semi-empirical approaches (UNIFAC,^[1] modified UNIFAC,^[2] ASOG,^[3] MOSCED,^[4] SPACE,^[5] etc.) were successfully developed in the last few decades. We think that these approaches mainly resolve the second from above-mentioned tasks.

Unfortunately, there are quite a few papers in this field, which seem to consider the good description of experimental data as the unique purpose. In our opinion, these works are sometimes rather harmful because they entail the false assurance in the fidelity of background model.

Over the last few decades most solvation studies made use of the linear solvation–energy relationships (LSER) formulated by Kamlet, Taft, and Abboud.^[6–9] More recently, this approach was widely used predominantly in the works of Abraham *et al.*^[10–23] and Carr *et al.*^[24,25]

According to this approach, the thermodynamic parameter (TP) of solvation or transfer depends on a number of solute parameters (Eqns (1) and (2)):

$$TP = i + vV_X + s\pi_2^H + rR_2 + a\sum\alpha_2^H + b\sum\beta_2^H \quad (1)$$

$$TP = i + l\log L_{16} + s\pi_2^H + d\delta_2 + a\sum\alpha_2^H + b\sum\beta_2^H \quad (2)$$

where V_X is the McGowan characteristic volume,^[26] which, along with $\log L_{16}$ (Ostwald coefficient of solute in hexadecane), defines the contributions into TP of cavity formation and general dispersion interaction;^[12] π_2^H relates to the ability of solute to dipole and induction interactions with solvent; R_2 is the excess molar refraction;^[10] δ_2 is an empirical correction factor which compensates for the impossibility of describing electrostatic interactions by a single parameter (0 for aliphatic compounds, 0.5 for polychlorinated aromatic compounds, and 1 for any other aromatic compound);^[24] $\sum\alpha_2^H$ and $\sum\beta_2^H$ are the apparent acidity and basicity of solute.^[11] The first three terms of Eqns (1) and (2) relate to nonspecific solvation and the latter two to specific solute–solvent interaction. The coefficients i , v , l , s , r , d , a , and b characterize the given solvent and are found by the multiple linear regression technique.

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Despite the parameters in Eqns (1) and (2) are used to describe data on Gibbs energies of solvation and solution, these equations were also used for solvation enthalpies.^[23,24,27–33] It was confirmed that the LSER approach is quite good for the description of calorimetric data.

Authors who intensively employ the LSER approach always stress that it not only possesses a predictive power, but also is an excellent tool for gaining insight into the nature of intermolecular interactions in solution. They write that the terms in Eqns (1) and (2) can be for most part directly identified with particular solute–solvent interactions.^[10,14] In our opinion these pretensions are rather inconsistent.^[31,34] The parameters reflecting the nonspecific solvation (V_X , $\log L_{16}$, π_2^H , R_2 , and δ_2) are the most vulnerable in this respect.

The authors of the LSER approach have defined that $\log L_{16}$ (and V_X) is the parameter related to cavity formation and dispersion solute–solvent interactions.^[9] We can add that because of the approximate proportionality of solute polarizability and the volume of a molecule this parameter must contain the contribution of inductive interactions. Dispersion and inductive contributions seem to be inseparable because they depend on the same molecular parameter (polarizability).

Parameter π_2^H reflects 'polarity/polarizability' of a solute,^[12,24,35–37] while the product $s\pi_2^H$ is a measure of the dipolar and inductive interactions between the solute and the solvent.^[24] Owing to the above-mentioned reason this parameter must contain the contribution of dispersion interactions. Indeed, this parameter is based on the solvent π^* parameter of Kamlet, Taft, and Abboud, which was derived to be free from specific interactions. But is it free from dispersion interactions? Furthermore, if the dispersion interactions depend not only on solute polarizability (e.g., well-known London's equation for the energy of two spherical molecules in addition to polarizabilities contains the ionization potentials of the molecules) then the differentiating part of dispersion interactions is included exclusively into π_2^H .

The term rR_2 'represents dispersion interactions'^[12] and 'is the interactions due to the presence of π - and n -electron pairs'.^[13] Since the excess molar refraction is the excess polarizability, this parameter (along with δ_2) must be related to inductive interactions (not to mention that π - and n -electron pairs are in particular the factors determining the hydrogen bond acceptor ability). In addition we can mention that this term may contain some part of cavity formation enthalpy. Indeed, we do not intend to dispute the assertion that cavity formation energy depends on the volume of solute molecule. But what physical parameter is the measure of this volume? Is it molar volume, characteristic volume, or molar refraction? In the latter case the excess molar refraction of aromatic, halogenated, and fluorinated compounds conjugate with their 'excess' (relatively to calculated via V_X) cavity formation energy.

So, none of the independent parameters related to nonspecific interactions (V_X , π_2^H , or R_2) directly corresponds to any particular type of solute–solvent interactions.

The parameters of specific interaction ($\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$) seem to be more reasonable, but it is evident that description of specific interactions in the form of $a\Sigma\alpha_2^H + b\Sigma\beta_2^H$ is acceptable for simplest systems only. For example, solvation of proton acceptors in the solvents associated via hydrogen bonding can be accompanied by the cleavage of hydrogen bonds between solvent molecules. On the other hand, the contribution of hydrophobic effect to thermodynamic parameters was analyzed

separately in References^[38–40]. It was found to be very substantial for alkane solutes and zero for rare gases. It is not clear how this effect is taken into account by Eqns (1) and (2). It should be pointed out that the LSER approach is often used for aqueous solutions^[15,21–23,25] and other solvents associated via hydrogen bonding^[16,18–20] and it is not surprising that 'for distribution systems in which one phase is water, some solutes exhibit variable hydrogen-bond basicity'.^[17]

In a recent paper Vitha and Carr^[41] presented an excellent review of the LSER model in its historical development. They brightly demonstrated the great value of this approach for practical use in chromatography. Nevertheless, our doubts about the physical meaning of solute descriptors become rather strengthened. These doubts are shared partially by the authors of the review.^[41]

The LSER approach was undoubtedly very useful for the investigation of the solvent effects in various physico-chemical and biological processes. Nevertheless, the foregoing analysis^[31,34] shows that the solvent parameters obtained from Eqns (1) and (2) are mainly formal parameters. The bright illustration is the good description^[31] of experimental values of vaporization enthalpies for 140 liquid solutes by the equation similar to Eqns (1) and (2). Vaporization enthalpy is the solvation enthalpy in itself with opposite sign. So, resulted 'solvent' parameters have no physical sense by default. Nevertheless, standard deviations and correlation coefficients are not worse than those in the cases of solvation enthalpies in single solvents.

We think that it is more productive to analyze successively the separate types of intermolecular interactions in solutions. The example of such an approach based on solvation enthalpy data is presented in this paper. This approach is developed during the last three decades by the authors' research group. The paper is predominantly the review and generalization of our own publications. References to other authors whose works influenced our investigations (Richard Fuchs, Edward M. Arnett, Harold L. Friedman, Javier Catalán *et al.*) must be mostly found in our original publications.

SEPARATION OF DIFFERENT TYPES OF SOLUTE–SOLVENT INTERACTIONS FROM THE SOLVATION ENTHALPY

The transfer of the solute molecules from the standard state of solute (298 K; 1 atm; solid, liquid, or gas) to the solvent at infinite dilution is named 'solvation'. The term 'solvation' means the transfer from the ideal gas phase to the solvent at infinite dilution. The standard molar enthalpies of these processes are interrelated by a simple Eqn (3)

$$\Delta_{\text{solv}}H^{A/S} = \Delta_{\text{soln}}H^{A/S} - \Delta_{\text{vap}}H^A \quad (3)$$

where A is any solute (organic nonelectrolyte); S is any solvent; $\Delta_{\text{solv}}H^{A/S}$ is the solvation enthalpy of A in S , $\Delta_{\text{soln}}H^{A/S}$ is the solution enthalpy, and $\Delta_{\text{vap}}H^A$ is the standard molar vaporization enthalpy of solute.

Note: In order to simplify the equations we will omit the superscript 'A/S' in all the following cases. So, for solution, solvation, interaction, and cavity formation enthalpies ΔH without specifying solute and solvent will represent $\Delta H^{A/S}$.

Solution enthalpies are the experimental basis obtained from calorimetry for the analysis of solute–solvent interactions. But for the most part, the solvation enthalpies are preferable for this

analysis because they are free from contribution of solute–solute interactions.

The driving force for solvation is the solute–solvent intermolecular interaction. It should be kept in mind, however, that ‘solvation’ and ‘interaction’ are not identical terms. It is generally accepted that solvation enthalpy in addition to solute–solvent interaction enthalpy ($\Delta_{\text{int}}H$) includes some endothermic contribution owing to partial breaking of solvent–solvent interactions. This contribution is named the cavity formation enthalpy ($\Delta_{\text{cav}}H$):

$$\Delta_{\text{solv}}H = \Delta_{\text{cav}}H + \Delta_{\text{int}}H \quad (4)$$

Cavity formation enthalpy cannot be measured experimentally, but there are some theoretical approaches, which enable to calculate this value.^[42–44] Usually such approaches conceive the cavity formation as an inserting to the solvent of hard noninteracting sphere with size and shape of solute molecule. The volume of molecule is commonly considered as the major solute molecule parameter determining the cavity formation enthalpy. Sometimes^[45] the solvation enthalpy is considered as the sum of not two but three components:

$$\Delta_{\text{solv}}H = \Delta_{\text{cav}}H + \Delta_{\text{int}}H + \Delta_{\text{str}}H \quad (5)$$

where $\Delta_{\text{str}}H$ is the enthalpy associated with the structural change produced in the solvent by the solute (or by the cavity). It is also named the structural reorganization enthalpy of the solvent. This term is probably small for the majority of organic solvents but is particularly relevant to aqueous solution.

We assume the following possible contributions to the solvent interaction enthalpy. First of all, the splitting of intermolecular interactions into nonspecific and specific ones is universally accepted by chemists:

$$\Delta_{\text{int}}H = \Delta_{\text{int}(\text{nonsp})}H + \Delta_{\text{int}(\text{sp})}H \quad (6)$$

Specific interactions enthalpy [$\Delta_{\text{int}(\text{sp})}H$] is the enthalpy of localized donor–acceptor interactions, including hydrogen bond formation. Nonspecific interactions enthalpy is commonly considered as a sum of dispersion, dipolar, and inductive contributions:

$$\Delta_{\text{int}(\text{nonsp})}H = \Delta_{\text{int}(\text{disp})}H + \Delta_{\text{int}(\text{dip})}H + \Delta_{\text{int}(\text{ind})}H \quad (7)$$

The second term [$\Delta_{\text{int}(\text{dip})}H$] on the right-hand side of Eqn (7) reflects the electrostatic solute–solvent interaction arising from dissymmetry of charge distribution in the molecules. This type of interaction is often named the orientational or dipolar interaction. The parameters for describing this dissymmetry are first of all, the dipole moments of the molecules and secondly, the multipole moments of higher order. The third term [$\Delta_{\text{int}(\text{ind})}H$] is also of electrostatic nature, but one of the two interacting dipoles (or multipoles) arises from polarization of initially nonpolar molecule in the electrostatic field of another molecule. In addition to the parameters of charge dissymmetry of the second molecules, the polarizability of the first molecule plays a decisive role. Sometimes the sum of the electrostatic contributions is named ‘enthalpy of polar interactions’:

$$\Delta_{\text{int}(\text{polar})}H = \Delta_{\text{int}(\text{dip})}H + \Delta_{\text{int}(\text{ind})}H \quad (8)$$

The first term on the right-hand side of Eqn (7) [$\Delta_{\text{int}(\text{disp})}H$] is the enthalpy of dispersion interaction, which is of quantum–chemical nature. The particular feature of dispersion interactions is that it is attributed to all molecules without any exception. For the simplest molecular-pair systems the value of this term is readily

computable and depends on polarizability and ionization potential of both partners. Sometimes the term ‘van der Waals interactions’ is used as a synonym of ‘dispersion interactions’.^[45–53] But in other papers^[54–58] the term ‘van der Waals interactions’ is used as a synonym of ‘nonspecific interactions’.

The regular solution theory^[59,60] is the most widely used among the semiempirical approaches to analyze the thermodynamic parameters of solvation. It establishes the cohesive energy density (Hildebrand solubility parameter, δ_H) as the parameter characterizing the ability of the solute (δ_H^A) and the solvent (δ_H^S) to interact:

$$\delta_H = \sqrt{\frac{\Delta_{\text{vap}}H - RT}{V_M}} \quad (9)$$

where V_M is molar volume of solute or solvent. This approach gives Eqn (10) for the calculation of solvation enthalpy^[61,62]:

$$\Delta_{\text{solv}}H = V_M^A \cdot (\delta_H^S)^2 - 2 \cdot V_M^A \cdot \delta_H^S \cdot \delta_H^A - RT \quad (10)$$

where $[V_M^A \cdot (\delta_H^S)^2]$ and $(2 \cdot V_M^A \cdot \delta_H^S \cdot \delta_H^A)$ are the internal energies of cavity formation and interaction, respectively.

Hildebrand's original theory was only intended to apply to mixtures of nonpolar liquids, and for such liquids their intermolecular forces are only of one type, namely dispersion forces. Consequently, the solubility parameter for nonpolar substances can be considered as a measure of the dispersion interactions. Nevertheless, it was shown^[63] that even if one component of the system (solute or solvent) is alkane the terms in Eqn (10) poorly represent the interaction and cavity formation enthalpies despite the fact^[64,65] that the total solvation enthalpy of some polar solutes in hexane is satisfactorily described by Eqn (10).

The separation of electrostatic and specific interaction contributions to various physico-chemical parameters including the solvation enthalpy is very often performed by using the homomorph concept.^[66–74] The latter can be expressed mathematically by

$$\Delta_{\text{solv}}H - \Delta_{\text{solv}}H^{h/S} = \Delta_{\text{int}(\text{polar})}H + \Delta_{\text{int}(\text{sp})}H \quad (11)$$

where $\Delta_{\text{solv}}H^{h/S}$ is the solvation enthalpy of homomorph.

Homomorph is the compound with similar dispersion forces^[66] but incapable of polar and specific interactions. Assuming this definition of homomorph, Eqn (11) can be considered as rigorous. Unfortunately, the enthalpy of dispersion interaction cannot be measured directly or calculated for any real compound and this definition is partially useless for the choice of a definite compound as homomorph. Another definition formulated in papers^[74–76] states that homomorphs are the molecules, which have the same or closely similar molecular geometry. For example, alkanes with similar molar volume or ethers with the same number of carbon atoms were often used as homomorphs for aliphatic alcohols. It must be understood that the second definition of homomorph being applied to Eqn (11) means that the dispersion interaction enthalpy depends only on the size (volume) and shape (branching) of solute molecule. Despite the high allure of this supposition, it is not proven and we consider it as erroneous. This opinion agrees with the conclusion of Graziano who made it clear^[77] that the difference in hydration Gibbs energy for benzene and for alkane of equal size should be attributed to the different strength of van der Waals interaction with water.

Before extracting the polar and specific contributions from solvation enthalpies we will consider the systems for which the dispersion interactions play the decisive role.

Systems with dispersion solute–solvent interactions only

If there exist among the many organic nonelectrolytes substances capable of dispersion solute–solvent interaction only, then these substances are first of all alkanes. Indeed, it is generally accepted that alkanes do not interact specifically with common organic compounds. Molecular dipole moments of alkanes are practically equal to zero. The polarity of C–H and C–C bonds is low so the multipole moments of alkanes must be minimal. Besides, alkanes have the smallest polarizability among all organic substances. This allows to suppose a minor contribution of inductive interactions.

We will consider both cases: (i) alkane is a solute and (ii) alkane is a solvent.

Solvation enthalpies of alkanes in various solvents

Solution and solvation of alkanes in various media were studied thermochemically in a series of works.^[62,78–81] It was ascertained that solvation enthalpy of alkyl derivatives of various substances is the additive function of the number of methylene groups in solute molecule.^[62,80] Besides, it was shown in References^[78,82] that solution enthalpy for alkanes of various structure is proportional to the volume of alkane molecule. Molar volume and molar refraction (Lorenz–Lorentz equation) were used as the measure of alkane molecule volume. We consider molar refraction as a preferable parameter because molar volume also contains the intermolecular interstices. Examples of such proportional dependences are shown in Fig. 1, where the solution enthalpy values were obtained from References^[62,78–80,83–89]

A very significant result was obtained by Fuchs *et al.*^[78] They concluded that a *n*-alkane and a branched isomer having one or

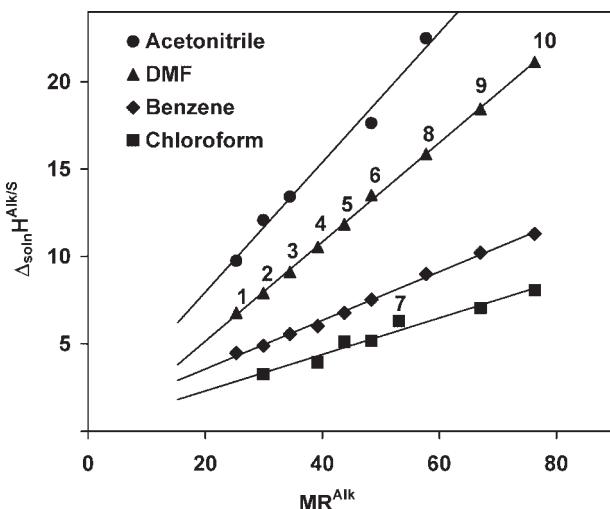


Figure 1. Correlations of solution enthalpies (kJ mol^{-1}) for some *n*-alkane solutes with their molar refraction ($\text{cm}^3 \text{mol}^{-1}$) in acetonitrile, DMF, benzene, and chloroform. Solutes: 1 – *n*-pentane, 2 – *n*-hexane, 3 – *n*-heptane, 4 – *n*-octane, 5 – *n*-nonane, 6 – *n*-decane, 7 – *n*-undecane, 8 – *n*-dodecane, 9 – *n*-tetradecane, 10 – *n*-hexadecane. $\Delta_{\text{soln}} H^{\text{Alk}/S}$ and MR^{Alk} values taken from References [62,78–80,83–89]

more quaternary carbon atoms have similar molar volumes, and should, therefore, as solutes, exhibit about the same amount of cavity formation energy in a given solvent. On the other hand, the molecular surface area and opportunities for effective short-range dispersion interactions with solvents are considerably greater for the *n*-alkane. The observation that the quantity $[\Delta_{\text{soln}} H^{\text{Alk(normal)}/S} - \Delta_{\text{soln}} H^{\text{Alk(branched)}/S}]$ has nearly the same value for methanol, DMF, benzene, and cyclohexane would be likely only if the dispersion interactions between the *n*-alkane and each of four solvents were also similar.^[78] It means that interaction enthalpy of an alkane as a solute is approximately the same in the solvents of various polarity and the differences in solvation or solution enthalpies in these cases arise primarily from the differences in cavity formation energy. This result was used as a basis of the method for determining the relative cavity formation enthalpy of a solvent.^[82,90]

If the solute is alkane (Alk) Eqns (3) and (4) gives

$$\Delta_{\text{soln}} H^{\text{Alk}/S} = \Delta_{\text{vap}} H^{\text{Alk}} + \Delta_{\text{cav}} H^{\text{Alk}/S} + \Delta_{\text{int}} H^{\text{Alk}/S} \quad (12)$$

In a series of solvents, vaporization enthalpy is a constant. Any solvent of the series can be defined as the standard solvent (S_0) for the comparison with other solvents. Assuming the constancy of interaction enthalpy of alkane with various solvents it can be written as

$$\Delta_{\text{soln}} H^{\text{Alk}/S} - \Delta_{\text{soln}} H^{\text{Alk}/S_0} = \Delta_{\text{cav}} H^{\text{Alk}/S} - \Delta_{\text{cav}} H^{\text{Alk}/S_0} \\ = \{\delta_{\text{cav}} H^{\text{Alk}}\}_{S_0}^S \quad (13)$$

where $\{\delta_{\text{cav}} H^{\text{Alk}}\}_{S_0}^S$ is the relative cavity formation enthalpy. It is convenient to define the standard solvent as the hypothetical solvent (*n*-hexane is good approximation) for which the solution enthalpies of any *n*-alkane are zero. In this case the relative cavity formation enthalpy is the solution enthalpy of the *n*-alkane with the same volume^[82].

$$\{\delta_{\text{cav}} H^{\text{Alk}}\}_{S_0}^S = \Delta_{\text{soln}} H^{\text{Alk}/S} \quad (14)$$

The specific relative cavity formation enthalpy ($\delta_{\text{cav}} h^S$)^[82] was defined owing to the proportionality between the solution enthalpy of alkanes and volume of their molecules.

In addition to molar refraction the characteristic volume was used as a measure of solute molecule volume. We consider that validities of both functions are approximately the same. But since the atomic and bond contributions are essentially additive, characteristic volumes are simpler for calculations. So, the specific relative cavity formation enthalpy can be calculated as

$$\delta_{\text{cav}} h^S = \frac{\Delta_{\text{soln}} H^{\text{Alk}/S}}{V_x^{\text{Alk}}} \quad (15)$$

It should be emphasized that the value calculated using Eqns (14) and (15) is not absolute but relative cavity formation enthalpy; nevertheless, it can be used for calculations of the solute–solvent interaction enthalpy relative to any standard solvent.

Parameter $\delta_{\text{cav}} h^S$ reflects the solvent–solvent intermolecular interactions. In this respect, it is somewhat similar to the Hildebrand solubility parameter calculated by Eqn (9). However, the Hildebrand parameter for real solvents reflects both nonspecific and specific solvent–solvent interactions being obtained from vaporization enthalpy, while $\delta_{\text{cav}} h^S$ seems to reflect only the nonspecific interactions. It was confirmed not

only with calorimetric,^[91] but also with IR spectroscopic data.^[92,93] The solvent effect on the stretching vibration frequencies of different bonds of the solute was successfully described using this parameter.

Solvation enthalpies of various nonelectrolytes in alkanes

The thermochemistry of solvation of various nonelectrolytes in alkanes has been studied in a number of studies.^[58,63,65,81,94–99] The most interesting result^[63,96,98] is the linear correlation of the solvation enthalpies [kJ/mol] in cyclohexane for solutes of various classes with their molar refraction [cm³/mol] (Fig. 2):

$$-\Delta_{\text{solv}}H^A/\text{C}_6\text{H}_{12} = 5.09 + 1.03 \cdot MR^A \quad (16)$$

$n = 102, r = 0.994, s = 1.56$

where n , r , and s are number of points, correlation coefficient, and standard deviation, respectively.

This was the first quantitative correlation between the thermodynamic parameters of solvation and the solute structural parameters for a wide range of organic nonelectrolytes. However, this relationship is not universal. It was noted^[63] that the solvation enthalpies of linear and cyclic alkanes in cyclohexane are described by linear correlations with different intercepts. Moreover, the equations for normal and branched aliphatic derivatives are different.

The linear correlation described by Eqn (16) allows to conclude that the solvation enthalpy of various nonelectrolytes in alkanes is caused by the presence of only dispersion interactions in this case. Despite the wide variation in dipole moments of solute (from 0 to 3.8 D) and the nonzero polarizability of the solvent, the contribution of the inductive interactions is negligible.

Combining Eqns (16) and (3) gives the method of estimation for vaporization enthalpy:^[63,96]

$$\Delta_{\text{vap}}H^A = \Delta_{\text{solv}}H^A/\text{C}_6\text{H}_{12} + 5.09 + 1.03 \cdot MR^A \quad (17)$$

Molar refraction is known for many compounds or can be easily calculated using the additive models. The experimental determination of solution enthalpy in many cases is noticeably simpler than that of vaporization enthalpy. This method of estimation of vaporization enthalpy may be almost the only one for some compounds, which are hardly volatile or unstable at high temperatures.

Solvation enthalpies of various nonelectrolytes in tetrachloromethane

Tetrachloromethane does not interact specifically with the overwhelming majority of solutes. Although this statement was challenged in some cases^[100–102] it underlies practically all quantitative methods for determining the thermodynamic parameters of specific interactions,^[103] in so far as they use tetrachloromethane as the inert solvent. Dipolar interactions also should not be present because of zero dipole moment of tetrachloromethane. Thus, only inductive and dispersion interactions seem to exist.

As it is evident from the previous section, dispersion interactions can be successfully analyzed using the correlation of solvation enthalpy with solute molar refraction. This analysis was performed in References^[98,104] for tetrachloromethane as a solvent. Correlation of solvation enthalpy in tetrachloromethane for various solutes with their molar refraction is shown in Fig. 3.

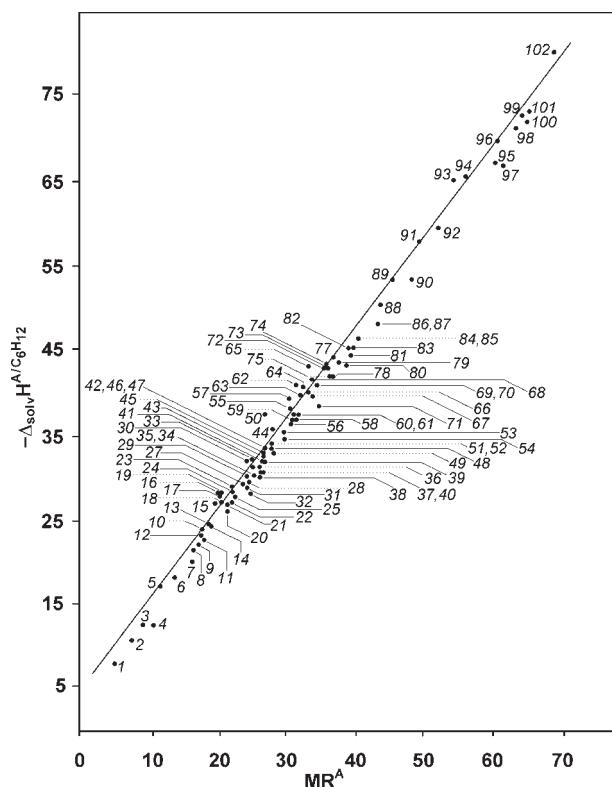


Figure 2. Correlation of solvation enthalpies in cyclohexane (kJ mol⁻¹) with molar refractions (cm³ mol⁻¹) of solutes. Solutes: 1 – water; 2 – hydrogen chloride; 3 – methanol; 4 – hydrogen bromide; 5 – ethane nitrile; 6 – ethanol; 7 – acetone; 8 – propanal; 9 – acrylonitrile; 10 – allyl alcohol; 11 – 1-propanol; 12 – methyl acetate; 13 – allylamine; 14 – iodomethane; 15 – ethyl nitrate; 16 – THF; 17 – chloroform; 18 – *cis*-1,2-dichloroethylene; 19 – *trans*-1,2-dichloroethylene; 20 – butanone; 21 – carbon disulphide; 22 – 1-butanol; 23 – methyl propionate; 24 – ethyl acetate; 25 – dimethyl sulfoxide; 26 – 1,4-dioxane; 27 – *n*-propanethiol; 28 – *n*-butylamine; 29 – 1,2-dimethoxyethane; 30 – pyridine; 31 – thiophene; 32 – hexafluorobenzene; 33 – 1-cyclopropylethanone; 34 – 2-pentanone; 35 – 3-pentanone; 36 – trichloroethylene; 37 – 1-chlorobutane; 38 – 1,4-difluorobenzene; 39 – fluorobenzene; 40 – benzene; 41 – tetrachloromethane; 42 – piperidine; 43 – 1-pentanol; 44 – ethyl chloroacetate; 45 – methyl butanoate; 46 – *n*-propyl acetate; 47 – cyclohexane; 48 – 1-bromobutane; 49 – iodine; 50 – phenol; 51 – 1-butanethiol; 52 – 1-iodopropane; 53 – 2-hexanone; 54 – 3-hexanone; 55 – aniline; 56 – 1,1-dichlorobutane; 57 – 1,1,2,2-tetrachloroethane; 58 – 1-hexanol; 59 – chlorobenzene; 60 – *n*-butyl acetate; 61 – methyl pentanoate; 62 – benzonitrile; 63 – benzaldehyde; 64 – methyl trichloroacetate; 65 – nitrobenzene; 66 – anisole; 67 – bromobenzene; 68 – thiophenol; 69 – 2-heptanone; 70 – 4-heptanone; 71 – phenylacetylene; 72 – 1,4-dichlorobenzene; 73 – 1,2-dichlorobenzene; 74 – 1-heptanol; 75 – styrene; 76 – acetophenone; 77 – ethyl trichloroacetate; 78 – phenyl acetate; 79 – methyl benzoate; 80 – 2-octanone; 81 – iodobenzene; 82 – 1,3-dinitrobenzene; 83 – thioanisole; 84 – 1-octanol; 85 – *N*,*N*-dimethylaniline; 86 – 2-nonanone; 87 – 5-nonanone; 88 – naphthalene; 89 – 1,2,4,5-tetrachlorobenzene; 90 – 2-decanone; 91 – 1-decanol; 92 – diphenyl; 93 – hexachlorobenzene; 94 – benzophenone; 95 – *cis*-azobenzene; 96 – phenanthrene; 97 – benzil; 98 – *trans*-azobenzene; 99 – anthracene; 100 – 1-bromodecane; 101 – 1,2-diphenylacetylene; 102 – diphenylmercury. $\Delta_{\text{solv}}H^A/\text{C}_6\text{H}_{12}$ and MR^A values taken from References [63,96,98].

The main conclusions drawn from this correlation^[104] can be summarized as follows:

1. The overall picture of solvation enthalpies in tetrachloromethane is noticeably more complex than in cyclohexane.

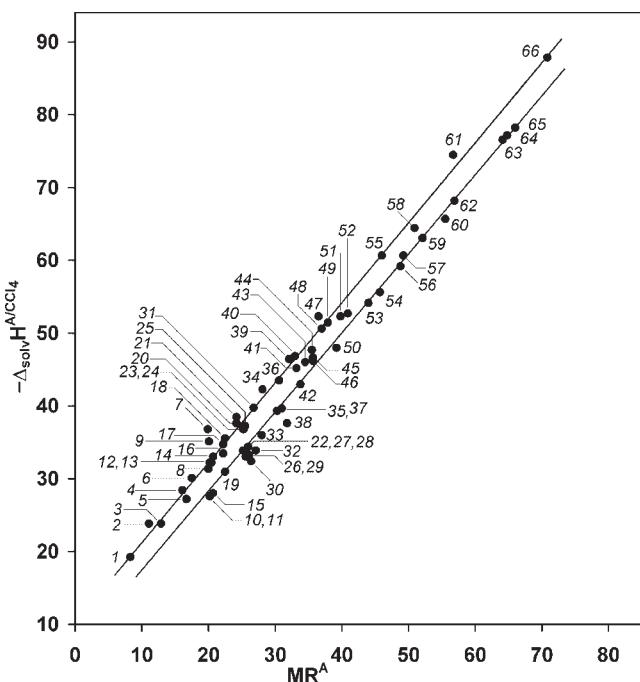


Figure 3. Correlation of solvation enthalpies in tetrachloromethane (kJ mol^{-1}) with molar refractions ($\text{cm}^3 \text{mol}^{-1}$) of solutes. Solutes: 1 – methanol; 2 – acetonitrile; 3 – ethanol; 4 – acetone; 5 – acrylonitrile; 6 – 1-propanol; 7 – DMF; 8 – THF; 9 – DMSO; 10 – chloroform; 11 – *cis*-1,2-dichloroethylene; 12 – thiazole; 13 – pyrrol; 14 – butanone; 15 – *trans*-1,2-dichloroethylene; 16 – 1-butanol; 17 – ethyl acetate; 18 – dimethyl sulfite; 19 – diethyl ether; 20 – 1,2-dimethoxyethane; 21 – pyridine; 22 – 1-chlorobutane; 23 – *N*-methylpyrrol; 24 – 2-pentanone; 25 – phosphorus oxichloride; 26 – trichloroethylene; 27 – 1,4-difluorobenzene; 28 – fluorobenzene; 29 – benzene; 30 – tetrachloromethane; 31 – ethyl chloroacetate; 32 – *n*-butyl methyl ether; 33 – iodine; 34 – phenol; 35 – tetrachloroethylene; 36 – aniline; 37 – chlorobenzene; 38 – dipropyl ether; 39 – benzaldehyde; 40 – nitrobenzene; 41 – anisole; 42 – bromobenzene; 43 – 2-heptanone; 44 – *N*-methylaniline; 45 – 1,2-dichlorobenzene; 46 – 1,4-dichlorobenzene; 47 – acetophenone; 48 – *p*-chlorobenzaldehyde; 49 – *p*-chloronitrobenzene; 50 – iodobenzene; 51 – thioanisole; 52 – *N,N*-dimethylaniline; 53 – naphthalene; 54 – 1,2,4,5-tetrachlorobenzene; 55 – 1-naphthol; 56 – 1-chloronaphthalene; 57 – 1,3,5-tribromobenzene; 58 – 1-nitronaphthalene; 59 – diphenyl; 60 – hexachlorobenzene; 61 – benzophenone; 62 – 1,3,4,5-tetrabromobenzene; 63 – *trans*-azobenzene; 64 – anthracene; 65 – *trans*-diphenylethylene; 66 – 9-anthraldehyde. $\Delta_{\text{solv}}H^A/\text{CCl}_4$ and MR^A values taken from References [98,104].

As a rough approximation all solute points at Fig. 3 are divided into two groups. Good linear correlations are observed within each group with approximately the same slope.

2. The difference between two groups (difference in intercepts) cannot be explained by the contribution of inductive interactions since the dipole moments of solutes within each group vary over a wide range.

Analysis of solvation enthalpies in other solvents (thoroughly selecting the solute–solvent systems without specific interactions) shows that division into groups remains unchanged while the value of difference in intercepts depends on the solvent. For example, this difference in cyclohexane does not exceed the experimental accuracy.

It was supposed that this difference arises from the different abilities of solutes to dispersion interactions.

In other words, it means that the volume of the solute molecule (molar refraction) is not the only solute parameter defining the value of dispersion interaction enthalpies.

Electrostatic solute–solvent interactions enthalpy

According to Eqn (8) the enthalpy of electrostatic (polar) interactions is the sum of dipolar and inductive contributions. They are similar in nature and are commonly described by various modifications of the continuum model.^[105] In the majority of cases the values of static dipole (multipole) moments noticeably exceed the values of induced dipole (multipole) moments. Therefore, we will consider the dipolar interactions firstly.

According to the continuum models the solvation enthalpy is generally proportional to the square of the solute dipole moment (μ^2) and to a function of the relative permittivity (ϵ_r) of the solvent (such as Kirkwood function $(\epsilon_r - 1)/(\epsilon_r + 2)$, or Onsager function $(\epsilon_r - 1)/(\epsilon_r + 1)$, or more simple function $(1/\epsilon_r)$). Classical electrostatic continuum models consider the solute as a point dipole (or multipole of higher order). This means that the distance between the positive and negative charges in solute molecule must be substantially smaller than the distance between the solute and solvent molecules. On the other hand, the solvent is considered as a structureless medium with definite relative permittivity. It is evident that both assumptions are rather rough for real solute–solvent systems.

Despite the wide usage and intensive development of continuum models it is quite difficult to prove definitely their applicability to the description of the experimental values of solvation enthalpies. Indeed, the correlations of solvation enthalpy for a wide series of solutes in a given solvent with the square of solute dipole moments are rather unsuccessful because solutes with widely varied dipole moments vary in their ability to specifically interact with the solvent. These correlations are totally absent for inert solvents (cyclohexane and tetrachloromethane) as it is shown in previous sections. More frequently, the correlations of solvation enthalpies for a given polar solute with Kirkwood or Onsager functions are considered as a confirmation of the applicability of continuum models to solvation enthalpies. However, it was shown^[83] that the solvation enthalpies of the nonpolar *n*-hexane in a series of solvents correlate similarly with these functions. In other words, the cavity formation enthalpy of the solvents depends on their permittivity.

There exist some attempts^[106] to extract the electrostatic contribution to solvation enthalpy using Eqn (11) (homomorph concept). We consider these attempts rather incorrect because they suppose the independency of dispersion interactions on any solute parameter except for molecular volume.

Our attempt to extract this contribution is based on comparing the solvation enthalpies in a series of solvents for some geometrical isomers as solutes. Indeed, *cis*- and *trans*-disubstituted ethylenes or *o*-, *m*-, and *p*-disubstituted benzenes are the substances maximally similar to each other regarding their ability to interact intermolecularly with solvents. Isomers have approximately the same volume of molecules that results in equal cavity formation enthalpies. In addition to the equality of molecular volume, the identical group composition gives the solid argumentation for assuming the equality of dispersion interaction enthalpies. Even if specific interactions with a solvent do occur, as a rough approximation they should be the same for isomers. Consequently, the differences in solvation enthalpies for isomers with polar substituents must be the differences in their

dipolar interactions. The only difficulty is often the absence of vaporization enthalpies for highly polar solutes. In these cases the differences in solution enthalpies for a series of solvents must be examined because according to Eqn (3) they are the differences in solvation enthalpies.

Comparison of solution enthalpies for isomers in a series of solvents was performed in Reference [98]. The solutes examined were: *cis*- and *trans*-dichloroethylenes *cis*- and *trans*-dicyanoethylenes (DCE); *o*-, *m*-, and *p*-dichlorobenzenes; *o*-, *m*-, and *p*-dinitrobenzenes (DNB); *o*-, *m*-, and *p*-dicyanobenzenes. The differences in the dipole moments for isomeric solutes were up to 5.8 D. The solvents used for this study varied highly in polarity (relative permittivities were from 2.8 to 45 and dipole moments of solvent molecule were from 0 to 4.2 D). In all cases linear correlations of solution enthalpies for isomers with the slope being close to unity were found. The examples of such correlations for *m*-, and *p*-DNB and *cis*- and *trans*-DCE^[98] are shown in Fig. 4.

Standard deviations for all the correlations do not exceed 2 kJ mol⁻¹. Therefore, it can be concluded that the dipolar contribution to the solvation enthalpies caused by dipole moment of solute molecule (up to 5.8 D) either is absent or does not exceed 2 kJ mol⁻¹.

A similar result was obtained in Reference [107] for solvation of *cis*- and *trans*-1,2-dihaloethylenes and in Reference [108] for solvation of 1,3- and 1,4-dioxanes, but the authors interpreted the similarity of the solvation thermodynamic parameters for these pairs of isomers by higher values of quadrupole moments for *trans*-1,2-dichloroethane and 1,3-dioxane. Taking into account the facts reported in current and two previous sections it seems as if the electrostatic contributions due to dipole moments are compensated for those due to quadrupole moments in all cases without any exception. It seems very improbable.

We tested the role of quadrupole interactions^[109] comparing the solvation enthalpies for three isomers (*o*-, *m*-, and *p*-dichlorobenzenes). Solvation enthalpies in a wide range of solvents are practically equal for these solutes. The dipole moments of these three isomers are different but the quadrupole

moments of *o*- and *m*- isomers are equal. So, the observed equality of solvation enthalpies cannot be explained by the compensation of differences in dipole and quadrupole interactions.

However, as it is well known, the multipole expansion is infinite and the authors of the paper^[110] discovered that 'the small influence of the long-range interactions on the energetics of the equilibrium of *cis-trans* isomerization for dichloroethylenes can be only explained if electric multipole moments of higher order than quadrupole are considered'.

In such a way, two alternative conclusions can be drawn. (i) Electrostatic interactions do not contribute to the solvation enthalpy, even for highly polar solutes within the accuracy of 2 kJ mol⁻¹. (ii) Following the opinion of the specialists in continuum solvation models,^[107,108,110] we must conclude that electrostatic interactions contribute. However, the contribution from solute dipole moment is compensated for those from multipole moments of higher order.

In the latter case we must add that this compensation takes place practically always. For example, the solvation enthalpies for the series of solutes in 17 solvents with various relative permittivities (from 2.3 for tetrachloromethane to 62.9 for propylene carbonate) were considered in Reference [98]. The solutes were: benzene; naphthalene; anthracene; diphenyl; fluoro-, chloro-, bromo-, and iodo- benzenes; *o*- and *p*-dichlorobenzenes (*m*-dichlorobenzene can be added by the reader from Reference [109]); and 1-chloronaphthalene. These solutes noticeably vary in their dipole moments and relative numbers of polar groups. Nevertheless, excellent linear correlations with molar refraction of the solutes (with correlation coefficients from 0.994 to 0.998 and standard deviations from 0.8 to 1.4 kJ mol⁻¹) were found for all the solvents. If dipolar interactions contribute, they are compensated for in a so successful manner that the enthalpy of electrostatic interactions with their multipole expansion must be linearly related to the simplest parameter which is the molar refraction! But where has polarity gone to? Is it a grin without a cat?

As long ago as in 1930, Hildebrand and Carter have shown that 'it is the number and polarity of the substituent groups rather than the electric moment of the whole molecule which determines deviations from Raoult's law'.^[111] Probably, this conclusion might be altered to consider the role of dispersion interaction but the latter was discovered on the other continent some months later.^[112] Nevertheless, up to now there are some researchers who think that solvent effects can be described in general by the simplest Kirkwood equation.

Specific solute–solvent interaction enthalpy

Solution calorimetry is often used for the determination of the enthalpies of donor–acceptor complex formation including the enthalpies of hydrogen bonding.

In many cases, the values of complex formation enthalpies obtained by the calorimetric method are considered as more reliable than those obtained by spectroscopic (UV-vis, IR, NMR) methods based on the temperature dependence of equilibrium constants.

On the other hand, calorimetry gives a complex value which depends on a variety of types of intermolecular interactions existing in solutions. So, the reliability of calorimetrically obtained complex formation enthalpies entirely depends on the correctness of the extraction of specific interaction enthalpy from the

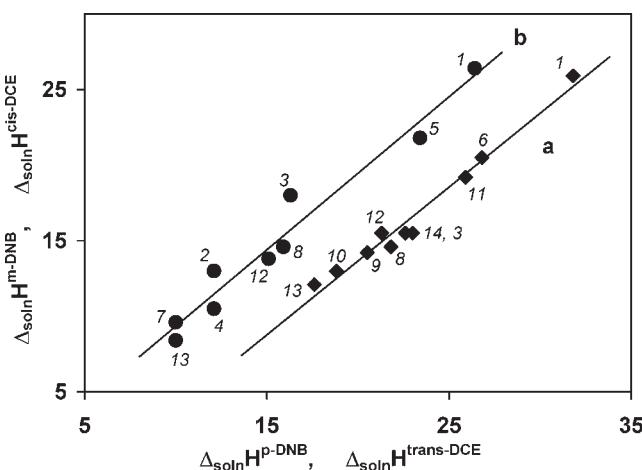


Figure 4. Correlations of solution enthalpies (kJ mol⁻¹): **a** – *m*-DNB versus *p*-DNB and **b** – *cis*-DCE versus *trans*-DCE. Solvents: 1 – tetrachloromethane; 2 – 1,4-dioxane; 3 – benzene; 4 – ethyl acetate; 5 – 1-chloropentane; 6 – 1-chlorobutane; 7 – THF; 8 – 1,2-dichloroethane; 9 – acetone; 10 – benzonitrile; 11 – methanol; 12 – acetonitrile; 13 – DMF; 14 – DMSO. $\Delta_{\text{soln}}H$ values taken from Reference [98]. The slopes of lines **a** and **b** obtained by regression analysis are 0.98 and 1.01, respectively

solution enthalpy. Furthermore, the specific interaction enthalpy [$\Delta_{\text{int(sp)}}H$] is related to complex formation enthalpy ($\Delta_c H^{A,S}$) by simple Eqn (18) only if single type of complexes is present in solution:

$$\Delta_{\text{int(sp)}}H = \alpha \cdot \Delta_c H^{A,S} \quad (18)$$

where α is the degree of complex formation. In some cases (e.g., in 'pure base' method^[113]) α is regarded as practically equal to unity owing to the overwhelming excess of one of the components and the enthalpy of complex formation is equated with the specific interaction enthalpy.

Generally, all solute–solvent systems with hydrogen bonding can be subdivided into four types:

- (I) there are no intramolecular hydrogen bond (IMHB) in the solute and solvent molecules and no intermolecular solvent–solvent hydrogen bonds;
- (II) there are no IMHBs in A and S molecules, but the solvent is associated via intermolecular hydrogen bonds;
- (III) there are IMHBs in A molecules but intermolecular hydrogen bonds in the solvent are absent;
- (IV) both IMHBs in A and intermolecular hydrogen bonds in the solvent are present.

Eqn (18) is applied to systems of type (I) only. In other cases the cleavage of solute intramolecular or solvent–solvent intermolecular hydrogen bonds should be taken into account.

We think that thorough investigation of specific interactions in solution must include both spectral and calorimetric methods, spectral methods being preferable for the ascertainment of the contribution of specific interactions.

Solvation enthalpy can be regarded as the sum of specific interaction enthalpy and nonspecific solvation enthalpy [$\Delta_{\text{solv(nonsp)}}H$]:

$$\Delta_{\text{solv}}H = \Delta_{\text{solv(nonsp)}}H + \Delta_{\text{int(sp)}}H \quad (19)$$

where $\Delta_{\text{solv(nonsp)}}H$ is [$\Delta_{\text{cav}}H + \Delta_{\text{int(nonsp)}}H$] and $\Delta_{\text{int(sp)}}H$ is the specific interaction enthalpy (enthalpy of localized donor–acceptor interactions, including hydrogen bond formation).

Numerous approaches were developed to extract the contribution made by specific interactions to the enthalpy of solvation. They include the pure base method^[113] and its modification,^[67] the non-hydrogen bonding baseline method^[85] and the method of base solutes.^[114,115] These methods are actually based on the estimation of the nonspecific solvation enthalpy in Eqn (19) using 'model' solutes or 'model' solvents. The essential inadequacy of the approach is the poorly founded choice of 'models', that is, the substances having the same properties as the explored solute (or solvent) except for its ability to undergo specific interaction. This problem has been substantially solved in the method of base solutes, but the application of this method requires the analysis of a bulk of solvation enthalpy values in each case.^[115]

Recently we proposed a new, very general method for the extraction of specific interaction enthalpy from the enthalpy of solvation.^[91,116] It requires the minimum of experimental solution enthalpy data and does not require the choice of certain 'model' compounds for a given solute. This method is based on our presupposition that the difference between the enthalpies of nonspecific interactions for some solvent S and cyclohexane (as a solvent) is proportional to the same difference for tetrachlor-

methane and cyclohexane (as solvents):

$$\Delta_{\text{int(nonsp)}}H - \Delta_{\text{int(nonsp)}}H^{A/C_6H_{12}} = q_S \cdot \left[\Delta_{\text{int(nonsp)}}H^{A/CCl_4} - \Delta_{\text{int(nonsp)}}H^{A/C_6H_{12}} \right] \quad (20)$$

where q_S is the solvent-dependent proportionality factor. If solutes do not interact specifically with the solvents the differences between the enthalpies of nonspecific interactions can be calculated from experimental data by combining Eqns (4), written for each solvent, and (15) for relative cavity formation enthalpy:

$$\begin{aligned} \Delta_{\text{int(nonsp)}}H - \Delta_{\text{int(nonsp)}}H^{A/C_6H_{12}} \\ = \Delta_{\text{solv}}H - \Delta_{\text{solv}}H^{A/C_6H_{12}} - (\delta_{\text{cav}}h^S - \delta_{\text{cav}}h^{C_6H_{12}}) \cdot V_X^A \end{aligned} \quad (21)$$

The values of the proportionality factor q_S for 27 solvents were calculated by regression analysis using the experimental data of nonspecific solvation enthalpies for 59 solutes. The standard deviations of calculated solvation enthalpies from experimental ones vary from 0.28 to 2.88 kJ mol⁻¹ (1.33 kJ mol⁻¹ on average). The value of q_S depends on the solvent and reflects its nonspecific interaction with solutes. So it would be reasonable to find correlations of q_S with some solvent parameter such as Hildebrand solubility parameter, Kirkwood function, Dimroth–Reichardt, or Kamlet–Aboud–Taft (π^*) solvatochromic parameters, etc. Indeed, some correlations with these parameters are observed but a substantially better correlation (correlation coefficient is 0.98) was found with the square root of specific relative cavity formation enthalpies ($\sqrt{\delta_{\text{cav}}h^S}$):

$$q_S = a + b \cdot \sqrt{\delta_{\text{cav}}h^S} \quad (22)$$

where a and b values obtained by linear regression analysis are 0.34 and 0.61 respectively if the units for all the enthalpies in Eqns (20) and (15) are kJ mol⁻¹ and the unit for V_X in Eqn (15) is cm³ mol⁻¹ 10⁻².

Although the correlation with the square root of specific relative cavity formation enthalpies was found empirically, we think that it is not accidental. This parameter is to some extent the analog of the Hildebrand solubility parameter because in the theory for regular solutions δ_H^2 characterizes the specific cavity formation energy. The Hildebrand parameter reflects the overall breaking of solvent–solvent interactions, calculated from the vaporization enthalpy, whereas for cavity formation the breaking of only some part of these interactions is required. The parameter $\sqrt{\delta_{\text{cav}}h^S}$ probably reflects just this part of the interactions better. We designate this parameter as S_{vdW} to imply that it is the solvent parameter reflecting its nonspecific interactions (van der Waals interactions) with the solutes:

$$S_{\text{vdW}} = \sqrt{\delta_{\text{cav}}h^S} \quad (23)$$

The resulted equation for nonspecific solvation enthalpy is

$$\begin{aligned} \Delta_{\text{solv(nonsp)}}H \\ = \Delta_{\text{solv}}H^{A/C_6H_{12}} + (\delta_{\text{cav}}h^S - \delta_{\text{cav}}h^{C_6H_{12}}) \cdot V_X^A \\ + (a + b \cdot S_{\text{vdW}}) \\ \cdot \left[\Delta_{\text{solv}}H^{A/CCl_4} - \Delta_{\text{solv}}H^{A/C_6H_{12}} - (\delta_{\text{cav}}h^{CCl_4} - \delta_{\text{cav}}h^{C_6H_{12}}) \cdot V_X^A \right] \end{aligned} \quad (24)$$

It should be stressed that it is an empirical equation. Despite some similarity of S_{vdW} and the Hildebrand parameter, Eqn (24) is not based on regular solution theory and certainly is not the

modification or improvement of the latter. The above-mentioned similarity is rather the result of the fact that both approaches are based on the very old Berthelot rule^[117] which states that the interaction potential between two different molecules 1 and 2, U_{12} , is in many cases proportional to the square root of the potential between two molecules of a component 1...1 or 2...2: U_{11} or U_{22} :

$$U_{12} = \sqrt{(U_{11}U_{22})} \quad (25)$$

Combination of Eqn (24) in a somewhat more common form and Eqn (19) gives Eqn (26) for calculation of the specific interaction enthalpies:

$$\begin{aligned} \Delta_{\text{int(sp)}}H = & \Delta_{\text{soln}}H - \Delta_{\text{soln}}H^{A/C_6H_{12}} - (\delta_{\text{cav}}h^S - \delta_{\text{cav}}h^{C_6H_{12}}) \times V_X^A \\ & - (a_R + b_R \cdot S_{\text{vdW}}) \\ & \times \left[\Delta_{\text{soln}}H^{A/R} - \Delta_{\text{soln}}H^{A/C_6H_{12}} - (\delta_{\text{cav}}h^R - \delta_{\text{cav}}h^{C_6H_{12}}) \times V_X^A \right] \end{aligned} \quad (26)$$

where $\Delta_{\text{soln}}H$, $\Delta_{\text{soln}}H^{A/R}$, and $\Delta_{\text{soln}}H^{A/C_6H_{12}}$ are the solution enthalpies of solute A in the studied solvent S, standard solvent R, and cyclohexane, respectively; $\delta_{\text{cav}}h^S$, $\delta_{\text{cav}}h^R$, and $\delta_{\text{cav}}h^{C_6H_{12}}$ are the specific relative cavity formation enthalpies for each solvent calculated by Eqn (15) (these values slightly vary with the length of *n*-alkanes so that the averaged value for all available *n*-alkane solution enthalpies in each solvent is used in our work); R is the reference solvent; S_{vdW} is the solvent parameter calculated by Eqn (23); a_R and b_R are intercept and slope in Eqn (22) and subscript R in this case means that these values depend on the choice of the reference solvent. The reference solvent R is defined as a given non-alkane solvent that does not interact specifically with the solutes. This reference solvent in Eqn (24) is tetrachloromethane but in Eqn (26) it can be changed for another solvent. This can be useful because tetrachloromethane can interact specifically with some electron donor solutes^[100–102] (e.g., triethylamine, pyridine (Py), diethyl ether, 1,4-dioxane). For these solutes, another solvent (e.g., benzene) can be used as a reference (a_R and b_R for benzene as a reference solvent are 0.20 and 0.38, respectively).

In Reference [91], specific interaction enthalpies for 280 solute–solvent systems were calculated. For 82 of these 280 systems, the complexation enthalpy obtained by independent methods was documented in literature. Comparing the literature data with those determined via Eqn (26) gives a standard deviation of approximately 2 kJ mol⁻¹.

The main advantage of this method is its universality. Owing to the absence of 'model' compounds it can be applied to a wider range of solutes (e.g., chloroform) and used for the determination of specific interaction enthalpies of proton acceptor solutes with proton donor solvents.^[118] The essential disadvantage is the high dependence of the results upon the inaccuracies in the determination of $\Delta_{\text{soln}}H^{A/C_6H_{12}}$ and $\Delta_{\text{soln}}H^{A/R}$, particularly for solvents with high $\delta_{\text{cav}}h^S$. The precise determination of solution enthalpies in cyclohexane and tetrachloromethane can be a non-trivial task for some weakly soluble substances.

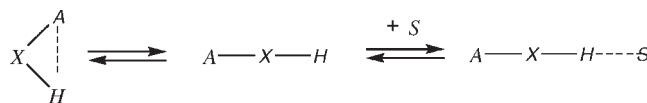
In contrast to nonassociated solvents, formation of hydrogen bonds of a solute with an associated solvent can generally involve cleavage of hydrogen bonds between solvent molecules. Correspondingly, the enthalpy of specific interaction with an associated solvent will depend in a complex manner on the solvent association and on structural features of solute molecules. These two factors determine the energy required to shift the

association equilibrium in the solvent during the formation of solute–solvent complexes (solvent reorganization energy). There was developed an approach^[119] that allows qualitative conclusions on the occurrence (or absence) of the solvent reorganization effect in the formation of solute–solvent complexes. This approach consists in comparing the numbers of lone electron pairs capable of hydrogen bonding and of active hydrogen atoms in the solvent molecule. The type of hydrogen bonding centers (active hydrogen atoms or lone electron pairs) present in excess determines the type of solutes with which the solvent reorganization energy should be manifested at a specific interaction. For example, in alcohols as solvents, the number of lone electron pairs is twice as much as the number of active hydrogen atoms. This means that solutes specifically interacting with a solvent via lone electron pairs (ketones, ethers, esters) should cause reorganization of an alcohol as solvent. With proton donor solutes, for example, chloroform, the solvent reorganization should not be manifested. If the numbers of lone electron pairs and active hydrogen atoms are equal, the solvent reorganization should be manifested as solvation of both proton donors and proton acceptors.

An example of the analysis of specific interaction enthalpies in a solvent associated via hydrogen bonding is presented in Reference [120]. Eqn (26) was used to calculate the specific interaction enthalpies for Py dissolved in aliphatic alcohols $[\Delta_{\text{int(sp)}}H^{\text{Py/ROH}}]$, where ROH are methanol, ethanol, 1-butanol, 1-hexanol, or 1-octanol. The resulting values vary from -5.8 kJ mol^{-1} for methanol to -1.0 kJ mol^{-1} for 1-octanol. The specific interaction enthalpies for the alcohols dissolved in Py $[\Delta_{\text{int(sp)}}H^{\text{ROH/Py}}]$ were found to be within the interval from -15.9 to $-16.7 \text{ kJ mol}^{-1}$. This strong difference between $\Delta_{\text{int(sp)}}H^{\text{Py/ROH}}$ and $\Delta_{\text{int(sp)}}H^{\text{ROH/Py}}$ values is not surprising because aliphatic alcohols are solvents associated via hydrogen bonding. To form the Py-alcohol H-bonded complex during dissolution of Py in alcohols, some alcohol–alcohol hydrogen bonds must be disrupted (endothermic process). That is why the self-association enthalpies of aliphatic alcohols must be taken into account.

The self-association enthalpies for aliphatic alcohols $[\Delta_{\text{int(sp)}}H^{\text{ROH/ROH}}]$ were determined in Reference [121] using Eqn (26). This value is in the range $-16.4 \pm 0.4 \text{ kJ mol}^{-1}$ for above-mentioned alcohols. The sum of $\Delta_{\text{int(sp)}}H^{\text{Py/ROH}}$ and $\Delta_{\text{int(sp)}}H^{\text{ROH/ROH}}$ represents the average enthalpy of hydrogen bonding of Py with associated species of alcohols. Its values vary from $-20.9 \text{ kJ mol}^{-1}$ for methanol to $-18.7 \text{ kJ mol}^{-1}$ for 1-octanol and exceed the corresponding values of $\Delta_{\text{int(sp)}}H^{\text{ROH/Py}}$ by 20–30%. This excess was interpreted^[120] as the result of cooperativity effect for associated species of alcohols. This interpretation was confirmed by using combined calorimetric and IR spectral methods for calculating the cooperative hydrogen bonding enthalpies of Py with dimers of the aliphatic alcohols in tetrachloromethane solutions.

If a solute molecule contains an IMHB, then intermolecular hydrogen bond with proton acceptor solvent (S) can be formed only through the destruction of IMHB. This can be presented by the following equation:



So, the specific interaction enthalpy for a solute with IMHB and a proton acceptor solvent will be determined by the difference in

their intermolecular hydrogen bond formation enthalpies and the enthalpy of IMHB:

$$\Delta_{\text{int(sp)}}H = \alpha_1 \cdot \Delta_c H^{A..S} - \alpha_2 \cdot \Delta_c H^{\text{IMHB}} \quad (27)$$

where α_1 and α_2 are the degrees of complex formation for intermolecular solute–solvent and solute IMHB formations, respectively.

Eqn (27) was used in Reference [122] for the determination of $\Delta_c H^{\text{IMHB}}$ in *ortho*-substituted phenols. Additional assumption about the equality of solute–solvent hydrogen bond formation enthalpies for *ortho*- and *para*-substituted phenols was required in this case.

Some peculiarities of water as a solvent

It is well known that apolar substances are poorly soluble in water. This fact is usually attributed to their hydrophobicity. Repeated attempts were made to separate the hydrophobic effect contribution from the thermodynamic parameters of nonelectrolyte hydration. A brief review of these attempts is presented in Reference [123].

The new method of experimental determination of the hydrophobic effect enthalpy is proposed in References [123] and [124]. It was supposed that the feature of liquid water in comparison with other solvents is the presence of a hydrophobic effect term in hydration thermodynamic functions. In this case Eqn (19) is transformed to Eqn (28):

$$\Delta_{\text{hydr}}H^A = \Delta_{\text{hydr(nonsp)}}H^A + \Delta_{\text{int(sp)}}H^{A/H_2O} + \Delta_{\text{h.e.}}H^A \quad (28)$$

where $\Delta_{\text{hydr}}H^A$ is the hydration (i.e., solvation in water) enthalpy, $\Delta_{\text{hydr(nonsp)}}H^A$ is the nonspecific hydration enthalpy, $\Delta_{\text{int(sp)}}H^{A/H_2O}$ is the specific interaction enthalpy, and $\Delta_{\text{h.e.}}H^A$ is the hydrophobic effect enthalpy.

We do not consider the hydrophobic effect term as the result of a certain additional physical process taking place in water (e.g., strengthening of the hydrogen bond network around an apolar molecule). However, we cannot reject the possibility of such processes *a priori*. We consider the enthalpy of hydrophobic effect as a quantitative characteristic of deviation of water from the rules found for other solvents.

If solutes do not interact specifically with water, then the $\Delta_{\text{h.e.}}H^A$ value can be calculated as the difference between the experimentally determined hydration enthalpy and nonspecific hydration enthalpy calculated by Eqn (26) for water. It should be added that Eqn (24) contains the specific relative cavity formation enthalpies ($\delta_{\text{cav}}h^S$), which is usually calculated by Eqn (15) from solution enthalpy of *n*-alkane in the solvent. But solution enthalpy of *n*-alkane in water contains the hydrophobic effect enthalpy. So, the equation for calculation of specific relative cavity formation enthalpy for water should be modified:

$$\delta_{\text{cav}}h^{H_2O} = \frac{\Delta_{\text{soln}}H^{\text{Alk}/H_2O} - \Delta_{\text{h.e.}}H^{\text{Alk}}}{V_x^{\text{Alk}}} \quad (29)$$

The hydrophobic effect enthalpies for *n*-alkanes ($\Delta_{\text{h.e.}}H^{\text{Alk}}$) were determined by this method.^[125]

The hydrophobic effect enthalpies were calculated by the new method for noble gases, alkanes, and aromatic hydrocarbons.^[124] It was found that this value is negative (exothermic) for noble gases and alkanes. This fact corresponds with the classic interpretation of the hydrophobic effect as the strengthening of the hydrogen bond network around apolar molecules.^[126–130]

The hydrophobic effect enthalpy for aromatic hydrocarbons is positive (endothermic) and grows up with the size of the solute.^[124]

The hydrophobic effect enthalpies for normal aliphatic alcohols were estimated^[124] by assuming that the specific interaction enthalpies of alcohols in water and in methanol are equal. The rough equality of the hydrophobic effect enthalpies for the aliphatic alcohols ($-10.0 \pm 0.9 \text{ kJ/mol}$) and alkanes ($-10.7 \pm 1.5 \text{ kJ/mol}$) is likely evidence for the additivity of the hydrophobic effect contribution to the enthalpy of hydration.

CONCLUSION

This review was written mainly to demonstrate that, despite the solution calorimetry gives the gross measurement of interactions in solutions, the consecutive analysis with an accurate selection of solutes and solvents allows substantial insights into many detailed features of intermolecular interactions in solution. The application of a unified methodology is the determining factor for a fruitful use of solution calorimetry. We think that results described in this paper are good illustrations of this.

LIST OF SYMBOLS AND ABBREVIATIONS USED

A	any solute (organic nonelectrolyte)
S	any solvent
$\Delta_{\text{solv}}H^{A/S}$, $\Delta_{\text{solv}}H$	solvation enthalpy of A in S
solv	solvation
soln	solution
vap	vaporization
int	interaction
sp	specific
nonsp	nonspecific
disp	dispersion
dip	dipolar
ind	inductive
cav	cavity formation
δ_H	Hildebrand solubility parameter
Alk	alkane (normal if other not indicated)
S_0	standard solvent
$\{\delta H^A\}_{S_1}^{S_2}$	difference in enthalpies of some process (e.g., solvation or cavity formation) for solute A in two solvent. Example: $\{\delta_{\text{solv}}H^A\}_{S_0}^{S_1} = \Delta_{\text{solv}}H^{A/S} - \Delta_{\text{solv}}H^{A/S_0}$ ($= \Delta_{\text{solv}}H^{A/S} - \Delta_{\text{solv}}H^{A/S_0}$). The later value is often named the transfer enthalpy from standard solvent.
$\delta_{\text{cav}}h^S$	specific relative cavity formation enthalpy
V_x	McGowan characteristic volume (see definition in Reference [26]). In our works it is a measure of solute molecule volume as well as the molar refraction.
$\Delta_c H^{A..S}$	enthalpy of complex formation (calculated per mole of complex in contrast to specific interaction enthalpy)

α	degree of complex formation
S_{vdW}	solvent parameter reflecting its possibility to nonspecific interactions. It is calculated using Eqn (23)
R	reference solvent in Eqn (26). It is certain non-alkane solvent that does not interact specifically with the solutes.
hydr	hydration (that is solvation in water)
h.e.	hydrophobic effect

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