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HYDROGEN BONDING IN PURE BASE MEDIA. CORRELATIONS BETWEEN CALORIMETRIC AND INFRARED SPECTROSCOPIC DATA

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The known correlations between calorimetric and IR spectroscopic data on hydrogen bonding were reinvestigated for hydrogen bond donors (AH) dissolved in pure bases (B). Ninety-five AH···B systems were considered for which the enthalpies of specific interaction due to hydrogen bonding AH···B ($\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}}$, kJ mol^{-1}), the weight centers of A–H stretching bands (ν, cm^{-1}) and their integral absorption coefficients (a, 10^4 cm mmol^{-1}) had been measured. The relationships between $\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}}$ and the parameters of the infrared absorption spectra [weight center shifts $\Delta\nu$ and the changes in the square roots of a ($\Delta a^{1/2}$)] were analyzed. It was found that the dependence of $\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}}$ on $\Delta a^{1/2}$ consists of two nearly parallel straight lines: the first ($-\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}} = 12{\cdot}0\ \Delta\alpha^{1/2} + 0{\cdot}4$) corresponds to water and the weak C—H and O—H H-bond donors (chloroethylenes, acetylenes acetonitrile, nitromethane, chloroform, *o*,o'-di-*tert*-butylphenol); the second ($-\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}} = 12{\cdot}1\ \Delta a^{1/2} - 4{\cdot}2$) corresponds to the stronger N—H and O—H H-bond donors (*N*-methylaniline, pyrrole, alcohols, phenol, carbon acids). Non-linear dependences of $\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}}$ on $\Delta\nu$ were obtained for all C—H, N—H and O—H H-bond donors except water [$-\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}} = 59{\cdot}9\ \Delta\nu/(\Delta\nu + 674)$]. Enthalpies of specific interaction for water obey another dependence [$-\Delta H^{\mathrm{H_2O/B}}_{\mathrm{sp.int.}}/2 = 28{\cdot}5\ \Delta\nu/(\Delta\nu + 269)$]. The $\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}}$ values can be estimated by the above correlations with an accuracy of ±3 to ±6 kJ mol^{-1}. These relationships obtained for solutions of H-bond donors in pure bases differ from the well known dependences determined for the AH···B hydrogen bonding in carbon tetrachloride medium.

INTRODUCTION

Intermolecular interactions due to hydrogen bonding have been of considerable interest for several decades.[1] The most extensively studied are 1:1 complexes between hydrogen bond donors (AH) and acceptors (B) in media of 'inert' solvents (carbon tetrachloride, alkanes, benzene, chloroform, etc.):

$$\mathrm{AH} + \mathrm{B} \xrightleftharpoons{K,\,\Delta H^{\mathrm{AH\cdots B}}_{\mathrm{h.b.}}} \mathrm{AH\cdots B} \tag{1}$$

where K is the equilibrium constant and $\Delta H^{\mathrm{AH\cdots B}}_{\mathrm{h.b.}}$ is the enthalpy of H-bond formation. Infrared (IR) spectroscopy is widely used for the determination of both K and $\Delta H^{\mathrm{AH\cdots B}}_{\mathrm{h.b.}}$. To determine the enthalpy of hydrogen bonding, the temperature dependence of the equilibrium constant is usually studied.[1,2] This direct method enables the enthalpy of hydrogen bonding to be evaluated if (i) Beer's law is valid and (ii) there is no effect of the H-bond acceptor concentration on the extinction coefficient of the 'non-bonded' A—H band. The latter assumption is fulfilled when relatively small (*ca* 10^{-2} mol l^{-1}) concentrations of H-bond acceptor are used.

However, there are some systems for which it is difficult to determine the equilibrium constant of complex formation. Thus, in the case of weak H-bond donors the amount of the A—H···B complexes becomes measurable only when relatively large concentrations of bases (*ca* 1 mol l^{-1}) in $\mathrm{CCl_4}$ or even solutions of the H-bond donor in pure bases are used. The increase in the base concentration can affect the extinction coefficient of the non-bonded A—H group.[3] Moreover, the weak hydrogen bonding is often followed by the strong overlapping of the 'free' and 'bonded' A—H bands.[4,5]

In specific cases, the equilibrium is strongly shifted towards the H-bond complex. Polymers, low-molecular-weight crystalline and glassy solids with hydrogen bonds and self-associated liquids are the examples of such systems. Furthermore, there are numerous systems where the hydrogen bond formation takes place just in the pure base medium. The analysis of the contributions of the hydrogen bonding of solutes in pure bases is especially important when considering the solubilities of gases or the distribution of solutes between two liquid phases (e.g. water–octanol). It appears that the determi-

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nation of $\Delta H^{\mathrm{AH\cdots B}}_{\mathrm{h.b.}}$ by measuring the temperature dependence of the equilibrium constant is not an easy procedure for such systems.

When dealing with the above-mentioned systems, it is better to consider the value of specific interaction enthalpy $\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}}$ of an H-bond donor (AH) in a base (B) as a measure of the interaction via hydrogen bonds

$$\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}} = \alpha\, \Delta H^{\mathrm{AH\cdots B}}_{\mathrm{h.b.}} \tag{2}$$

where α is the degree of complexation of the H-bond donor. The degree of complexation takes into account that (i) a solute molecule may possess more than one H-bond donor group and therefore 1:2, 1:3, etc., complexes may be formed along with the 1:1 complexes; (ii) there may be a noticeable quantity of solute molecules which are not engaged in the H-bond complexes. Thus, in general the $\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}}$ value is governed both by the enthalpy of hydrogen bonding and the equilibrium constants. In a special case the $\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}}$ value may be equal or very close to $\Delta H^{\mathrm{AH\cdots B}}_{\mathrm{h.b.}}$ (if α is close to 1). Note that the latter situation is frequently realized.[2]

To estimate the enthalpies of specific interaction various approaches can be used. First, the $\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}}$ values can be determined by separating the contribution of non-specific solvation from the calorimetric values of solvation enthalpies of the acid (AH) in the base (B).[6-10] Second, following Abraham *et al.* [11,12] Mishima *et al.*[13] or Raevsky *et al.*[14] one may use the correlations between the empirical parameters of molecules engaged in the complexation and the equilibrium constants or enthalpies of H-bond formation. However, these approaches are based on the data obtained for carbon tetrachloride solutions and therefore characterize 1:1 hydrogen bond complexation in the inert medium. Thus, the assumption of the equality of $\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}}$ to $\Delta H^{\mathrm{AH\cdots B}}_{\mathrm{h.b.}}$ should be made. Third, one may use correlations between $\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}}$ and some spectral characteristics. IR methods based on the correlations between the $\Delta H^{\mathrm{AH\cdots B}}_{\mathrm{h.b.}}$ values and weight center shifts of the A–H stretching bands ($\Delta\nu$) or their integral absorption coefficients ('integrated intensities' $a^{\mathrm{AH\cdots B}}$) are widespread. We shall consider these correlations in detail in order to establish whether they can be applied to solutions of H-bond donors in pure bases.

Badger and Bauer[15] were the first to propose the linear dependence of $\Delta\nu/\nu$ on $\Delta H^{\mathrm{AH\cdots B}}_{\mathrm{h.b.}}$ with the intercept equal to zero. More thorough investigations performed by Drago and co-workers,[16-19] Rao and co-workers,[20,21] Sherry and Purcell,[22,23] Thijs and Zeegers-Huyskens,[24,25] Kleeberg and co-workers,[26,27] Perelygin[28,29] and others showed that there are good linear correlations

$$-\Delta H^{\mathrm{AH\cdots B}}_{\mathrm{h.b.}} = a\,\Delta\nu + b \tag{3}$$

when the hydrogen bonding of one H-bond donor with a series of relative H-bond acceptors is considered. The coefficients a and b were found to be the function of the nature of the H-bond donor. Further, as a rule, the coefficient a decreases and b increases on going to another type of H-bond acceptor series with a higher average $\Delta H^{\mathrm{AH\cdots B}}_{\mathrm{h.b.}}$ value.[17] The standard deviations of the dependences (3) were usually *ca* 2–3 kJ mol^{-1} and the correlation coefficients were in the range 0·83–0·98. All the measurements were carried out in carbon tetrachloride.

Orville-Thomas and co-workers[30-32] attempted to find a universal $\Delta\nu$ against $\Delta H^{\mathrm{AH\cdots B}}_{\mathrm{h.b.}}$ dependence for H-bonds formed by O—H groups. They plotted on the same graph all the $\Delta H^{\mathrm{AH\cdots B}}_{\mathrm{h.b.}} - \nu$ pairs for phenols and alcohols with various bases It was noted that the experimental data can be described by a non-linear dependence. Hence, the following relationship based on the charge-transfer model of H-bonds was proposed:

$$-\Delta H^{\mathrm{AH\cdots B}}_{\mathrm{h.b.}} = C(\nu_0^2 - \nu^2)^{1/2} + d \tag{4}$$

where ν_0 and ν are the wavenumbers of 'free' and 'bonded' O—H bands and c and d are coefficients derived from the theory.

Iogansen[33] considered the same experimental data and proposed an empirical relationship which better describes them:

$$-\Delta H^{\mathrm{AH\cdots B}}_{\mathrm{h.b.}} = 75{\cdot}24\ \Delta\nu/(\Delta\nu + 720) \tag{5}$$

where $\Delta H^{\mathrm{AH\cdots B}}_{\mathrm{h.b.}}$ is in kJ mol^{-1} and $\Delta\nu$ is in cm^{-1}. According to Iogansen,[33] the value 75·24 kJ mol^{-1} corresponds to the 'proton transfer limit' for hydrogen bonding; the meaning of the second coefficient 720 in equation (5) is not known.

It should be noted that there are two types of intermolecular interactions responsible for the ν^{AH} frequency shifts. Only specific interactions with the H-bond acceptor cause the frequency shift $\Delta\nu$ when the 1:1 complex is formed in the carbon tetrachloride surrounding. However, when comparing the frequencies of an H-bond donor dissolved in CCl_4 and the analogous solutions in a pure base, both the differences in specific and non-specific interactions should be taken into account. It is well known that changes in the medium perturb significantly the IR spectra of A—H···B complexes in the range of A–H stretching bands.[34,35] In particular the weight center (ν) could be shifted by 600 cm^{-1} on going from the gaseous phase to a solution.[35] The enhancement of $\Delta\nu$ on going from CCl_4 to the H-bond acceptor solution is usually 10–20% of the $\Delta\nu$ value. Therefore, it is reasonable to correlate separately the data obtained for solutions in carbon tetrachloride and those obtained for pure base media.

Relationships (4) and (5) are based on the experimental data obtained for the following conditions: all the $\Delta H^{\mathrm{AH\cdots B}}_{\mathrm{h.b.}}$ values were measured for the AH···B hydrogen bonding in carbon tetrachloride; at the same time, the $\Delta\nu$ values were partly obtained for hydrogen bonding in the CCl_4 medium (about 80% of the data) and partly for solutions of H-bond donors in pure bases (about 20%). Since most of the $\Delta\nu$ values were obtained for the carbon tetrachloride surrounding, expressions (4) and (5) can be applied to these experimental conditions only.

Relationships between $\Delta H_{\rm h.b.}^{\rm AH\cdots B}$ and integral absorption coefficients $\alpha^{\rm AH\cdots B}$ of the A–H stretching bands have been proposed by different workers.[36–38] Becker[36] correlated the $\Delta H_{\rm h.b.}^{\rm AH\cdots B}$ values with $\alpha^{\rm AH\cdots B}$ values, whereas Perkampus and Kerin[37] considered the enhancement of the integral absorption coefficient ($\alpha^{\rm AH\cdots B} - \alpha_{\rm CCl}^{\rm AH}$) as a measure of the $\Delta H_{\rm h.b.}^{\rm AH\cdots B}$ value. A great body of data was considered by Iogansen (cf. References 33 and 38 and references cited therein), who proposed the expression (6) known as the 'Iogansen intensity rule:'

$$-\Delta H_{\rm h.b.}^{\rm AH\cdots B} = 12{\cdot}12\ \Delta\alpha^{1/2} \qquad (6)$$

where

$$\alpha^{\rm AH\cdots B} = (2{\cdot}303/lc)\int_{\rm band} \log(I_0/I)\,{\rm d}\nu \qquad (7)$$

l is the cell path length, c is the concentration of the H-bond donor and I and I_0 are the percentage transmittance readings for the solution and the solvent spectra, respectively. The value $\Delta\alpha^{1/2}$ equals $(\alpha^{\rm AH\cdots B})^{1/2} - (\alpha_{\rm free}^{\rm AH})^{1/2}$; $\alpha_{\rm free}^{\rm AH}$ and $\alpha^{\rm AH\cdots B}$ are the integral absorption coefficients of the H-bond donor in non-bonded and bonded states, respectively. The units of the values in equation (6) are kJ mol^{-1} for $\Delta H_{\rm h.b.}^{\rm AH\cdots B}$ and 10^4 cm mmol^{-1} for $\alpha^{\rm AH\cdots B}$.

Although the existence of correlations of type (6) for separate classes of H-bond complexes is accepted by many investigators,[28,29,39–41] the universality of the intensity rule is questioned. Thus, according to Perelygin,[28,29] the empirical coefficient in equation (6) differs for various types of H-bond donors. For the alcohol complexes, as an example, the slope in equation (6) equals 10·9, while for carbon acids it is 16·7.

IR measurements for more than 100 H-bond donor–acceptor systems were performed in order to check correlation (6).[33] The applicability of equation (6) to Cl—H, O—H, N—H, C—H, P—H and S—H H-bond donors was established. The experimental points were obtained under the following conditions. The enthalpies of H-bonding were measured mainly by three methods, calorimetry, gas–liquid chromatography (GLC) and the IR spectroscopic investigation of the equilibrium constant as a function of temperature. Calorimetric $\Delta H_{\rm h.b.}^{\rm AH\cdots B}$ values were obtained both for solutions of H-bond donors in pure bases and for H-complexes in $\rm CCl_4$ medium. The GLC method was applied only to solutions in pure bases; the IR technique was applied only to the H-complexes in carbon tetrachloride. The $\alpha^{\rm AH\cdots B}$ values were partly determined for hydrogen bonding in carbon tetrachloride medium (about 85% of the data) and partly for H-bond donors in pure bases (about 15%).

However, it is well known that $\alpha^{\rm AH\cdots B}$ usually increases by 10–20% on going from $\rm CCl_4$ to more polar solutions.[34,35] Thus, again, it would be more reasonable to divide all the experimental data into (i) those obtained for the carbon tetrachloride medium and (ii) those obtained for solutions in pure bases.

The goal of this work was to reinvestigate the well known relationships between the specific interaction enthalpy due to hydrogen bond formation, $\Delta\nu$ and $\alpha^{\rm AH\cdots B}$ on the basis of the calorimetric and IR spectroscopic data obtained recently by our group for the solutions of various H-bond donors in pure bases.[42–47]

RESULTS AND DISCUSSION

Calorimetric determination of specific interaction enthalpies

To reinvestigate the empirical equations (2)–(6), we compared the specific interaction enthalpies and IR data for H-bond donors in pure base media.

The solvation enthalpy of an H-bond donor AH in a solvent (base) B ($\Delta H_{\rm solv.}^{\rm AH/B}$) can be obtained according to the equation

$$\Delta H_{\rm solv.}^{\rm AH/B} = \Delta H_{\rm solut.}^{\rm AH/B} - \Delta H_{\rm vap.}^{\rm AH} \qquad (8)$$

where $\Delta H_{\rm solut.}^{\rm AH/B}$ is the solution enthalpy of AH in B (298 K, finite concentrations 10^{-2}–10^{-1} mol l^{-1}) and $\Delta H_{\rm vap.}^{\rm AH}$ is the enthalpy of vaporization of AH. Both $\Delta H_{\rm solut.}^{\rm AH/B}$ and $\Delta H_{\rm vap.}^{\rm AH}$ are experimentally measurable values. On the other hand, the solvation enthalpy may be perceived as a sum of two terms: enthalpy of non-specific solvation of AH in B ($\Delta H_{\rm nonsp.solv.}^{\rm AH/B}$) and specific: interaction enthalpy ($\Delta H_{\rm sp.int.}^{\rm AH/B}$) of the H-bond donor AH in the base B:

$$\Delta H_{\rm solv.}^{\rm AH/B} = \Delta H_{\rm nonsp.solv.}^{\rm AH/B} + \Delta H_{\rm sp.int.}^{\rm AH/B} \qquad (9)$$

The latter value is defined according to the equation (2).

It follows from equation (9) that the specific interaction enthalpy can be determined by subtracting the enthalpy of non-specific solvation from the experimental $\Delta H_{\rm solv.}^{\rm AH/B}$ value. There are several approaches to estimating the enthalpy of non-specific solvation: the 'pure base' method (pB)[6] or its modification,[7] the 'non-hydrogen-bonding baseline' method (NHBB)[8] and the method based on the dependences of the solvation enthalpies of the compounds on their molecular refractivities.[9,10] These approaches differ in the method of finding the inert model compound (M) for which the solvation enthalpy ($\Delta H_{\rm solv.}^{\rm M/B}$) is equal to $\Delta H_{\rm nonsp.solv.}^{\rm AH/B}$.

The derivatives of the H-bond donor molecules in which the active H-atoms are replaced by a methyl group (AMe) are usually taken as the model compounds in PB method. The discussion of this method has been presented in earlier papers.[8,9,48–50] It was noted that the non-specific solvation enthalpy of the H-bond acceptor molecule can differ from that for the methyl-substituted model compound.[9,48] The $\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}}$ values obtained by the PB method were shown to be dependent on the choice of the inert solvent.[49] It is reasonable to say that such a dependence is the result of the above-mentioned differences between the non-specific solvation enthalpies of the AH and AMe molecules in the pure base and in the inert solvent.

In accordance with the NHBB method, the possible discrepancies of modeling the solute non-specific solvation can be corrected by the correlation between the difference $[\Delta H^{\mathrm{AH}}_{\mathrm{solv.}} - \Delta H^{\mathrm{M}}_{\mathrm{solv.}}]$ and the well known Taft–Kamlet π^* constants in a number of the non-hydrogen-bonding solvents (i.e. *n*-heptane, cyclohexane, carbon tetrachloride, α,α,α-trifluorotoluene and 1,2-dichloroethane).[8,51–54] However, in some cases such correlations can be unsatisfactory.[50] Justifying the inertness of some chosen 'non-hydrogen-bonding' solvents such as α,α,α-trifluorotoluene and 1,2-dichloroethane is also a problem in the NHBB method.

The method[9] is based on studying the correlations between solvation enthalpies of various compounds in carbon tetrachloride and the solute's molecular refractivity (*MR*). This approach made it possible to classify the different solutes according to the type of their non-specific solvation. Thus, aromatic hydrocarbons and their halogen-substituted derivatives belong to the same group of solutes. Nitrile-, carbonyl-, nitro-, amino- and hydroxyl-substituted aromatic compounds form another group. Such a classification offers a means of determining the enthalpies of non-specific solvation. To obtain the $\Delta H^{\mathrm{AH/B}}_{\mathrm{nonsp.solv.}}$, the correlations between solvation enthalpies $\Delta H^{\mathrm{M_i/B}}_{\mathrm{solv.}}$ of various solutes $\mathrm{M_i}$ and their $MR^{\mathrm{M_i}}$ values are considered for the compounds $\mathrm{M_i}$ incapable of specific interaction with the solvent B. It is assumed that a hypothetical model compound $\mathrm{M_h}$ with $MR^{\mathrm{M_h}} = MR^{\mathrm{AH}}$ has the same enthalpy of non-specific solvation as the H-bond donor under investigation. To verify the validity of this method, the $\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}}$ values obtained were compared with the $\Delta H^{\mathrm{AH\cdots B}}_{\mathrm{h.b.}}$ values measured from the IR spectra for 1:1 complexes in carbon tetrachloride. Good agreement was found for a wide series of the acid–base pairs.

A comparison of the last approach with the PB and NHBB methods was carried out in more detail earlier.[9,50] It has been shown[50] that notwithstanding the significantly different assumptions used to separate the contribution of the non-specific solvation, the methods[6–9] give nearly the same results for many investigated systems. It should be also noted that all the above-mentioned approaches are not entirely universal. However, the method[9] is favoured by our group, as (i) it is free of the shortcomings of the PB and NHBB methods (see above) and (ii) its validity has been tested on a wider range of solute structures. Thus, only the calorimetric data obtained by this method[9] is considered below.

Data processing

We considered the weight center shifts $\Delta\nu$ and the enhancements of the integral absorption coefficients $\Delta\alpha^{1/2}$. The $\nu^{\mathrm{AH\cdots B}}$ and $\alpha^{\mathrm{AH\cdots B}}$ values correspond to the solutions of H-bond donors (AH) in pure bases (B) while $\nu^{\mathrm{AH}}_{\mathrm{free}}$ and $\alpha^{\mathrm{AH}}_{\mathrm{free}}$ are determined for solutions of AH in carbon tetrachloride.

We found about 100 systems for which both spectros-

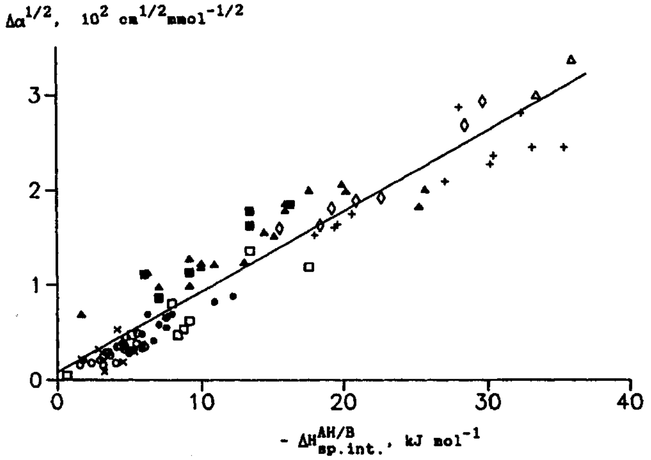

Figure 1. The correlation between $\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}}$ and $\Delta\alpha^{1/2}$ for all available data. The symbols correspond to the following H-bond donors (cf. Table 1): ○, chloroethylenes and chloroform; ×, acetonitrile and nitromethane; ●, acetylenes; ■, NH-donors; □, *o,o'*-di-*tert*-butylphenol; ◇, phenol; △, carbon acids; ▲, *n*-alkanols; +, water. The straight line is drawn according to equation (10) for all the data

copic and calorimetric measurements had been performed. In addition to our data,[42,46] all available $\Delta\nu$ and $\alpha^{AH\cdots B}$ values for the solutions of H-bond donors in pure bases were taken into consideration.[55–68] All these systems are listed in Table 1 and plotted in Figures 1–5. Values determined independently in different studies are averaged. The errors are generally about 5–10% for $\Delta\alpha^{1/2}$ and $\Delta\nu$ and 2–3 kJ/mol for $\Delta H^{AH/B}_{sp.int.}$. In order to obtain the correlations for calculating both the IR spectral characteristics and the specific interaction enthalpy the latter value was considered as both the dependent and independent variable. Following Ioganson,[33] the $\Delta H^{AH/B}_{sp.int.}$ values were correlated with the $\Delta\alpha^{1/2}$ values by a linear regression model. A non-linear model was applied to the $\Delta H^{AH/B}_{sp.int.}$–$\Delta\nu$ values. Marquardt's method of minimizing the dispersion was used in the latter case.

Correlations between $\Delta H^{AH/B}_{sp.int.}$ and $\Delta\alpha^{1/2}$

The experimental values of $\Delta\alpha^{1/2}$ plotted against $\Delta H^{AH/B}_{sp.int.}$ are shown in Figure 1. The points were fitted by straight lines:

$$-\Delta\alpha^{1/2} = a\,\Delta H^{AH/B}_{sp.int.} + b \qquad (10)$$

Table 1. Spectroscopic and thermodynamic data for hydrogen bonding in pure bases[a]

H-bond donor	Base[b]	$-\Delta H^{AH/B}_{sp.int.}$	Ref.	$\Delta\alpha^{1/2}$	$\Delta\nu$	Ref.
cis-Dichloroethylene	Dioxane	3·0	42	0·21	6	42
	Acetone	4·1	42	0·18	1	42
	Acetonitrile	3·2	42	0·16	−3	42
	DMF	4·7	42	0·32	15	42
	DMSO	6·1	42	0·35	28	42
trans-Dichloroethylene	Dioxane	1·8	42	0·21	10	42
	Acetone	2·4	42	0·18	6	42
	Acetonitrile	1·6	42	0·16	1	42
	DMF	3·6	42	0·29	20	42
	DMSO	4·7	42	0·36	35	42
Trichloroethylene	Dioxane	3·4	42	0·29	17	42
	Acetone	3·2	42	0·24	12	42
	Acetonitrile	3·2	42	0·25	4	42
	THF	4·2	42	0·35	25	42
	Ethyl acetate	3·7	42	0·26	7	42
	DMF	4·8	42	0·45	33	42
	DMSO	5·0	42	0·31	45	42
Chloroform[c]	Acetone	4·4	55	0·54	—	56
	Dioxane	5·3	55	0·48	—	56
	THF	5·5	55	0·58	—	56
	Pyridine	5·6	55	0·74	—	56
Acetonitrile	Benzene	3·3	46	0·09	—	46
	Acetonitrile	1·7	46	0·22	—	46
	Acetone	2·9	46	0·32	—	46
	DMSO	4·2	46	0·53	—	46
Nitromethane	Benzene	4·6	44	0·19	—	44
	Acetonitrile	5·4	44	0·30	—	44
	Acetone	5·9	44	0·38	—	44
	DMSO	7·5	44	0·67	—	44
Phenylacetylene	Dioxane	5·0	45	0·28	67	45
	Acetone	5·9	45	0·33	57	45
	DMF	7·6	45	0·55	92	45
	DMSO	6·3	45	0·69	122	45
p-Bromophenylacetylene	Dioxane	6·7	45	0·41	71	45
	Acetone	5·9	45	0·48	59	45
	DMSO	8·0	45	0·69	124	45
Methyl propiolate	Dioxane	7·1	45	0·58	88	45
	Acetone	7·6	45	0·65	72	45
	DMF	10·9	45	0·82	126	45
	DMSO	12·2	45	0·88	162	45
o,o′-di-*tert*-butyl phenol	Benzene	0·7	43	0·05	12	43
	Ethyl acetate	5·2	43	0·47	90	43

Continued

Table 1. *Continued*

H-bond donor	Base[b]	$-\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}}$	Ref.	$\Delta\alpha^{1/2}$	$\Delta\nu$	Ref.
o,o'-di-*tert*-butyl phenol *continued*						
	THF	8·0	43	0·80	170	43
	Dioxane	9·2	43	0·62	110	43
	Acetone	8·8	43	0·53	100	43
	Acetonitrile	8·4	43	0·47	80	43
	DMF	13·4	43	1·36	270	43
	DMSO	17·6	43	1·19	330	43
Phenol	Acetonitrile	15·5	9	1·60	210	59,61
	Pyridine	29·7	9	2·93	681	61
	Acetone	20·9	9	1·89	260	59,62
	Ethyl acetate	18·4	9	1·63	173	62
	THF	22·6	9	1·92	320	62
	Benzene	4·6	9	0·38	54	59,60,63
	DMSO	28·4	9	2·68	553	61
	Dioxane	19·2	9	1·81	285	59,63
Benzoic acid	DMSO	36·0	9	3·37	967	65
Acetic acid	DMSO	33·5	9	3·00	840	65
N-methylaniline	Pyridine	6·1	56	1·11	124	57
Pyrrole	Acetonitrile	7·1	9	0·86	87	58
	Dioxane	9·2	9	1·13	142	58
	Pyridine	13·4	9	1·78	337	58
	DMF	13·4	9	1·63	229	58
	DMSO	16·3	9	1·85	295	58
Methanol	Acetonitrile	6·3	9	1·13	109	59,67
	Dioxane	9·2	47	1·28	142	59,67
	Acetone	10·0	9	1·23	128	59,67
	DMSO	15·9	9	1·86	269	59,67
n-Butanol	Nitrobenzene	1·7	47	0·69	55	47
	Acetonitrile	7·1	47	0·98	101	47,66
	Ethyl acetate	9·2	47	0·99	93	47
	Dioxane	10·9	47	1·22	140	47,66
	Acetone	10·0	47	1·19	130	47,66
	Octan-2-one	13·0	47	1·24	164	47
	Pyridine	17·6	47	2·00	311	47,66
	DMF	15·1	47	1·52	194	47
	DMSO	15·9	47	1·79	267	47,66
	TEP	14·4	47	1·56	191	47
	Benzylamine	19·9	47	2·06	404	47
	HMPTA	20·2	47	1·99	308	47
	Triethylamine	25·6	47	2·01	382	47
	Isopropylamine	25·2	47	1·83	409	47
Water	Nitrobenzene	9·0	47	—	74	47
	Acetonitrile	18·0	47	1·53	127	47
	Dioxane	19·4	47	1·61	172	47,68
	Acetone	20·6	47	1·75	157	47
	Octan-2-one	22·4	47	—	164	47
	Pyridine	28·0	47	2·87	309	47
	DMSO	33·2	47	2·45	258	47
	TEP	27·0	47	2·09	196	47
	Benzylamine	32·4	47	2·81	414	47
	HMPTA	30·4	47	2·36	263	47
	Triethylamine	30·2	47	2·27	365	47
	Isopropylamine	35·4	47	2·45	383	47
	THF	19·6	47	1·64	—	68

[a] The $\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}}$ values are in kJ mol^{-1}, $\Delta\alpha^{1/2}$ in 10^2 cm$^{1/2}$ mmol$^{-1/2}$ and $\Delta\nu$ in cm^{-1}.

[b] Abbreviations: DMF = dimethylformamide; DMSO = dimethyl sulfoxide; HMPTA = hexamethylphosphoric triamide; TEP = triethyl phosphate; THF = tetrahydrofuran.

[c] The $\Delta\alpha^{1/2}$ values for the C–D stretching band of chloroform-*d* are multiplied by $(m_{\mathrm{CD}}/m_{\mathrm{CH}})^{1/2} \approx 1{\cdot}37$, where m_{CX} are the reduced masses of C—X groups.

Table 2. Regression parameters for $\Delta H^{AH/B}_{sp.int.}-\Delta\alpha^{1/2}$ data

System	Equation[a]	a (c)[b]	b (d)[c]	N[d]	r^2[e]	SD[f]	F[g]
All points	(10)	0·085 ± 0·006	−0·080 ± 0·085	93	0·910	0·25	919
	(11)	10·7 ± 0·7	0·2 ± 1·0	93	0·910	2·81	919
Group A	(10)	0·080 ± 0·004	0·00 ± 0·06	59	0·956	0·16	1201
	(11)	12·0 ± 0·7	0·4 ± 0·7	59	0·956	1·94	1201
Group B	(10)	0·077 ± 0·008	−0·44 ± 0·14	34	0·928	0·18	399
	(11)	12·1 ± 1·3	−4·2 ± 2·2	34	0·928	2·26	399

[a] Number of equation in text.
[b] The units of the coefficient a of equation (10) are 10^7 cm kJ^{-1}; the coefficient c of equation (11) is in 10^{-7} kJ cm^{-1}.
[c] The units of the coefficient b of equation (10) are 10^4 cm mmol^{-1}; the coefficient d of equation (11) is in kJ mol^{-1}.
[d] The total number of points included in the regression.
[e] Squared correlation coefficient.
[f] Standard deviation.
[g] Fisher F-statistic.

and

$$-\Delta H^{AH/B}_{sp.int.} = c\,\Delta\alpha^{1/2} + d \qquad (11)$$

using $\Delta H^{AH/B}_{sp.int.}$ as both the independent and dependent variable. The regression parameters obtained are given in Table 2.

The parameters of equation (11) are close to those suggested by Iogansen[33] [equation (6)]. Hence, in general, equation (6) may be applied both to hydrogen bonding in the CCl_4 medium and to the solutions of H-bond donors in pure base media. Nevertheless, one can see from Figure 1 that the $\Delta\alpha^{1/2}$ values for strong H-bond donors such as N—H donors, alcohols, phenol and carbon acids are systematically larger than those predicted by equation (6). Points corresponding to relatively weak H-bond donors (ethylenes, acetylenes, nitromethane, acetonitrile, and *o,o'*-di-*tert*-butylphenol) lie below the straight line of the dependence according to equation (6). Hence it appears that the scattering of the points around the straight line in Figure 1 is not completely occasional. We then used an artificial approach. All the studied H-bond donors were separated into two groups according to location of their points with reference to the line in Figure 1. We denote by A and B the groups of H-bond donors for which the points fall systematically below and above the straight line, respectively. As a result, group A includes all weak H-bond donors and water. The stronger H-bond donors (N—H donors, alcohols, phenol and carbon acids) appear in group B. The presence of water and the weak H-bond donors in the same group seems curious. No explanation of this fact has been found.

Such a separation of the experimental data is shown in Figure 2 and 3 and the regression coefficients are presented in Table 2.

The slopes of equations (11) and (6) for compounds

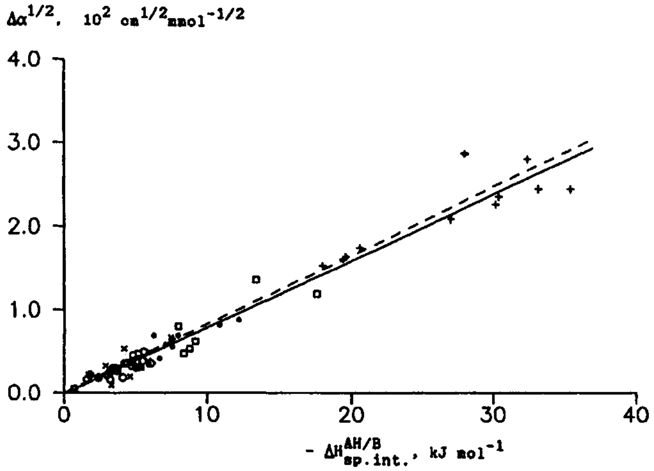

Figure 2. The correlation between $\Delta H^{AH/B}_{sp.int.}$ and $\Delta\alpha^{1/2}$ for C—H H-bond donors, *o,o'*-di-*tert*-butylphenol and water. Symbols as in Fig 1. The solid line corresponds to equation (10) for group A, and the dashed line corresponds to equation (6).

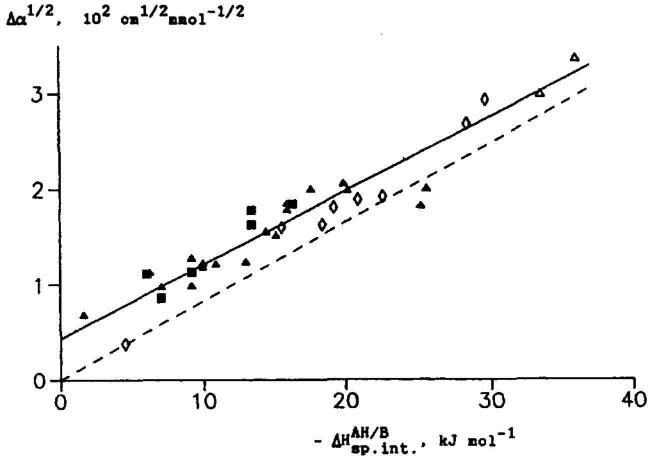

Figure 3. The correlation between $\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}}$ and $\Delta a^{1/2}$ for N—H H-bond donors, *n*-alkanols, phenol and carbon acids. Symbols are the same as in Fig. 1. The solid line corresponds to equation (10) for group B and the dashed line corresponds to equation (6).

of group A are the same, and the intercept of equation (11) is negligible. It appears that equation (6) is applicable to weak H-bond donors and water (group A) even if the experimental data refer to pure base media.

The data on group B show straight lines which are nearly parallel to those for group A, however there are systematic shifts (Figure 3). It is well established that the H-bond donors included in group B obey the 'intensity rule' [equation (6)] when the measurements are performed in carbon tetrachloride.[58,61–63] Thus, the intercepts in equations (10) and (11) can be supposedly attributed to the change in the non-specific solvation of the AH···B complex on going from carbon tetrachloride to pure base surrounding. The intercept is negligible for the weak H-bond donors and essential for the stronger ones. The non-zero intercept in equation (11) indicates that the usage of equation (6) for N—H and O—H and strong H-bond donors in pure bases leads to the mean systematic error of 4·2 kJ mol^{-1}.

Correlation between $\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}}$ and $\Delta\nu$

It is well known that there are H-bond donors which do not show noticeable frequency shifts on H-bond formation. The most extensively studied are the complexes of haloforms, for which even positive frequency shifts had been observed.[4,56,69] Also no weight center shifts of acetonitrile and nitromethane methyl stretchings were found, notwithstanding the significant enhancement of their integrated intensities.[44,46] Thus, chloroform, acetonitrile and nitromethane were not taken into consideration below.

Since the frequency shift characterizes only one hydrogen bond, the $\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}}$ values were divided by 2 for the compounds having two H-bond donor groups (dichloroethylenes, water). The correlation between $\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}}$ and $\Delta\nu$ is shown in Figure 4.

The form of the relationship between $\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}}$ and $\Delta\nu$ was taken as that of equation (5):

$$-\Delta\nu = a\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}}/(b+\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}}) \qquad (12)$$

$$-\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}} = d\,\Delta\nu/(\Delta\nu + c) \qquad (13)$$

The coefficients *a*, *b*, *c* and *d* were used as the adjustable parameters. Their starting values were taken to be $a = c = 720\ \mathrm{cm}^{-1}$ and $b = d = 75{\cdot}24\ \mathrm{kJ\,mol}^{-1}$. The regression parameters obtained for all the points are presented in Table 3. The solid line in Figure 4 corresponds to equation (12). The dashed line shows the known dependence determined from the data obtained in carbon tetrachloride.[31–33] The distance between the curves increases proportionally to $\Delta\nu$ (and $-\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}}$) and reaches *ca* 15% of $-\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}}$.

There is no separation of the data into A and B groups as was observed in the $\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}}$–$\Delta a^{1/2}$ correlations (see above). However, the $\Delta\nu$ values for water seem to be slightly larger than those predicted by equation (13). Therefore, the data for water were considered separately.

The regression parameters obtained for water and for all the data except water are presented in Table 3. It should be kept in mind that by the $-\Delta H^{\mathrm{AH/B}}_{\mathrm{sp.int.}}$ value in equations (12) and (13), half of this enthalpy ($-\Delta H^{\mathrm{H_2O/B}}_{\mathrm{sp.int.}}/2$) is meant for water.

The dependence in equation (12) for water is shown in Figure 5. According to Iogansen,[33] the first coefficient in equation (7) (28·5 ± 4·8 kJ mol^{-1}) shows the 'proton transfer limit' of the H-bonds. It is of interest that this value for water is approximately half that for the other H-bond donors (59·9 ± 5·3 kJ mol^{-1}).

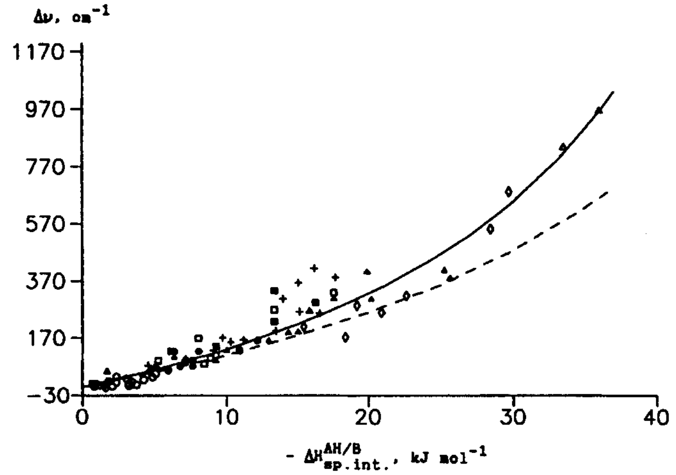

Figure 4. Correlation between $\Delta H^{AH/B}_{sp.int.}$ and $\Delta\nu$ for all available data. Symbols as in Fig. 1. The solid curve corresponds to equation (12) for all the data and the dashed curve corresponds to equation (5).

Table 3. Regression parameters for $\Delta H^{AH/B}_{sp.int.} - \Delta\nu$ data

System	Equation[a]	a (c)[b]	b (d)[c]	N[d]	r^2[e]	SD[f]	F[g]
All points	(12)	795 ± 84	66·4 ± 4·2	82	0·927	48	1023
	(13)	696 ± 101	59·3 ± 5·8	82	0·914	2·3	855
All points minus water	(12)	667 ± 60	60·9 ± 2,9	70	0·951	41	1328
	(13)	674 ± 91	59·9 ± 5·3	70	0·933	2·1	938
Water	(12)	481 ± 317	39·7 ± 16·3	12	0·796	52	40
	(13)	269 ± 90	28·5 ± 4·8	12	0·874	1·4	70

[a,d–g] See footnotes to Table 2.
[b] The units of the coefficient *a* of equation (12) and *c* of equation (13) are cm^{-1}.
[c] The units of the coefficient *b* of equation (12) and *d* of equation (13) are kJ mol^{-1}

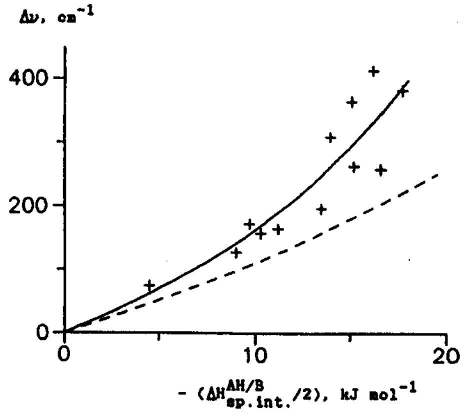

Figure 5. Correlation between $\Delta H^{H_2O/B}_{sp.int.}/2$ and $\Delta\nu$. The solid curve corresponds to equation (12) for water and the dashed curve corresponds to equation (5).

In previous work[47] we compared the values of specific interaction enthalpies of *n*-alkanols (ROH) and water in a number of pure bases. It was found that the ratio ($\Delta H^{H_2O/B}_{sp.int.}/\Delta H^{ROH/B}_{sp.int.}$) is close to 2 when B is a weak base. On going to stronger bases, both $\Delta H^{ROH/B}_{sp.int.}$ and $\Delta H^{H_2O/B}_{sp.int.}$ increase, but the $\Delta H^{H_2O/B}_{sp.int.}$ values show saturation in strong H-bond acceptor solvents.[47] Thus, the above ratio decreases to ca 1·5 when strong bases such as pyridine or dimethyl sulfoxide are used. A decrease in the 'proton transfer limit' for water in comparison with other H-bond donors is likely to reflect this tendency for a decrease in the $\Delta H^{H_2O/B}_{sp.int.}/\Delta H^{ROH/B}_{sp.int.}$ ratio observed previously.[47]

CONCLUSIONS

The empirical relationships (10)–(13) were obtained from the analysis of the available infrared and calorimetric data in pure base media. Such relationships enable one to estimate the $\Delta H^{AH/B}_{sp.int.}$ values of liquid or amorphous solid pure bases by simple measurements of the band integral intensities or the weight centers. The dependence of $\Delta H^{AH/B}_{sp.int.}$ on $\Delta a^{1/2}$ is made up of two straight lines (Figures 2 and 3). Hence, the preliminary assignment of an H-bond donor to group A or B is desirable for evaluating its specific interaction enthalpy. However, if such an assignment is questionable, the less accurate equation (11) for all the points can be used.

Most of the $\Delta\nu$–$\Delta H^{AH/B}_{sp.int.}$ data can be described by a single dependence. This confirms the applicability of the same correlation to H-bonds formed by O—H, C—H and N—H groups. However, there are some exceptions to this rule (chloroform, acetonitrile, nitromethane and water). Generally, it is difficult to predict whether a certain H-bond donor should be assigned to one of the exceptions or whether its $\Delta H^{AH/B}_{sp.int.}$ value can be estimated by using equation (13). Nevertheless, it seems likely that phenols, alcohols, carbon acids, acetylenes and ethylenes (i.e. the classes of H-bond donors for which representatives were considered in the regression (13) for all the data except water) should obey this rule.

The accuracy of the evaluation of the $\Delta H^{AH/B}_{sp.int.}$ values via equations (10)–(13) can be estimated from the standard deviations (SD) of the correlations. Table 4 shows the accuracy (at the 95% confidence level) of such evaluations. It seems reasonable to compare these values with the corresponding values for other methods. Thus, the approach proposed by Raevsky *et al.*[14] permits the determination of $\Delta H^{AH\cdots B}_{h.b.}$ for a 1:1 complex in carbon tetrachloride via the empirical parameters of the solutes (acidity and basicity). The standard deviation of this method ($SD = 2{\cdot}7\ kJ\,mol^{-1}$) falls in the range of our SD values (see Tables 2 and 3). At the same time, the accuracy attainable in calorimetric and infrared[1,2] measurements of $\Delta H^{AH\cdots B}_{h.b.}$ is 1·5–3·0 times higher than the mean values presented in Table 4.

Application of the spectral–thermodynamic correlations (10)–(13) seems to be useful as an alternative method to the currently accepted approaches[1,2,6–14] to the determination of $\Delta H^{AH/B}_{sp.int.}$ values (the latter may be close to $\Delta H^{AH\cdots B}_{h.b.}$ measured in CCl_4 if $\alpha \approx 1$). Moreover, series of systems can be mentioned (e.g. solutions of low-molecular-weight H-bond donors in amorphous polymers; competitive equilibria of inter- and intramolecular H-bonds;[39] H-bonding in the melts of bases; AH···B bonding in the medium of a weaker base) for which the spectral–thermodynamic correlations offer several advantages over the other methods.

Table 4. Standard deviations of the correlations

Independent parameter	Equation	Standard deviation (kJ mol^{-1})
Intensity[a]	(11)	5·9
Intensity[b]	(11)	4·1
Intensity[c]	(11)	4·7
Weight center[a]	(13)	4·4
Weight center[d]	(13)	3·0

[a] All the experimental data.
[b] Group A.
[c] Group B.
[d] Only water considered.

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