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Calorimetric determination of hydrogen-bonding enthalpy for neat aliphatic alcohols

Boris N. Solomonov,* Vladimir B. Novikov, Mikhail A. Varfolomeev and Alexander E. Klimovitskii

Chemical Institute, Kazan State University, Kremlevskaya 18, Kazan 420008, Russia

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ABSTRACT: Hydrogen bonding in pure aliphatic alcohols is investigated using a novel calorimetric approach. Average enthalpies of hydrogen bonding were determined for methanol, ethanol, propan-1-ol, propan-2-ol, butan-1-ol, hexan-1-ol and octan-1-ol. For all the studied alcohols except methanol the average hydrogen-bonding enthalpies fall in the range from -16.9 to $-17.7\,\mathrm{kJ\,mol^{-1}}$. A slightly smaller value of $-15.1\,\mathrm{kJ\,mol^{-1}}$ was observed for methanol. From the enthalpies of the specific interactions of the alcohols and chloroform (as proton donors) formed with the alcohols and diethyl ether (as proton acceptors), the dimerization enthalpies were determined for the investigated alcohols: $-8.6 \pm 0.7\,\mathrm{kJ\,mol^{-1}}$. The specific interaction and dimerization enthalpies obtained are concurrent with the Badger–Bauer rule and the hydrogen-bond cooperativity effects. The calorimetric data obtained are supported by literature Fourier transform infrared data on dimer and multimer formation for ethanol and octan-1-ol in tetrachloromethane solution.

KEYWORDS: hydrogen bond; aliphatic alcohols; enthalpy of solution; calorimetry: infrared spectroscopy; cooperativity factors

INTRODUCTION

Solute–solvent specific interactions (commonly considered as localized donor–acceptor interactions, including hydrogen bonding) play an important role in a variety of chemical and biochemical processes. From this point of view, aliphatic alcohols are of special interest because they represent the simplest highly self-associated solvents. The self-association network in the alcohols is formed due to hydrogen bonding (H-bonding). As a class of solvents, aliphatic alcohols are intermediate between non-associated organic solvents (like alkanes) and water.

The important physical and chemical properties of self-associated solvents are due to the fact that a wide range of associative complexes of different stoichiometry and structure are formed, and these associative complexes are in thermodynamic equilibrium with each other.[1–3] One of the most significant parameters of such equilibria is their enthalpy. The enthalpy value obtainable from calorimetric measurements is that determined most directly but it is an average over all the associated species. In contrast, spectroscopic methods (e.g. IR or NMR) typically deal with particular associative complexes. However, information on particular complex species is obtainable only when the species are isolated in an inert medium (solvent, matrix or gas phase). Furthermore, even under this condition it is not always possible to account for all types of associations that may arise, therefore generally only several of the most significant species are considered. Thus, calorimetric and spectroscopic methods are mutually complementary.

To the best of our knowledge there is still a significant uncertainty in the methods of calorimetric determination of the average H-bonding enthalpy for liquid aliphatic alcohols. This is confirmed by the wide scatter of experimental values for H-bonding enthalpies in ethanol, which are summarized by Blainey and Reid.[4] These authors state that reported enthalpies range from -10 to $-40\,\mathrm{kJ\,mol^{-1}}$ and the majority of studies have found enthalpies in the range of -16 to $-25\,\mathrm{kJ\,mol^{-1}}$.

In the present article we develop a new method of determining the H-bond enthalpy for neat aliphatic alcohols. This approach is based on our previous calorimetric studies where we succeeded in extracting a specific interaction enthalpy from the enthalpy of solution.[5]

EXPERIMENTAL

Materials

All solutes and solvents were commercial products of the best grade available that, additionally, were dried and fractionally distilled. Chloroform was washed with water to remove ethanol and then dried by $CaCl_2$ and distilled over P_2O_5. Diethyl ether and cyclohexane were dried by refluxing and further distillation over metallic sodium. Methanol was refluxed and distilled over magnesium

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**Correspondence to:* B. N. Solomonov, Chemical Institute, Kazan State University, Kremlevskaya 18, Kazan 420008, Russia.
E-mail: boris.solomonov@ksu.ru

methylate. Ethanol was dried by consecutive refluxing and distillation over CaO and magnesium ethylate. The rest of the aliphatic alcohols were dried by refluxing and distillation over BaO. Tetrachloromethane was fractionally distilled over P_2O_5.

The residual water content was controlled by Karl Fischer titration and did not exceed 3×10^{-2} vol. % for alcohols and 5×10^{-3} vol. % for the other chemicals.

Calorimetry

Enthalpies of solution were measured at 298 K using a differential quasi-adiabatic calorimeter. The technique for the determination of these values was described in more detail earlier[6,7] and the volume of the calorimetric cell was 100 cm^3. Absence of a concentration dependence of the heat effects was used as a criterion for the infinite dilution condition, which was controlled in special experiments by successive dissolution of several weighed samples in the same solvent.

A concentration dependence of the heat effects is most probable for systems where the solute is an alcohol and the solvent is cyclohexane or tetrachloromethane. For those systems, the maximum solute concentration was selected below 0.007 $\text{mol}\,\text{l}^{-1}$. As an independent test, infrared spectra of the same solute–solvent systems were collected. Absence of the alcohol dimer bands indicates that self-association of the alcohol molecules is negligible (i.e. below the infrared detection limit, which is believed to be ca. 2%). For other solute—solvent systems the final solute concentration did not exceed 0.02 $\text{mol}\,\text{l}^{-1}$.

The solution enthalpies obtained were averaged over four to six measurements. The uncertainty of calorimetric measurements was evaluated as the average deviation from the average value and was ca. $\pm 0.3\,\text{kJ}\,\text{mol}^{-1}$ for solution enthalpies of propan-2-ol in cyclohexane and tetrachloromethane and of hexan-1-ol in tetrachloromethane and chloroform. Uncertainty for all other solute–solvent systems was below $\pm 0.2\,\text{kJ}\,\text{mol}^{-1}$.

Infrared spectroscopy

Infrared spectra were recorded using an FTIR Bruker Vector 22 spectrometer. Interferograms were collected and Fourier-transformed using Blackman–Harris apodization to provide spectra at a resolution of 1 cm^{-1}. The number of scans varied between 64 and 128. Sodium chloride cells were utilized with different spacers (0.1–1.0 mm) to achieve the best signal-to-noise ratio.

RESULTS AND DISCUSSION

Determination of the specific interaction enthalpy $\left(\Delta_{\text{int}(sp)}H^{A/S}\right)$ is one of the methods for estimating the H-bonding enthalpy between solute (A) and solvent (S). This value can be derived from the definition that the solvation enthalpy $\left(\Delta_{solv}H^{A/S}\right)$ is the sum of the non-specific solvation enthalpy $\left(\Delta_{solv(nonsp)}H^{A/S}\right)$ and the enthalpy of solute–solvent specific interaction $\left(\Delta_{\text{int}(sp)}H^{A/S}\right)$:

$$\Delta_{solv}H^{A/S} = \Delta_{solv(nonsp)}H^{A/S} + \Delta_{\text{int}(sp)}H^{A/S} \qquad (1)$$

The term on the left-hand side of Eqn (1) is determined experimentally as the difference between the solution enthalpy $\left(\Delta_{soln}H^{A/S}\right)$ and the vaporization enthalpy of the solute $\left(\Delta_{vap}H^{A}\right)$:

$$\Delta_{solv}H^{A/S} = \Delta_{soln}H^{A/S} - \Delta_{vap}H^{A} \qquad (2)$$

The term $\Delta_{solv(nonsp)}H^{A/S}$ accounts for two factors: the formation of a cavity in solvent S, which requires partial breaking of solvent–solvent interactions; and all other types of solute–solvent interactions, excluding the specific ones. For solutes able to interact specifically with the solvent, the value of $\Delta_{solv(nonsp)}H^{A/S}$ cannot be determined directly but it can be evaluated using appropriate models.

In our case, the solute is an aliphatic alcohol (ROH) and the solvent is the same compound. The solution enthalpy of the alcohol in itself is zero, so the solvation enthalpy is equal to the vaporization enthalpy but with opposite sign. Luck and co-workers[8] showed that the fraction of non-associated (monomeric) molecules in aliphatic alcohols is negligibly small ($<2\%$ in methanol and even less in other alcohols), therefore the enthalpy of specific interaction of an alcohol with itself $\left(\Delta_{\text{int}(sp)}H^{ROH/ROH}\right)$ represents the H-bond formation enthalpy averaged statistically over different associate species in the neat alcohol.

There are a number of approaches for extracting the specific interaction enthalpy from the solvation enthalpy values: the pure base method and its modification;[9,10] the non-hydrogen-bonding baseline method;[11] and the method of base solutes,[12] etc. These methods require model compounds (homomorphs) for evaluating the non-specific solvation enthalpy term of Eqn (1).

It should be noted that the choice of model compounds becomes a problem for alcohols as solvents because of the ability of alcohols to interact specifically with the majority of solutes. For example, according to the homomorph concept, the average H-bond formation enthalpy in neat alcohol is equal to the difference between the vaporization enthalpies of the aliphatic alcohol and an isomeric aliphatic ether, but with opposite sign. The average enthalpies of H-bonding $\left(\Delta_{HB}H^{ROH}\right)$ calculated by using the homomorph concept are shown in Table 1.

For the studied series, the $\Delta_{HB}H^{ROH}$ magnitudes fall in the range from -23.5 to $-27.1\,\text{kJ}\,\text{mol}^{-1}$. These results are in good agreement with the values of solution

Table 1. Average H-bonding enthalpies[a] ($\Delta_{HB}H^{ROH}$) of aliphatic alcohols calculated using the homomorph concept

Aliphatic alcohol (ROH)	Homomorph (R′OR″)	$\Delta_{vap}H^{ROH}$	$\Delta_{vap}H^{R'OR''}$	$\Delta_{HB}H^{ROH}$
C_2H_5OH	CH_3OCH_3	42.6[13]	18.5[14]	−24.1
n-C_3H_7OH	$CH_3OC_2H_5$	47.4[13]	23.9[14]	−23.5
n-C_4H_9OH	n-$C_3H_7OCH_3$	52.3[13]	27.9[15]	−24.4
n-C_4H_9OH	$C_2H_5OC_2H_5$	52.3[13]	27.2[13]	−25.1
n-$C_5H_{11}OH$	n-$C_4H_9OCH_3$	56.9[13]	32.5[15]	−24.4
n-$C_5H_{11}OH$	n-$C_3H_7OC_2H_5$	56.9[13]	31.4[14]	−25.5
n-$C_6H_{13}OH$	$(n$-$C_3H_7)_2O$	62.8[13]	35.7[14]	−27.1
n-$C_6H_{13}OH$	n-$C_4H_9OC_2H_5$	62.8[13]	36.8[14]	−26.0
n-$C_8H_{17}OH$	$(n$-$C_4H_9)_2O$	71.1[13]	44.4[14]	−26.7

[a] All enthalpy values are in kJ mol^{-1} (298 K).

enthalpy of aliphatic alcohols in alkanes.[16] Sometimes the latter values are also used as a measure of alcohol self-association.[17] Note that if one assumes that the solution enthalpy of an alcohol in an alkane is equal to the H-bonding enthalpy of the alcohol, it is the same as admitting that the alcohol–alcohol, alkane–alkane, and alkane–alcohol non-specific interaction enthalpies are equivalent. The use of the homomorph concept also implies that the alcohol–alcohol and ether–ether non-specific interaction enthalpies are equivalent. To the best of our knowledge, the above assumptions are incorrect.

Previously, we have proposed a simple method for extracting the specific interaction enthalpy from the enthalpy of solvation.[5] This approach is based on analyses of 634 solvation enthalpy values obtained for systems with no specific interaction. These data were collected using 27 different solvents. The data clearly indicate that for each solute there is a certain relationship between non-specific interaction enthalpies obtained with different solvents. As a result, an equation for the enthalpy of solute–solvent specific interaction was derived:

$$\begin{aligned}\Delta_{\mathrm{int}(sp)}H^{A/S} &= \Delta_{\mathrm{soln}}H^{A/S} - \Delta_{\mathrm{soln}}H^{A/C_6H_{12}} \\ &- \left(\delta_{cav}h^{S} - \delta_{cav}h^{C_6H_{12}}\right) \times V_X^A - \left(a^R + b^R\sqrt{\delta_{cav}h^S}\right) \\ &\times \left[\Delta_{\mathrm{soln}}H^{A/R} - \Delta_{\mathrm{soln}}H^{A/C_6H_{12}} - \left(\delta_{cav}h^{R} - \delta_{cav}h^{C_6H_{12}}\right) \times V_X^A\right]\end{aligned} \tag{3}$$

where: $\Delta_{\mathrm{soln}}H^{A/S}$, $\Delta_{\mathrm{soln}}H^{A/R}$ and $\Delta_{\mathrm{soln}}H^{A/C_6H_{12}}$ are solution enthalpies of solute A in the studied solvent S, standard solvent R and cyclohexane, respectively; and $\delta_{cav}h^S$, $\delta_{cav}h^R$ and $\delta_{cav}h^{C_6H_{12}}$ are specific relative cavity formation enthalpies[18,19] for each solvent:

$$\delta_{cav}h^S = \frac{\Delta_{\mathrm{soln}}H^{Alkane/S}}{V_X^{Alkane}} \tag{4}$$

where V_X^A is the characteristic volume[20] of the solute. Values calculated by Eqn (4) for a certain solvent and different n-alkanes are approximately the same. The empirical coefficients a^R and b^R can be obtained from linear regression analyses, with magnitudes depending upon the choice of standard solvent. For example, if R is tetrachloromethane, then $a^R = 0.34$ and $b^R = 0.61$; whereas if R is benzene, then $a^R = 0.20$ and $b^R = 0.38$.

Taking into account that for the 634 solute–solvent systems without specific interactions $\Delta_{\mathrm{int}(sp)}H^{A/S}$ must be zero, we obtained a standard deviation for Eqn (3) of 1.5 kJ mol^{-1}. In Ref. 5, specific interaction enthalpies for 280 solute–solvent systems were calculated. For 82 of these 280 systems the complexation enthalpy is documented in the literature. By comparing the literature data with those determined via Eqn (3) we obtained a standard deviation of 2 kJ mol^{-1}.

Standard solvent R is defined as a certain non-alkane solvent that does not interact specifically with the solutes. Thus, tetrachloromethane can be utilized as a standard solvent in the majority of cases. However, some electron-donor solutes (e.g. triethylamine, pyridine, diethyl ether, 1,4-dioxane, etc.) are known to interact specifically with tetrachloromethane.[21–23] Exothermicity of the solution enthalpy in tetrachloromethane for the above-listed solutes is indirect evidence of such interactions, therefore a different solvent (e.g. benzene) should be selected as a standard solvent for such solutes.

For analysis of the specific interaction of alcohols we used tetrachloromethane as a standard solvent. For calculating $\Delta_{\mathrm{int}(sp)}H^{ROH/ROH}$ via Eqn (3) it is necessary to know the following values: the solution enthalpy of the alcohol (ROH) in cyclohexane; the solution enthalpy of ROH in tetrachloromethane; and the relative cavity formation enthalpy of ROH as a solvent. These values are given in Table 2. The solution enthalpy of any alcohol in itself is zero by definition and the specific relative cavity formation enthalpies for tetrachloromethane and cyclohexane are 1.9 and 1.4×10^2 kJ cm^{-3}, respectively.[5] The calculated values of the specific interaction enthalpies of alcohols with themselves $\left(\Delta_{\mathrm{int}(sp)}H^{ROH/ROH}\right)$ are also shown in Table 2. These values characterize the average enthalpies of H-bonding in pure alcohols per mole of ROH.

Note that the specific interaction enthalpies obtained are similar for all the examined alcohols except methanol. At the same time, by comparing the data in Tables 1 and 2 one can see that the average enthalpies of H-bonding $\left(\Delta_{\mathrm{int}(sp)}H^{ROH/ROH}\right)$ calculated from Eqn (3) are substantially lower than those obtained using the homomorph concept $\left(\Delta_{HB}H^{ROH}\right)$. Taking into account that the homomorph concept is based on the aforementioned debatable assumptions, we believe that the results obtained from Eqn (3) are more realistic.

The reliability of the results obtained from Eqn (3) can be confirmed by comparing them with infrared data on H-bonding enthalpies of ethanols[4,35] and octan-1-ol[36] in an

Table 2. Enthalpies[a] of solution in cyclohexane ($\Delta_{\mathrm{soln}}H^{ROH/C_6H_{12}}$) and tetrachloromethane ($\Delta_{\mathrm{soln}}H^{ROH/R}$), specific relative cavity formation enthalpies[b] ($\delta_{cav}h^S$, $kJ\,cm^{-3}\,10^2$), characteristic volumes (V_X^{ROH}, $\mathrm{cm^3\,mol^{-1}}\ 10^{-2}$) and average enthalpies[a] of H-bonding ($\Delta_{\mathrm{int}(sp)}\ H^{ROH/ROH}$) for aliphatic alcohols calculated using Eqn (3)

Aliphatic alcohol (ROH)	$\Delta_{\mathrm{soln}}H^{ROH/C_6H_{12}}$	$\Delta_{\mathrm{soln}}H^{ROH/R}$	$\delta_{cav}h^S$	V_X^{ROH}	$\Delta_{\mathrm{int}(sp)}H^{ROH/ROH}$
Methanol	24.3 (Refs. 5, 24)	18.4	5.1	0.308	−15.1
Ethanol	23.3 (Ref. 25)	18.4 (Ref. 26)	2.8	0.449	−16.9
Propan-1-ol	24.5 (Ref. 5, 24)	18.5	1.5	0.590	−17.7
Propan-2-ol	23.8	18.8	2.8	0.590	−17.3
Butan-1-ol	23.5 (Ref. 25)	18.5 (Ref. 27)	1.6	0.731	−17.7
Hexan-1-ol	24.4 (Ref. 5, 24)	18.6	1.2	1.013	−17.7
Octan-1-ol	24.6 (Ref. 5, 24)	18.7	1.1	1.295	−17.7

[a] All enthalpy values are in kJ mol^{-1} (298 K).

[b] Relative cavity formation enthalpies were calculated using Eqn (4) as the average for all alkanes whose solution enthalpies are available from the literature;[25,28–34] solution enthalpies in hexan-1-ol were obtained in this work and are 1.5, 1.9 and 2.5 kJ mol^{-1} for *n*-octane, *n*-decane and *n*-tetradecane, respectively.

inert solvent (tetrachloromethane). The monomer–dimer and monomer–multimer equilibria were considered in those studies. The following magnitudes were obtained for the dimerization enthalpies: for ethanol, −19.5 kJ mol^{-1} (Ref. 35) and -17.6 ± 1.3 kJ mol^{-1} (Ref. 4); for octan-1-ol, −8.9 kJ mol^{-1} (Ref. 36). The multimer formation enthalpies were found to be − 17.4 kJ mol^{-1} (Ref. 35) and -15.6 ± 2.1 kJ mol^{-1} (Ref. 4) for ethanol and −19.1 kJ mol^{-1} (Ref. 36) for octan-1-ol. One can see that the values calculated from Eqn (3) (i.e. average H-bonding enthalpies) are in good agreement with the infrared spectroscopic data for multimer formation. Such agreement is not surprising because, in neat aliphatic alcohols the fraction of dimeric complexes must be relatively small.

The dimerization enthalpy obtained from Refs 4, 35 and 36 for ethanol is approximately double that determined for octan-1-ol, which is strange because the structure of both dimers was assumed to be the same.[4,35,36]

Unfortunately, the alcohol dimerization enthalpy cannot be obtained directly from Eqn (3) but can be estimated by assuming that the proton-acceptor ability of an aliphatic alcohol relative to a certain standard proton-acceptor does not depend on the nature of the proton-donors. If diethyl ether (DEE) and chloroform (CF) are chosen as the standard proton-acceptor and the second proton-donor, respectively, then the above assumption can be written as:

$$\frac{\Delta_{HB}H^{ROH\ldots CF}}{\Delta_{HB}H^{DEE\ldots CF}} = \frac{\Delta_{HB}H^{ROH\ldots ROH}}{\Delta_{HB}H^{DEE\ldots ROH}} \tag{5}$$

In this equation the dimerization enthalpy ($\Delta_{HB}H^{ROH\ldots ROH}$) is an unknown value whereas the other three values can be calculated from Eqn (3) using calorimetric data. Chloroform is taken as the second proton-donor because it is a pronounced proton-donor but hardly exhibits proton-acceptor properties. Accordingly, chloroform as a solvent is not associated by H-bonding. The latter statement can be confirmed by the fact that the solvation enthalpy of chloroform in cyclohexane is relatively low (2.9 kJ mol^{-1}).[25] The latter magnitude is not the self-association enthalpy of chloroform because it also contains the difference between the chloroform–chloroform and chloroform–cyclohexane non-specific interaction enthalpies, but the self-association enthalpy of chloroform does not exceed this magnitude. Moreover, the self-association enthalpy of chloroform calculated by Eqn (3) is −0.8 kJ mol^{-1}, thus the use of chloroform does not require the solvent reorganization effects to be taken into account (i.e. the breaking of the solvent–solvent H-bonds).

When considering possible diethyl ether–chloroform interacions, it must be kept in mind that the formation of 1:2 complexes is viable theoretically, because the oxygen atom of diethyl ether has two lone electron pairs. The probability of 1:2 complexes can be reduced significantly when diethyl ether is used as a solvent owing to an excess of diethyl ether molecules (e.g. the chloroform: diethyl ether molar ratio in calorimetric experiments is ca. 1:1000). We performed calorimetric measurements for the two extreme cases: chloroform dissolved in diethyl ether; and diethyl ether dissolved in chloroform. Then, by applying Eqn (3), we calculated the values of $\Delta_{\mathrm{int}(sp)}H^{CF/DEE}$ and $\Delta_{\mathrm{int}(sp)}H^{DEE/CF}$: −8.6 and −9.6 kJ mol^{-1}, respectively. The relatively small difference between these two magnitudes indicates that in both cases it is mostly the 1:1 complex that is formed.

For determining the H-bonding enthalpy of diethyl ether with aliphatic alcohols ($\Delta_{HB}H^{DEE\ldots ROH}$) it is more convenient to use the alcohol not as a solvent but as a solute, because in that case it is not necessary to account for the solvent reorganization effect (breaking of the solvent–solvent H-bonds). Thus, Eqn (5) is transformed into Eqn (6):

$$\Delta_{HB}H^{ROH\ldots ROH} = \Delta_{\mathrm{int}(sp)}H^{ROH/DEE} \times \frac{\Delta_{\mathrm{int}(sp)}H^{ROH/CF}}{\Delta_{\mathrm{int}(sp)}H^{DEE/CF}} \tag{6}$$

Table 3. Enthalpies[a] of solution in chloroform $(\Delta_{soln}H^{ROH/CF})$ and diethyl ether $(\Delta_{soln}H^{ROH/DEE})$, specific interaction enthalpies[a] with these solvents $(\Delta_{int(sp)}H^{ROH/CF}$ and $\Delta_{int(sp)}H^{ROH/DEE})$, dimerization enthalpy $(\Delta_{HB}H^{ROH...ROH})$ calculated[b] using Eqn (6) for aliphatic alcohols and the cooperativity factor $(A_b = \Delta_{int(sp)}H^{ROH/ROH}/\Delta_{HB}H^{ROH...ROH})$

Solute (ROH)	$\Delta_{soln}H^{ROH/CF}$	$\Delta_{soln}H^{ROH/DEE}$	$\Delta_{int(sp)}H^{ROH/CF}$	$\Delta_{int(sp)}H^{ROH/DEE}$	$\Delta_{HB}H^{ROH...ROH}$	A_b
Methanol	9.2	4.3	−6.7	−13.3	−9.3	1.6
Ethanol	9.5	5.2 (Ref. 25)	−7.1	−12.5	−9.2	1.8
Propan-1-ol	10.0	5.1 (Ref. 25)	−6.4	−12.5	−8.3	2.1
Butan-1-ol	10.1	5.3 (Ref. 25)	−6.9	−12.4	−8.9	2.0
Hexan-1-ol	10.4	5.5	−6.7	−12.0	−8.4	2.1
Octan-1-ol	11.0	5.8	−6.5	−11.7	−8.0	2.2

[a] All enthalpy values are in kJ mol^{-1} (298 K).

[b] Enthalpies of solution of diethyl ether in chloroform, cyclohexane and benzene were utilized in Eqn (6) and are −9.5, 2.3 (Ref. 25) and 0.84 (Ref. 37) kJ mol^{-1}, respectively. Specific relative cavity formation enthalpies for chloroform, diethyl ether and benzene are 3.5, 1.6 and 5.0 kJ cm^{-3} 10^{2}, respectively. These values were calculated using solution enthalpies of alkanes.[11,19,25,30,38,39]

The dimerization enthalpies calculated using Eqn (6) are shown in Table 3. It is evident from Table 3 that the dimerization enthalpies are very close for all the studied aliphatic alcohols: -8.6 ± 0.7 kJ mol^{-1}.

Note that each value in Eqn (6) contains some uncertainty. We estimate the uncertainty of the resulting dimerization enthalpies to be ca. 2 kJ mol^{-1}. It follows that for the studied alcohols the dimerization enthalpy should not exceed 11 kJ mol^{-1}. It has been mentioned above that the majority of previously documented alcohol–alcohol H-bonding enthalpies are in the range of −16 to −25 kJ mol^{-1}, which is two to three times higher than the magnitudes obtained in this work (Table 3). Thus, the dimerization enthalpies of the alcohols obtained from Eqn 6 (-8.6 ± 0.7 kJ mol^{-1}) could be considered as a non-trivial conclusion of our approach.

The correctness of our dimerization enthalpy data can be supported by infrared spectroscopy. According to the Badger–Bauer rule[40] there is a correlation between the H-bonding enthalpy and the O—H stretching frequency shift. Ratajczak, Orville-Thomas and Rao[41] investigated this rule in a wide frequency range and found a good correlation between the enthalpy and infrared spectroscopic parameters of H-bonding expressed by Eqn (7):

$$-\Delta_{HB}H = C\left(\nu_0^2 - \nu^2\right)^{1/2} + d \qquad (7)$$

where ν_0 and ν are the frequencies of 'free' and 'bonded' O—H bands and C and d are coefficients that can be derived from theory.

To obtain a dependence of this type for butan-1-ol with different proton-acceptors, we utilized the H-bond enthalpies that were determined using Eqn (3) previously[5] (Fig. 1). The enthalpy of H-bonding of butan-1-ol with tetrachloromethane is taken as zero. The O—H stretching frequencies of the butan-1-ol complexes with different proton-acceptors were obtained from the literature.[42] The frequency of the 'free' O—H group of butan-1-ol was determined in the gas phase (3672 cm^{-1}). Parameters C and d were found to be 0.0183 and −9.2, respectively, by linear regression analysis. The correlation coefficient and standard deviation were found to be 0.99 and 1.3 kJ mol^{-1}, respectively.

We have measured the frequency of the hydroxyl stretching band, attributed to the butan-1-ol dimers in tetrachloromethane (3510 cm^{-1}). Then Eqn (7) was exploited to determine the dimer formation enthalpy of butan-1-ol in tetrachloromethane. This value was found to be equal to −10.6 kJ mol^{-1}, which is in good agreement with the data from Table 3 (−8.9 kJ mol^{-1}).

We also applied the above approach to butan-1-ol multimers. Using Eqn (7) and experimentally measuring the multimer hydroxyl stretching band frequency of butan-1-ol in tetrachloromethane (3345 cm^{-1}), we obtained a value of −18.6 kJ mol^{-1} for the multimer formation enthalpy. The value calculated using Eqn (3) (−17.7 kJ mol^{-1}, Table 2) agrees very well with the spectroscopic data.

As shown above, our calorimetric data are in striking disagreement with the documented dimerization

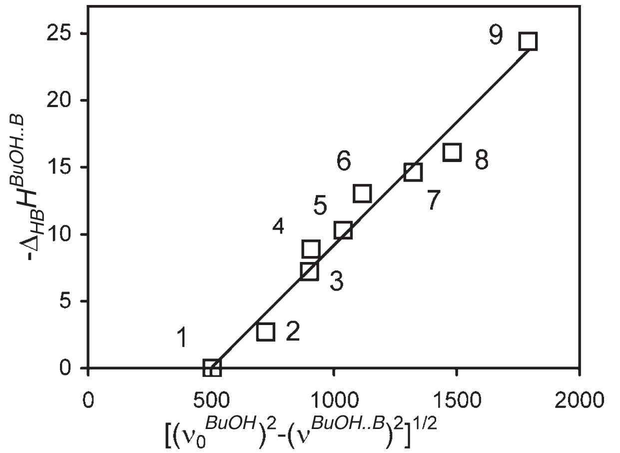

Figure 1. Correlation between the enthalpy of H-bond formation of butan-1-ol with some bases ($\Delta_{HB}H^{BuOH...B}$, kJ mol^{-1}) and the function $(\nu_0^2 - \nu^2)^{1/2}$ (cm^{-1}) from Eqn (7). The bases are: 1, tetrachloromethane; 2, nitromethane; 3, acetonitrile; 4, ethyl acetate; 5, acetone; 6, diethyl ether; 7, dimethyl sulfoxide; 8, pyridine; 9, triethylamine

enthalpies of ethanol in tetrachloromethane obtained by Schwager[35] and Blainey[4] (-19.3 and $-17.6\,\mathrm{kJ\,mol^{-1}}$, respectively). We would like to add that the data obtained by Schwager[35] and Blainey[4] are in disagreement with three other experimental results: data on dimerization of a similar alcohol, octan-1-ol;[36] the observed infrared frequency shifts, and the concept of H-bond cooperativity.[42]

The cooperativity factor, A_b, can be defined as a ratio of the average enthalpy of H-bonding in a certain complex to the dimer formation enthalpy. Thus, for pure alcohols, $A_b = \Delta_{\mathrm{int}(sp)}H^{ROH/ROH}/\Delta_{HB}H^{ROH\ldots ROH}$. The A_b magnitudes obtained are also presented in Table 3 and they are consistent with the results determined in Refs 43 and 44 for methanol and ethanol using infrared spectroscopy and *ab initio* calculations (1.5/1.9 and 1.9/2.7, respectively).

CONCLUSIONS

Average enthalpies of H-bonding for methanol, ethanol, propan-1-ol, propan-2-ol, butan-1-ol, hexan-1-ol and octan-1-ol in the liquid phase were determined using a new calorimetric approach. For all the alcohols studied, except methanol, the average enthalpies are in the range from -16.9 to $-17.7\,\mathrm{kJ\,mol^{-1}}$. A sligthly smaller value of $-15.1\,\mathrm{kJ\,mol^{-1}}$ was observed for methanol. The enthalpies obtained in this work are in contradiction with the results based on the homomorph concept but are in good agreement with infrared spectroscopic data. For all the alcohols investigated, the dimerization enthalpy was found to be in the range of $-8.6 \pm 0.7\,\mathrm{kJ\,mol^{-1}}$. With our new approach it is possible to evaluate H-bond enthalpies for any proton-donor in a neat aliphatic alcohol (e.g. methanol dissolved in octan-1-ol, phenol dissolved in methanol, etc). To the best of our knowledge such information cannot be obtained by any other method.

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