

A new method for the determination of cooperative hydrogen bonding enthalpy of proton acceptors with associated species of alcohols

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

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

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ABSTRACT: A calorimetric method for the determination of cooperative hydrogen bonding (HB) enthalpy of proton acceptors (B) with associated species of alcohols is proposed. The average enthalpy of cooperative HB of pyridine with associated species of alcohols was found to be $-19.8 \pm 0.6 \text{ kJ mol}^{-1}$ for all alcohols investigated. This value exceeds the enthalpy of HB in the complex $\text{ROH} \dots \text{NC}_5\text{H}_5$ (the average for all alcohols is $-15.8 \pm 0.2 \text{ kJ mol}^{-1}$) by 20–30%. Cooperativity factors (A_b , A_{Ox}) of hydrogen bonds for $(\text{ROH})_2 \dots \text{NC}_5\text{H}_5$ complexes were determined using the IR-spectroscopic method. The average values for the alcohols under consideration were found to be $A_b = 1.41 \pm 0.04$ and $A_{Ox} = 1.54 \pm 0.05$. On the basis of IR-spectroscopic and calorimetric data, the enthalpy of cooperative interactions of pyridine with the dimer $(\text{ROH})_2$ was estimated. This value for all the alcohols studied is, on average, $-20.9 \pm 0.1 \text{ kJ mol}^{-1}$. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: hydrogen bonding; aliphatic alcohols; pyridine; enthalpy of solution; calorimetry; IR spectroscopy; cooperativity

INTRODUCTION

Hydrogen bonding (HB) is one of the most important types of intermolecular interactions. It plays a huge role in various physicochemical and biological processes.^{1,2} HB is regarded as a non-covalent type of interaction³ and one of its basic properties is non-additivity or cooperativity. The cooperativity of HB exerts a marked influence on the behavior of biological and other supramolecular systems.^{4–9}

The concept of cooperativity between hydrogen bonds implies that the primary hydrogen bond between a proton-donor X-H and a proton-acceptor B ($\text{X-H} \dots \text{B}$) becomes stronger, when a third partner A forms a complex with a lone electron pair of atom X ($\text{A} \dots \text{X-H} \dots \text{B}$).^{10–13} A species A may be either a cation (Al^{3+} , Mg^{2+} , Ba^{2+} , Li^+ , K^+) or another proton-donor Y-H.^{14–17} In the latter case a complex $\text{Y-H} \dots \text{X-H} \dots \text{B}$ can be formed.¹⁷ The cooperativity phenomenon results not only in strengthening of the $\text{X-H} \dots \text{B}$ bond in ternary complex, but also in strengthening of the secondary H-bond ($\text{Y-H} \dots \text{X}$)^{14–16,18} in comparison with elementary $\text{X-H} \dots \text{B}$ or $\text{Y-H} \dots \text{X}$ complexes.

Authors of Ref. 15,16 have proposed two cooperativity factors A_b and A_{Ox} defined as the slopes of the linear correlations between the experimental frequencies of $\text{OH} \dots \text{B}$ and $\text{OH} \dots \text{O}$ bonds in the ternary complex $(\text{ROH})_2 \dots \text{B}$ and the frequency of the OH bond in $\text{ROH} \dots \text{B}$ complexes, respectively. Detailed information on H-bond cooperativity was obtained from matrix-isolation FTIR spectroscopy by Maes and Smets.¹⁸

Cooperativity factors are analyzed not only in terms of the frequency shifts of X-H stretching vibrations but also using the energy of the additional interaction (ΔE_{add}) which is calculated using quantum chemical methods.^{19–21}

Average enthalpies of HB for pure aliphatic alcohols were determined in our previous paper²² using a novel calorimetric approach. Being averaged over all associated species presented in neat alcohol these values are essentially the enthalpies of cooperative HB. For such cases a cooperativity factor A_b^I was proposed, defined as:

$$A_b^I = \frac{\Delta_{int(sp)} H^{ROH/ROH}}{\Delta_{HB} H^{ROH \dots ROH}} \quad (1)$$

where $\Delta_{int(sp)} H^{ROH/ROH}$ is the specific interaction enthalpy for ROH in neat alcohol, which is the HB enthalpy averaged over all associated species present; $\Delta_{HB} H^{ROH \dots ROH}$ is the enthalpy of linear dimer formation.

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

The cooperativity factor A_b^I reflects the strengthening of HB in associated species of alcohol relative to the HB in the dimer.

In the present work we propose a method for determining the averaged cooperative HB enthalpy for a proton-acceptor B with the associated species of alcohols. Pyridine is investigated as an example of such a proton-acceptor.

EXPERIMENTAL SECTION

Materials

All solutes and solvents were commercial products of the best grade available. They were additionally dried and fractionally distilled.²³

The residual water content was checked by Karl Fischer titration. It did not exceed $3 \times 10^{-2}\%$ (v) for alcohols and $5 \times 10^{-3}\%$ (v) 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.^{24,25} Concentrations of solutes did not exceed 0.01 M for alcohols and 0.02 M for others. The absence of a concentration dependence of the heat effects was used as a criterion for infinite dilution conditions. The solution enthalpies obtained were averaged over 4–6 measurements. The uncertainty of the calorimetric measurements was evaluated as the average deviation from the average value. The uncertainty for all solute – solvent systems was (± 0.1 kJ mol⁻¹).

IR 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. CaF₂ cells were used with different spacers (0.1–1.0 mm) to achieve the best signal/noise ratio. Concentration of alcohols was in the range of 0.07–0.80% (v) in inert solvent (minimum for methanol and maximum for octan-1-ol) and 1–10% (v) in pyridine.

RESULTS AND DISCUSSION

Determination of cooperative interaction enthalpy of pyridine with associated species of alcohols using a calorimetric method

The essence of the method for the determination of averaged cooperative HB enthalpy for proton-acceptor B with associated species of alcohol is as follows.

The transfer of solute molecules from the ideal gas phase to the solvent at infinite dilution is named solvation. Standard molar enthalpy of this process are expressed by the simple Eqn (2):

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

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

The solvation enthalpy can be regarded as the sum of the non-specific solvation enthalpy ($\Delta_{\text{solv(nonsp)}}H^{A/S}$) and the enthalpy of solute-solvent specific interaction ($\Delta_{\text{int(sp)}}H^{A/S}$) (commonly considered as localized donor-acceptor interactions, including HB):

$$\Delta_{\text{solv}}H^{A/S} = \Delta_{\text{solv(nonsp)}}H^{A/S} + \Delta_{\text{int(sp)}}H^{A/S} \quad (3)$$

Previously we have proposed a simple method for extracting the specific interaction enthalpy from the enthalpy of solvation.²⁶ An equation for the enthalpy of solute-solvent specific interaction was derived:

$$\begin{aligned} \Delta_{\text{int(sp)}}H^{A/S} = & \Delta_{\text{soln}}H^{A/S} - \Delta_{\text{soln}}H^{A/C_6H_{12}} \\ & - (\delta_{\text{cav}}h^S - \delta_{\text{cav}}h^{C_6H_{12}}) \times V_X^A \\ & - \left(a^R + b^R \sqrt{\delta_{\text{cav}}h^S} \right) \\ & \times \left[\Delta_{\text{soln}}H^{A/R} - \Delta_{\text{soln}}H^{A/C_6H_{12}} \right. \\ & \left. - (\delta_{\text{cav}}h^R - \delta_{\text{cav}}h^{C_6H_{12}}) \times V_X^A \right] \quad (4) \end{aligned}$$

where $\Delta_{\text{soln}}H^{A/S}$, $\Delta_{\text{soln}}H^{A/R}$ and $\Delta_{\text{soln}}H^{A/C_6H_{12}}$ are the solution enthalpies of solute A in the 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^{27,28} for each solvent:

$$\delta_{\text{cav}}h^S = \frac{\Delta_{\text{soln}}H^{\text{Alkane}/S}}{V_X^{\text{Alkane}}} \quad (5)$$

where V_X^{Alkane} is the characteristic volume of the alkane²⁹; $\Delta_{\text{soln}}H^{\text{Alkane}/S}$ is the solution enthalpy of alkane in the solvent S.

The empirical coefficients a^R and b^R are calculated using linear regression analysis with magnitudes depending upon the choice of standard solvent.^{22,26} 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 $b^R = 0.38$. The standard solvent R is defined as a non-alkane solvent that does not interact specifically with the solutes. Thus, tetrachloromethane can be used as a standard solvent in the majority of cases. However, some electron donor solutes (for example, triethylamine, pyridine, diethyl ether, 1,4-dioxane, etc.) are known to interact specifically with tetrachloromethane.^{30,31} Therefore, another solvent (e.g., benzene) should be selected as a standard for such solutes.

In the present work we use Eqn (4) to determine the specific interactions enthalpies (298 K) of pyridine in a

Table 1. The enthalpies (kJ mol⁻¹, 298 K) of solution of pyridine in alcohols and alcohols in pyridine, the enthalpies of HB in the complex ROH...NC₅H₅, specific interaction enthalpies of pyridine in alcohols, self-association enthalpies of alcohols and average enthalpies of cooperative HB of pyridine with associated species of alcohols

Alcohol	$\Delta_{\text{soln}}\text{H}^{\text{C}_5\text{H}_5\text{N}/\text{ROH}}$	$\Delta_{\text{soln}}\text{H}^{\text{ROH}/\text{C}_5\text{H}_5\text{N}}$	$\Delta_{\text{int}(\text{sp})}\text{H}^{\text{ROH}/\text{C}_5\text{H}_5\text{N}}$	$\Delta_{\text{HB}}\text{H}^{\text{ROH}\dots\text{NC}_5\text{H}_5}_{\text{CCl}_4}$	$\Delta_{\text{int}(\text{sp})}\text{H}^{\text{C}_5\text{H}_5\text{N}/\text{ROH}}$	$\Delta_{\text{int}(\text{sp})}\text{H}^{\text{ROH}/\text{ROH}}$	$\Delta_{\text{int}(\text{sp})}\text{H}^{\text{ROH}}_{\text{ROH}\dots\text{NC}_5\text{H}_5}$
Methanol	-4.1 ³³	-1.9 ²⁶	-16.2 ²⁶	-16.3 ³⁴	-5.8	-15.1 ²²	-20.9
Ethanol	-1.5 ³⁵	0.0 ²⁶	-15.9 ²⁶	-15.9 ³⁴	-3.2	-16.9 ²²	-20.1
Butan-1-ol	-0.2 ³⁵	1.3 ²⁶	-15.8 ²⁶	-16.3 ³⁴	-1.9	-17.7 ²²	-19.6
Hexan-1-ol	-0.1	2.2 ²⁶	-15.5 ²⁶	—	-1.9	-17.7 ²²	-19.6
Octan-1-ol	0.8 ³²	3.3	-15.6	-16.7 ³⁴	-1.0	-17.7 ²²	-18.7

Table 2. IR frequencies (cm⁻¹, 298 K) of monomers of different alcohols in inert solvents

Alcohol	$\nu_{n\text{-hexane}}^{\text{ROH}}$	$\nu_{\text{CCl}_4}^{\text{ROH}}$	$\nu_{\text{CCl}_3}^{\text{ROH}}$	$\nu_{\text{CH}_2\text{Cl}_2}^{\text{ROH}}$
Methanol	3654 ³⁸	3644 ³⁸	3634 ³⁸	3627 ³⁸
Ethanol	3644 ³⁸	3633 ³⁸	3622 ³⁸	3614 ³⁸
Butan-1-ol	3648	3638	3625	3618
Hexan-1-ol	3646	3636	3624	3617
Octan-1-ol	3646 ³⁸	3637 ³⁸	3624 ³⁸	3617 ³⁸

series of aliphatic alcohols. Data on solution enthalpies for pyridine in alcohols are shown in Table 1. The solution enthalpy of pyridine in cyclohexane is taken from Ref. 32. Benzene was taken as the standard solvent ($\Delta_{\text{soln}}\text{H}^{\text{C}_5\text{H}_5\text{N}/\text{C}_6\text{H}_6} = 0.04 \text{ kJ mol}^{-1}$).³² Specific relative cavity formation enthalpies are taken from Ref. 26. The specific interaction enthalpies of pyridine in a series of aliphatic alcohols ($\Delta_{\text{int}(\text{sp})}\text{H}^{\text{C}_5\text{H}_5\text{N}/\text{ROH}}$) calculated by Eqn (4) are shown in Table 1. Specific interaction enthalpies of aliphatic alcohols in pyridine ($\Delta_{\text{int}(\text{sp})}\text{H}^{\text{ROH}/\text{C}_5\text{H}_5\text{N}}$) are also included in Table 1 for comparison. The latter values are calculated using Eqn (4) and the solution enthalpies of alcohols in pyridine ($\Delta_{\text{soln}}\text{H}^{\text{ROH}/\text{C}_5\text{H}_5\text{N}}$) which are also shown in Table 1. In this case tetrachloromethane was used as the standard solvent. Solution enthalpies of alcohols in cyclohexane and tetrachloromethane are taken from Ref. 22.

As it is evident from Table 1, $\Delta_{\text{int}(\text{sp})}\text{H}^{\text{C}_5\text{H}_5\text{N}/\text{ROH}}$ values are dramatically lower than $\Delta_{\text{int}(\text{sp})}\text{H}^{\text{ROH}/\text{C}_5\text{H}_5\text{N}}$. We are sure that this difference is not the result of the differences of HB enthalpies in the different media. This is confirmed by the near coincidence of $\Delta_{\text{int}(\text{sp})}\text{H}^{\text{ROH}/\text{C}_5\text{H}_5\text{N}}$ and $\Delta_{\text{HB}}\text{H}^{\text{ROH}\dots\text{NC}_5\text{H}_5}_{\text{CCl}_4}$ values which are also shown in Table 1. The latter values are determined using IR spectroscopy and calorimetric methods in tetrachloromethane as the solvent.³⁴ In our opinion the decrease in $\Delta_{\text{int}(\text{sp})}\text{H}^{\text{C}_5\text{H}_5\text{N}/\text{ROH}}$ relative to $\Delta_{\text{int}(\text{sp})}\text{H}^{\text{ROH}/\text{C}_5\text{H}_5\text{N}}$ is the result of competition for the most acidic H-atom in the alcoholic solvent between the alcohol and pyridine molecules. This phenomenon has been investigated in a series of papers.³⁵⁻³⁷

We consider that the specific interaction enthalpies of pyridine in alcohols can be presented as the difference:

$$\Delta_{\text{int}(\text{sp})}\text{H}^{\text{C}_5\text{H}_5\text{N}/\text{ROH}} = \Delta_{\text{int}(\text{sp})}\text{H}^{\text{ROH}}_{\text{ROH}\dots\text{NC}_5\text{H}_5} - \Delta_{\text{int}(\text{sp})}\text{H}^{\text{ROH}/\text{ROH}} \quad (6)$$

Table 3. IR frequencies (cm⁻¹, 298 K) of dimers of aliphatic alcohols in inert solvents

Alcohol	$\nu_{n\text{-hexane}}^{\text{ROH}\dots\text{ROH}}$	$\nu_{\text{CCl}_4}^{\text{ROH}\dots\text{ROH}}$	$\nu_{\text{benzene}}^{\text{ROH}\dots\text{ROH}}$	$\nu_{1,2\text{-C}_2\text{H}_4\text{Cl}_2}^{\text{ROH}\dots\text{ROH}}$
Methanol	3552 ³⁸	3523 ³⁸	3507 ³⁸	3493 ³⁸
Ethanol	3534 ³⁸	3509 ³⁸	3498 ³⁸	3484 ³⁸
Butan-1-ol	3533	3510	3496	3478
Hexan-1-ol	3534	3512	3496	3484
Octan-1-ol	3533 ³⁸	3510 ³⁸	3493 ³⁸	3483 ³⁸

Table 4. Correlation parameters of dependencies $\nu = a_{\text{ROH}} + b_{\text{ROH}} \times \sqrt{\delta_{\text{cav}} h^S}$ for IR frequencies of monomers and dimers of aliphatic alcohols, standard deviation of frequencies values (S_0) and correlation coefficients R

Alcohol	a_{ROH}	b_{ROH}	S_0	R
Monomers				
Methanol	3654.9	-10.3	3.1	0.98
Ethanol	3645	-11.4	3.4	0.98
Butan-1-ol	3649.2	-11.5	4.3	0.96
Hexan-1-ol	3647	-11.1	3.9	0.97
Octan-1-ol	3647.4	-11.1	4.5	0.96
Dimers				
Methanol	3551.8	-20.4	0.3	0.99
Ethanol	3533.8	-17.0	1.4	0.99
Butan-1-ol	3534.4	-18.6	2.9	0.99
Hexan-1-ol	3534.7	-17.4	1.3	0.99
Octan-1-ol	3533.3	-17.6	1.6	0.99

The second value on the right-hand side of Eqn (6) is the average self-association enthalpy of the alcohol.²² The first value on the right-hand side of Eqn (6) represents the average specific interaction enthalpy of pyridine with associated species of the alcohol. It is likely that an overwhelming majority of the pyridine molecules in alcohols reside in $(\text{ROH})_n \dots \text{NC}_5\text{H}_5$ complexes (the degree of complexation of pyridine is close to 1). The large difference between the HB enthalpies for alcohol dimer ($\Delta_{\text{HB}}\text{H}^{\text{ROH}\dots\text{ROH}} = -8.7 \pm 0.6 \text{ kJ mol}^{-1}$)²² and for $\text{ROH}\dots\text{NC}_5\text{H}_5$ complexes ($\Delta_{\text{int(sp)}}\text{H}^{\text{ROH}/\text{NC}_5\text{H}_5} = -15.8 \pm 0.2 \text{ kJ mol}^{-1}$) (Table 1) proves this conjecture. Consequently, the value of $\Delta_{\text{int(sp)}}\text{H}^{\text{(ROH)}_n \dots \text{NC}_5\text{H}_5}$, in our opinion, represent the average enthalpy of cooperative HB of pyridine with associated species of alcohols ($\Delta_{\text{HB}}\text{H}^{\text{(ROH)}_n \dots \text{NC}_5\text{H}_5}$). Values of the average enthalpy of cooperative HB ($\Delta_{\text{int(sp)}}\text{H}^{\text{(ROH)}_n \dots \text{NC}_5\text{H}_5}$), as obtained by Eqn (6), are presented in Table 1.

In accordance with the work carried out by Kleeberg et al.¹⁴⁻¹⁶, not only the $\text{OH}\dots\text{N}$ bond in the cooperative complex $(\text{ROH})_n \dots \text{NC}_5\text{H}_5$ becomes stronger, but also the $\text{OH}\dots\text{O}$ bond. This fact must be kept in mind when calculating the cooperativity factors from a comparison of $\Delta_{\text{int(sp)}}\text{H}^{\text{(ROH)}_n \dots \text{NC}_5\text{H}_5}$ with the enthalpy of HB in the alcohol + pyridine complex obtained in pyridine or in an

inert solvent (Table 1). The average cooperativity factor for all alcohols studied amounts to 1.25 ± 0.05 .

Determination of cooperative hydrogen bond enthalpy of pyridine with dimer $(\text{ROH})_2$ using IR spectroscopic and calorimetric methods

The IR spectroscopic method, in contrast to solution calorimetry, gives information about the strengthening of every HB participant in a cooperative interaction. The method of determining cooperativity factors in the ternary complex $\text{ROH}\dots\text{ROH}\dots\text{B}$ using IR spectroscopy was proposed by Kleeberg et al.¹⁴⁻¹⁶

In our opinion this method is not completely correct.¹⁷ We have suggested a new model for the description of solvent effects on stretching vibration frequency shifts.³⁸ Based on this model, a more correct method of determining cooperativity factors in the ternary complex $(\text{CH}_3\text{OH})_2 \dots \text{B}$ was proposed.¹⁷ To calculate the cooperativity factors A_b and A_{ox} in the system $(\text{ROH})_2 \dots \text{NC}_5\text{H}_5$, according to previous work,¹⁷ stretching vibration frequencies of aliphatic alcohols and their dimers in a series of solvents were obtained. Results are listed in Tables 2 and 3. Table 4 contains correlation parameters obtained from comparison of frequencies and solvent parameters ($\delta_{\text{cav}} h^S$) responsible for non-specific solvation.^{27,28} Using the data of Table 4 we have calculated OH stretching vibration frequencies of alcohol monomers ($\nu_{\text{C}_5\text{H}_5\text{N}}^{\text{ROH}}$) and dimers $\nu_{\text{C}_5\text{H}_5\text{N}}^{\text{ROH}\dots\text{ROH}}$ in pyridine. Moreover, OH vibration frequencies of $\text{OH}\dots\text{N}$ ($\nu_{\text{C}_5\text{H}_5\text{N}}^{\text{(ROH)}_2 \dots \text{NC}_5\text{H}_5}$) and $\text{OH}\dots\text{O}$ ($\nu_{\text{C}_5\text{H}_5\text{N}}^{\text{ROH}\dots\text{ROH}\dots}$) bonds of the ternary complex $(\text{ROH})_2 \dots \text{NC}_5\text{H}_5$ in pyridine were determined as described previously.^{15,16} These results are listed in Table 5. Using the values given above, cooperativity factors were calculated by Eqns (7) and (8):

$$A_{\text{Ox}} = \frac{\nu_{\text{C}_5\text{H}_5\text{N}}^{\text{ROH}} - \nu_{\text{C}_5\text{H}_5\text{N}}^{\text{ROH}\dots\text{ROH}\dots}}{\nu_{\text{C}_5\text{H}_5\text{N}}^{\text{ROH}} - \nu_{\text{C}_5\text{H}_5\text{N}}^{\text{ROH}\dots\text{ROH}}}$$
 (7)

$$A_b = \frac{\nu_{\text{C}_5\text{H}_5\text{N}}^{\text{ROH}} - \nu_{\text{C}_5\text{H}_5\text{N}}^{\text{(ROH)}_2 \dots \text{NC}_5\text{H}_5}}{\nu_{\text{C}_5\text{H}_5\text{N}}^{\text{ROH}} - \nu_{\text{C}_5\text{H}_5\text{N}}^{\text{ROH}\dots\text{NC}_5\text{H}_5}}$$
 (8)

Table 5. IR frequencies (cm^{-1} , 298 K) of monomers of aliphatic alcohols and their complexes with pyridine, cooperativity factors (A), enthalpy of cooperative HB of pyridine with dimer $(\text{ROH})_2$ (kJ mol^{-1} , 298 K)

Alcohol	$\nu_{\text{C}_5\text{H}_5\text{N}}^{\text{ROH}}$	$\nu_{\text{C}_5\text{H}_5\text{N}}^{\text{ROH}\dots\text{NC}_5\text{H}_5}$	$\nu_{\text{C}_5\text{H}_5\text{N}}^{\text{(ROH)}_2 \dots \text{NC}_5\text{H}_5}$	A_b	$\nu_{\text{C}_5\text{H}_5\text{N}}^{\text{ROH}\dots\text{ROH}}$	$\nu_{\text{C}_5\text{H}_5\text{N}}^{\text{ROH}\dots\text{ROH}}$	A_{Ox}	$\Delta_{\text{HB}}\text{H}^{\text{(ROH)}_2 \dots \text{NC}_5\text{H}_5}$
Methanol	3628 ¹⁷	3315 ¹⁷	3200 ¹⁷	1.37 ¹⁷	3499 ¹⁷	3436 ¹⁷	1.49 ¹⁷	-21.0
Ethanol	3616	3313	3185	1.38	3490	3419	1.56	-21.0
Butan-1-ol	3620	3314	3185	1.42	3486	3414	1.54	-21.0
Hexan-1-ol	3618	3316	3181	1.45	3490	3415	1.59	-20.9
Octan-1-ol	3619	3316	3190	1.42	3488	3417	1.54	-20.5

where $\nu_{\text{C}_5\text{H}_5\text{N}}^{\text{ROH}\dots\text{NC}_5\text{H}_5}$ is the OH stretching vibration frequency in the complex $\text{ROH}\dots\text{NC}_5\text{H}_5$. Results are shown in Table 5. One can see that the strengthening of $\text{OH}\dots\text{O}$ hydrogen bonds in the complexes $(\text{ROH})_2\dots\text{NC}_5\text{H}_5$ is greater than that of $\text{OH}\dots\text{N}$ hydrogen bonds (Table 5).

Badger and Bauer were the first to propose a linear dependence of $\Delta\nu/\nu$ on $\Delta_{\text{HB}}H^{\text{X}-\text{H}\dots\text{B}}$ with an intercept of zero.³⁹ Further investigations have shown that in a wider range of frequency shifts this dependency is not linear. More sophisticated and universal dependencies between HB enthalpy and HB frequency are given by the Ratajczak–Orville–Thomas–Rao equation⁴⁰ ($-\Delta_{\text{HB}}H^{\text{X}-\text{H}\dots\text{B}} = c(\nu_0^2 - \nu^2)^{1/2} + d$) and the Iogansen relations described in Ref. 41,42, where $\Delta_{\text{HB}}H \sim \sqrt{\Delta_{\text{HB}}\nu}$. These dependencies for HB in complexes of alcohols with different bases give approximately the same results. Therefore following Eqn (9) provides the dependence between cooperativity factors determined by Eqns (7) and (8) [$A(\Delta\nu)$] and those from enthalpies of HB [$A'(\Delta H)$]:

$$A'(\Delta H) = \sqrt{A(\Delta\nu)} \quad (9)$$

Equation (10) gives us the opportunity to calculate the enthalpy of a cooperative HB of pyridine with dimer $(\text{ROH})_2$:

$$\begin{aligned} \Delta_{\text{HB}}H^{(\text{ROH})_2\dots\text{NC}_5\text{H}_5} &= \Delta_{\text{HB}}H^{\text{ROH}\dots\text{ROH}}(\sqrt{A_{\text{Ox}}(\nu)} - 1) \\ &+ \Delta_{\text{int}(\text{sp})}H^{\text{ROH}/\text{C}_5\text{H}_5\text{N}} \cdot \sqrt{A_b(\nu)} \end{aligned} \quad (10)$$

The values of the cooperative HB enthalpy of pyridine with dimer $(\text{ROH})_2$ are listed in Table 5. The values of $\Delta_{\text{HB}}H^{\text{ROH}\dots\text{ROH}}$ are taken from Ref. 22. If we compare the values of $\Delta_{\text{HB}}H^{(\text{ROH})_2\dots\text{NC}_5\text{H}_5}$ (Table 5) with $\Delta_{\text{int}(\text{sp})}H^{(\text{ROH})_n\dots\text{NC}_5\text{H}_5}$ values (Table 1), we can conclude that they coincide within 2 kJ mol^{-1} . It means that the cooperativity effect will reach a certain value after which all additional molecules extending the chain will be stabilized by a constant amount. It was demonstrated by quantum chemical methods^{5,7} that the manifestation of the cooperative effect of HB extends to 3–4 molecules of associated species.

CONCLUSION

Average values of the cooperative HB enthalpy of pyridine with associated species of methanol, ethanol, butan-1-ol, hexan-1-ol, and octan-1-ol were determined using a new calorimetric approach. The average enthalpy of cooperative HB for all alcohols explored lies in the range from -20.9 kJ mol^{-1} (pyridine + methanol) to -18.7 kJ mol^{-1} (pyridine + octan-1-ol). The increase in the cooperative HB enthalpy is about 20–30% relative to the HB enthalpy in complex $\text{ROH}\dots\text{NC}_5\text{H}_5$.

Cooperativity factors of HB in the complexes $(\text{ROH})_2\dots\text{NC}_5\text{H}_5$ obtained by IR spectroscopy for all alcohols investigated amount to 1.41 ± 0.04 for A_b and 1.54 ± 0.05 for A_{ox} .

The average value of the cooperative HB enthalpy of pyridine with dimer $(\text{ROH})_2$ is about $-20.9 \pm 0.1\text{ kJ mol}^{-1}$.

The approach for the determination of the average cooperative HB enthalpy suggested in this work, may be used to determine the HB energies in the majority of systems involving proton acceptor solutes and associated solvents. It may also be valuable for water as the solvent.

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