liquids

MDPI

Article

Calculation of Hydrogen Bonding Enthalpy Using the Two-Parameter Abraham Equation

Boris N. Solomonov, Mansur B. Khisamiev and Mikhail I. Yagofarov *

Department of Physical Chemistry, Kazan Federal University, Kremlevskaya Str. 18, Kazan 420008, Russia; boris.solomonov@kpfu.ru (B.N.S.); mansur.khisamiev@mail.ru (M.B.K.)
* Correspondence: miiyagofarov@kpfu.ru

Abstract: In this work, an approach to the calculation of hydrogen bonding enthalpies is proposed. It employs the correlation proposed by M.H. Abraham, establishing the connection between the equilibrium constant (K_{HB}) and acidity (α_2^{H}) and basicity (β_2^{H}) parameters: $\log K_{\mathrm{HB}} = 7.354 \cdot \alpha_2^H \cdot \beta_2^H - 1.099$. Hydrogen bonding enthalpy ($\Delta_{\mathrm{HB}}H$) is found using the compensation relationship with Gibbs energy ($\Delta_{\mathrm{HB}}G$): $\Delta_{\mathrm{HB}}G = 0.66 \cdot \Delta_{\mathrm{HB}}H + 2.5$ kJ·mol^{-1}. This relationship enables the calculation of the enthalpy, Gibbs energy and entropy of hydrogen bonding. The validity of this approach was tested against 122 experimental hydrogen bonding enthalpies values available from the literature. The root mean square deviation and average deviation equaled 1.6 kJ·mol^{-1} and 0.5 kJ·mol^{-1}, respectively.

Keywords: hydrogen bonding enthalpy; complexation equilibrium; compensation relationship

check for updates

Citation: Solomonov, B.N.; Khisamiev, M.B.; Yagofarov, M.I. Calculation of Hydrogen Bonding Enthalpy Using the Two-Parameter Abraham Equation. *Liquids* **2024**, *4*, 624–631. https://doi.org/10.3390/liquids4030034

Academic Editors: William E. Acree, Jr., Juan Ortega Saavedra and Enrico Bodo

Received: 15 July 2024
Revised: 13 August 2024
Accepted: 2 September 2024
Published: 6 September 2024

1. Introduction

There is a continuing interest in the hydrogen bonding phenomenon [1–4]. This is evidenced by the growing number of publications using hydrogen bonding (HB) as a keyword. However, it is worth highlighting that the number of direct experimental studies on the thermodynamic parameters of hydrogen bond formation has been declining over the last 3 decades. Among the reasons for this is the technically complex and time-consuming measurement procedure. Several approaches for the simple prediction of the thermodynamic functions of HB have been proposed [5–8]. These works complement the existing data on the Gibbs energies ($\Delta_{\mathrm{HB}}G$) and enthalpies ($\Delta_{\mathrm{HB}}H$) of acid-base complexation. However, the use of these methods is limited by the available constants characterizing the proton acceptor and proton donor abilities.

Recently [9,10], we developed an approach for the calculation of complexation enthalpies (protic acid-base and charge-transfer complexes) using the experimental values of the equilibrium constants at 298.15 K. The determination of complexation enthalpies is a far more difficult procedure, compared with that of the Gibbs energies. This is evidenced by the better reproducibility of the Gibbs energies [1,9,10], and it naturally follows from the fact that most binding enthalpies values are found from the temperature dependences of the equilibrium constants (K_{HB}) [1,4].

The purpose of this work is to test the predictive capability of a successful method for K_{HB} prediction developed by Abraham et al. combined with the approach for $\Delta_{\mathrm{HB}}H$ calculation using K_{HB} values.

2. Methodology

Below, the complex formation equilibrium (1) between a proton donor, A-H, and proton acceptor, B, is considered:

$$\mathrm{A-H+B} \overset{K_{\mathrm{HB}}}{\rightleftarrows} \mathrm{A-H\cdots B} \quad (1)$$

The Gibbs energy of hydrogen bonding is related to the equilibrium constant of reaction (1) as follows:

$$\Delta_{\mathrm{HB}}G = -RT\ln K_{\mathrm{HB}} \tag{2}$$

The hydrogen bonding enthalpy can be determined from direct calorimetric experiments [11–13] or from the temperature dependence of K_{HB}, along with the entropy ($\Delta_{\mathrm{HB}}S$) [1,4]:

$$\ln K_{\mathrm{HB}} = -\frac{\Delta_{\mathrm{HB}}H}{R}\cdot\frac{1}{T} + \frac{\Delta_{\mathrm{HB}}S}{R} \tag{3}$$

K_{HB} depends on the proton acceptor ability of B and proton donor ability of A-H. Since the 1980s, several empirical two-parameter approaches have been proposed for predicting K_{HB} by multiplying the descriptors characterizing A-H and B, particularly by Raevsky et al. [6,7] and Abraham et al. [8]. M.H. Abraham and co-workers developed the acidity and basicity scales based on the analysis of 1:1 complexation constants in tetrachloromethane of (*a*) a set of acids with reference bases [14] and (*b*) a set of bases with reference acids [15]. In order to construct the scales, (1) two arbitrary acids (set *a*) or bases (set *b*) were chosen with the fixed acidity (log $K_{\mathrm{A}}^{\mathrm{H}}$) and basicity constants (log $K_{\mathrm{B}}^{\mathrm{H}}$), (2) the log K_{HB} values were correlated with the latter fixed log $K_{\mathrm{A}}^{\mathrm{H}}$ and log $K_{\mathrm{B}}^{\mathrm{H}}$ parameters to characterize the reference bases (set *a*) and acids (set *b*), and (3) the log $K_{\mathrm{A}}^{\mathrm{H}}$ and log $K_{\mathrm{B}}^{\mathrm{H}}$ values were obtained for the rest of the proton acceptors and proton donors from the correlations with log K_{HB}. As a result, the logarithm of the concentration constant of hydrogen bonding ($K_{\mathrm{HB,c}}$) in tetrachloromethane can be found using Equation (4):

$$\log K_{\mathrm{HB,c}} = (7.354 \pm 0.019)\cdot\alpha_2^{\mathrm{H}}\cdot\beta_2^{\mathrm{H}} - (1.094 \pm 0.007) \tag{4}$$

where α_2^{H} = (log $K_{\mathrm{A}}^{\mathrm{H}}$ + 1.1)/4.636 and β_2^{H} = (log $K_{\mathrm{B}}^{\mathrm{H}}$+1.1)/4.636 are re-scaled acidity and basicity parameters. For 1312 acid-base systems, the root mean square deviation of Equation (4) was 0.09 log units [8]. The acidity (α_2^{H}) and basicity (β_2^{H}) parameters have been derived for a wide range of organic compounds [14–16], which makes Equation (4) quite effective in the estimation of K_{HB} values. This methodology was later developed and fruitfully applied in the studies of hydrogen bonding and fluid phase equilibria by M.H. Abraham and his colleagues, particularly by W.E. Acree, Jr. [17–19], to whom the present issue is devoted.

In recent works [20,21], we studied the compensation relationship between the Gibbs energies and enthalpies of solvation and vaporization of organic non-electrolytes at 298.15 K and distinguished four types of solute–solvent systems, exhibiting different types of the Gibbs energy–enthalpy relationship, depending on their hydrogen bonding capabilities. Aromatic and short-chained aliphatic compounds incapable of hydrogen bonding dissolved in non-hydrogen-bonded solvents followed a general linear trend. Whenever hydrogen bonds were formed between a solute and non-hydrogen-bonded solvent, the Gibbs energies of solvation appeared to be systematically more positive; the slope of the relationship stayed the same. Based on these findings, we derived Equation (5), connecting the Gibbs energies and enthalpies of hydrogen bonding [9]:

$$\Delta_{\mathrm{HB}}G/\left(\mathrm{kJ}\cdot\mathrm{mol}^{-1}\right) = 0.660\ \cdot\ \Delta_{\mathrm{HB}}H/\left(\mathrm{kJ}\cdot\mathrm{mol}^{-1}\right) + 2.5\ \cdot\ n \tag{5}$$

where *n* is a number of hydrogen bonds in acid-base complex. Equation (5) was also applied to charge-transfer complexes with iodine and interhalogens [10]. The validity of Equation (5) was confirmed by comparing the complex formation enthalpies calculated using Equation (6) with the literature data on 293 acid-base systems [9] and 152 charge-transfer complexes:

$$\Delta_{\mathrm{HB}}H/(\mathrm{kJ}\cdot\mathrm{mol}^{-1}) = \frac{\Delta_{\mathrm{HB}}G/(\mathrm{kJ}\cdot\mathrm{mol}^{-1}) - 2.5\cdot n}{0.660} \tag{6}$$

The root mean square deviation was 1.2 kJ·mol^{-1} for the hydrogen-bonded complexes and 1.4 kJ·mol^{-1} for the complexes with iodine and interhalogens.

It is worth highlighting that, in our previous studies of solvation thermodynamics [20,21], the mole-fraction scale was adopted, so $\Delta_{\mathrm{HB}}G$ in Equations (5) and (6) is also a mole-fraction-scale-based quantity. The relationships between mole-fraction and concentration constants and the respective Gibbs energies of hydrogen bonding under infinite dilution conditions are given by Equations (6) and (7):

$$K_{\mathrm{HB}} = K_{\mathrm{HB,c}} / V_{\mathrm{m}}^{\mathrm{S}} \tag{7}$$

$$\Delta_{\mathrm{HB}}G = \Delta_{\mathrm{HB}}G_c + RT \ln\left(\frac{V_{\mathrm{m}}^{\mathrm{S}}}{\mathrm{L \cdot mol^{-1}}}\right) \tag{8}$$

where $V_{\mathrm{m}}^{\mathrm{S}}$ is the molar volume of solvent at 298.15 K.

In this work, Equation (6) was combined with Equation (4) to obtain the hydrogen bonding enthalpies in tetrachloromethane directly from the acidity and basicity parameters of the proton donor and proton acceptor. Taking into account the molar volume of tetrachloromethane of 0.0965 L·mol^{-1} and combining Equations (4) and (6), one comes to a two-parameter Equation (9) for the calculation of $\Delta_{\mathrm{HB}}H$:

$$\Delta_{\mathrm{HB}}H/(\mathrm{kJ \cdot mol^{-1}}) = -63.61 \cdot \alpha_2^{\mathrm{H}} \cdot \beta_2^{\mathrm{H}} + 3.03 \tag{9}$$

It was tested against 122 literature values of the hydrogen bonded enthalpies determined in tetrachloromethane medium. The quality of the prediction was judged based on the root mean square deviation (*RMS*) and average deviation (*AD*) between the calculated and literature values given by Equations (10) and (11):

$$RMS = \sqrt{\frac{\Sigma[\Delta_{\mathrm{HB}}H(\mathrm{calc}) - \Delta_{\mathrm{HB}}H(\mathrm{lit})]^2}{N-1}} \tag{10}$$

$$AD = \frac{\Sigma[\Delta_{\mathrm{HB}}H(\mathrm{calc}) - \Delta_{\mathrm{HB}}H(\mathrm{lit})]}{N} \tag{11}$$

3. Results

The experimental data on the Δ_{HB}H values were collected from comprehensive books by Joesten and Schaad [1] and Laurence and Gal [3], as well as original research papers. For some compounds, the specific interaction enthalpies derived using the data on solvation enthalpies in the inert solvents and the pure base according to Ref. [22] are provided. The comparison between the calculated and literature data, along with the Δ_{HB}G found using Equations (4) and (8), is shown in Table 1.

Table 1. The Gibbs energies of hydrogen bonding at 298.15 K calculated according to Equation (4), the enthalpies of hydrogen bonding calculated according to Equation (9), and the literature values.

Proton Donor	Proton Acceptor	$\frac{-\Delta_{\mathrm{HB}}G(\mathrm{Eq.\ 4})}{\mathrm{kJ \cdot mol^{-1}}}$ a	$\frac{-\Delta_{\mathrm{HB}}H(\mathrm{Eq.9})}{\mathrm{kJ \cdot mol^{-1}}}$ a	$\frac{-\Delta_{\mathrm{HB}}H(\mathrm{lit.})}{\mathrm{kJ \cdot mol^{-1}}}$	$\frac{\Delta}{\mathrm{kJ \cdot mol^{-1}}}$ b	Ref.
Phenol	Benzene	3.1	8.5	6.5	2.0	[1]
	Toluene	3.1	8.5	6.9	1.6	[1]
	m-Xylene	3.6	9.2	8.7	0.5	[1]
	p-Xylene	3.6	9.2	9.0	0.2	[1]
	Mesitylene	4.3	10.4	9.2	1.2	[1]
	Acetophenone	11.6	21.4	19.7	1.7	[1]
		11.6	21.4	21.1	0.3	[1]

Table 1. *Cont.*

Proton Donor	Proton Acceptor	$\frac{-\Delta_{HB}G(\text{Eq. 4})}{\text{kJ}\cdot\text{mol}^{-1}}$ a	$\frac{-\Delta_{HB}H(\text{Eq.9})}{\text{kJ}\cdot\text{mol}^{-1}}$ a	$\frac{-\Delta_{HB}H(\text{lit.})}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta}{\text{kJ}\cdot\text{mol}^{-1}}$ b	Ref.
	Cyclohexanone	13.7	24.5	22.7	1.8	[22]
	Butanone	12.4	22.6	21.8	0.8	[1]
	Acetone	11.9	21.8	19.7	2.1	[23]
		11.9	21.8	22.3	−0.5	[22]
		11.9	21.8	21.3	0.5	[24]
	Methyl acetate	10.9	20.3	18.8	1.5	[1]
	Ethyl acetate	10.9	20.3	21.8	−1.5	[1]
	Butyrolactone	11.9	21.8	20.5	1.3	[1]
	Dimethylformamide	18.2	31.4	28.7	2.7	[1]
		18.2	31.4	29.1	2.3	[22]
	Propanal	10.9	20.3	18.0	2.3	[1]
	Dimethylacetamide	19.2	32.9	30.8	2.1	[1]
		19.2	32.9	30.3	2.6	[22]
	Pyridine	15.2	26.8	27.2	−0.4	[1]
		15.2	26.8	26.8	0.0	[22]
	Diethyl ether	10.9	20.3	20.1	0.2	[1]
	Benzonitrile	7.9	15.7	13.8	1.9	[1]
		7.9	15.7	19.3	−3.6	[1]
	Tetrahydrofuran	11.6	21.4	22.1	−0.7	[1]
		11.6	21.4	23.0	−1.6	[1]
	Chlorocyclohexane	2.1	6.9	8.2	−1.3	[1]
	1-Bromohexane	2.6	7.7	6.7	1.0	[1]
	1-Chlorobutane	2.1	6.9	7.2	−0.2	[1]
		2.1	6.9	9.3	−2.4	[1]
	1-Bromobutane	2.6	7.7	7.2	0.5	[1]
	1-Iodobutane	3.3	8.8	5.4	3.4	[1]
	1-Iodohexane	3.3	8.8	7.3	1.5	[1]
	Diethyl sulfide	7.6	15.3	15.1	0.2	[1]
	Di-*n*-butyl sulfide	7.6	15.3	14.2	1.1	[1]
	Benzaldehyde	9.4	18.0	18.0	0.0	[1]
4-Fluorophenol	Benzene	3.3	8.7	7.3	1.4	[3]
		3.3	8.7	7.7	1.0	[3]
	Toluene	3.3	8.7	7.9	0.8	[3]
	p-Xylene	3.8	9.5	8.1	1.4	[3]
	Mesitylene	4.6	10.7	8.8	1.9	[3]
	Pentamethylbenzene	4.8	11.1	10.3	0.8	[3]
	Hexamethylbenzene	5.1	11.5	10.8	0.7	[3]
	1-Heptene	1.4	5.9	6.8	−0.9	[3]
	Diethyl ether	11.5	21.1	24.1	−3.0	[3]
		11.5	21.1	22.7	−1.6	[3]
	Acetophenone	12.2	22.3	20.8	1.5	[3]
	Acetone	12.5	22.7	22.4	0.3	[3]
	Butanone	13.0	23.6	21.1	2.5	[3]
		13.0	23.6	22.9	0.7	[3]
	Cyclohexanone	14.4	25.6	24.3	1.3	[3]
	Benzaldehyde	9.9	18.7	18.6	0.1	[3]
	Methyl formate	9.6	18.3	18.0	0.3	[3]
	Ethyl formate	9.6	18.3	18.0	0.3	[3]
	Ethyl acetate	11.5	21.1	20.8	0.3	[3]
	Methyl acetate	11.5	21.1	20.8	0.3	[3]
	Nitrobenzene	7.0	14.3	11.5	2.8	[3]
	Chlorocyclohexane	2.2	7.1	8.7	−1.6	[1]
	Bromocyclohexane	3.8	9.5	8.2	1.3	[1]
	1-Chlorobutane	2.2	7.1	8.1	−1.0	[1]
	1-Bromobutane	2.7	7.9	7.6	0.3	[1]
	1-Iodobutane	3.5	9.1	6.5	2.6	[1]

Table 1. *Cont.*

Proton Donor	Proton Acceptor	$\frac{-\Delta_{HB}G(\mathrm{Eq.\ 4})}{\mathrm{kJ\cdot mol^{-1}}}$ a	$\frac{-\Delta_{HB}H(\mathrm{Eq.9})}{\mathrm{kJ\cdot mol^{-1}}}$ a	$\frac{-\Delta_{HB}H(\mathrm{lit.})}{\mathrm{kJ\cdot mol^{-1}}}$	$\frac{\Delta}{\mathrm{kJ\cdot mol^{-1}}}$ b	Ref.
	Benzonitrile	8.3	16.3	17.5	−1.2	[3]
	Dimethyl sulfide	7.2	14.7	13.0	1.7	[3]
	Ethanethiol	5.9	12.7	10.4	2.3	[3]
	Diethyl sulfide	8.0	15.9	14.7	1.2	[3]
	Dibutyl sulfide	8.0	15.9	15.5	0.4	[3]
	Pyridine	16.0	28.0	29.6	−1.6	[3]
Chloroform	Pyridine	3.5	9.0	10.0	−1.0	[1]
	Tetrahydrofuran	2.6	7.7	9.2	−1.5	[22]
	Triethylamine	4.5	10.7	13.5	−2.8	[22]
	Benzene	0.4	4.4	7.1	−2.7	[1]
	Diethyl ether	2.4	7.4	7.2	0.2	[22]
	Acetone	2.6	7.8	7.3	0.5	[22]
	Dimethylformamide	4.2	10.2	11.8	−1.6	[22]
	Dimethylacetamide	4.5	10.6	13.0	−2.4	[1]
	Dimethyl sulfoxide	4.3	10.4	10.5	−0.1	[22]
	Ethyl acetate	2.4	7.4	7.7	−0.3	[1]
		2.4	7.4	7.4	0.0	[22]
	Diethyl sulfide	1.6	6.2	7.1	−0.9	[1]
	Acetonitrile	1.5	6.1	4.9	1.2	[22]
	Nitromethane	1.5	6.1	3.7	2.4	[22]
Pyrrole	Acetonitrile	4.0	9.8	10.3	−0.5	[25]
	Anisole	3.7	9.4	7.4	2.0	[25]
	Benzene	1.6	6.1	5.7	0.4	[25]
	Benzonitrile	4.3	10.3	10.3	0.0	[25]
	Chlorobenzene	0.6	4.6	4.1	0.5	[25]
	Cyclohexanone	7.5	15.2	13.7	1.5	[25]
	Dimethylformamide	10.1	19.1	16.6	2.5	[25]
	Dimethyl sulfoxide	10.4	19.5	18.0	1.5	[25]
	Ethyl acetate	6.0	12.8	13.1	−0.3	[25]
	HMPA c	13.8	24.7	24.0	0.7	[25]
	Nitrobenzene	3.6	9.2	8.8	0.4	[25]
	Nitromethane	4.0	9.8	8.8	1.0	[25]
	Pyridine	8.4	16.5	16.2	0.3	[25]
	Tetrahydrofuran	6.4	13.5	15.2	−1.7	[25]
	Toluene	1.6	6.1	6.1	0.0	[25]
N-methylaniline	Dimethylformamide	4.8	11.1	9.9	1.2	[22]
	Dimethyl sulfoxide	5.0	11.3	9.9	1.4	[22]
	Ethyl acetate	2.8	8.0	5.4	2.6	[22]
	Pyridine	4.0	9.8	8.5	1.3	[22]
Methanol	Benzylamine	12.6	22.8	22.3	0.5	[22]
	Triethylamine	13.8	24.7	24.1	0.6	[22]
Butan-1-ol	Dimethylformamide	11.0	20.5	19.2	1.3	[1]
	Dimethylacetamide	11.7	21.5	18.7	2.8	[1]
	Triethylamine	11.8	21.7	23.1	−1.4	[1]
	Pyridine	9.2	17.7	18.4	−0.7	[1]
	Diethyl ether	6.5	13.7	16.3	−2.6	[1]
		6.5	13.7	13.6	0.1	[22]
	Anisole	4.1	9.9	7.1	2.8	[1]
	Tetrahydrofuran	7.0	14.4	12.8	1.6	[1]
	Acetophenone	7.0	14.4	15.9	−1.5	[1]
	Butanone	7.5	15.1	12.8	2.3	[1]
	Cyclohexanone	8.3	16.3	17.2	−0.9	[1]

Table 1. *Cont.*

Proton Donor	Proton Acceptor	$\frac{-\Delta_{HB}G(\text{Eq. 4})}{\text{kJ}\cdot\text{mol}^{-1}}$ [a]	$\frac{-\Delta_{HB}H(\text{Eq.9})}{\text{kJ}\cdot\text{mol}^{-1}}$ [a]	$\frac{-\Delta_{HB}H(\text{lit.})}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta}{\text{kJ}\cdot\text{mol}^{-1}}$ [b]	Ref.
2-methylbutan-2-ol	Dimethylformamide	9.19	17.7	15.1	2.6	[22]
	Dimethyl sulfoxide	9.45	18.1	15.0	3.1	[22]
	Ethyl acetate	5.41	12.0	9.3	2.7	[22]
	Triethylamine	9.84	18.7	19.7	−1.0	[22]
Hexanol	Benzylamine	10.7	20.1	21.3	−1.2	[22]
	Pyridine	9.2	17.7	15.6	2.1	[22]
	Tetrahydrofuran	7.0	14.4	12.3	2.1	[22]

[a] The α_2^H and β_2^H values [16,26] used for the calculation are listed in Table S1 of Supplementary Materials. [b] The difference between columns 4 and 5. [c] Hexamethylphosphoramide.

The data on 122 acid-base pairs were collected in total. Among 50 proton acceptors, aromatic and aliphatic amines, amides, ethers, esters, ketones, nitriles, aromatic hydrocarbons, nitro-compounds, halohydrocarbons, sulfides, and hexamethylphosphoramide were considered. The proton donors included phenol and 4-fluorophenol, pyrrole, methanol, butan-1-ol, hexan-1-ol, 2-methylbutan-2-ol, *N*-methylaniline, and chloroform. When collecting the enthalpies values, we attempted to cover more systems (pyrrole, *N*-methylaniline, 2-methylbutan-2-ol as acids; amines—alcohols pairs) that were not included in our recent work [9] devoted to the calculation of hydrogen bonding enthalpies from the experimental binding constants.

4. Discussion

For the 122 acid-base systems considered, *RMS* equaled 1.6 kJ·mol^{-1} and *AD* was 0.5 kJ·mol^{-1}. The deviations greater than 3 kJ·mol^{-1} are rather inconsistent with other available data. Although the maximum positive deviation of 3.4 kJ·mol^{-1} can be seen for the 1-iodobutane–phenol pair, excellent agreement was observed for 1-bromobutane and 1-iodohexane. One of the values from the Ref. available for the benzonitrile–phenol pair [1], for which the deviation is minimal and equals −3.6 kJ·mol^{-1}, deviates from another value by 5.2 kJ·mol^{-1}.

When analyzing the deviations between the calculated and experimental values, one should consider the possible sources of uncertainties for each magnitude. First, the expected uncertainty of Equation (4) of 0.09 log units contributes ±0.8 kJ·mol^{-1} to $\Delta_{HB}H$ found using Equation (6) or (9). The uncertainty of Equation (6) itself was earlier estimated as 2 kJ·mol^{-1} [9]. On the other hand, the uncertainty of the $\Delta_{HB}H$ measurement (usually due to K_{HB} variation with temperature) depends on the error in K_{HB}. It was earlier evaluated at the level of ca. 0.05–0.1 log units [15]. Then, one can estimate the uncertainty in $\Delta_{HB}H$ determination from its temperature dependence, similarly to Refs. [27,28]. Assuming that the temperature uncertainty is 0.01 K and three measurements at 288–308 K are performed, the respective standard deviation of $\Delta_{HB}H$ would equal 1–2 kJ·mol^{-1}. The issues with maintaining infinite dilution conditions and temperature effects on extinction coefficients during spectroscopic measurement may lead to far greater errors in $\Delta_{HB}H$, which is reflected in poor agreement between data on some acid-base systems studied multiple times, e.g., phenol-pyridine. In this case, standard deviation of the literature $\Delta_{HB}H$ values exceeds 4 kJ·mol^{-1}. Based on these estimates, the agreement within 3 kJ·mol^{-1} for most compounds listed in Table 1 and a *RMS* of 1.6 kJ·mol^{-1} can be considered excellent.

Thus, the comparison between the hydrogen bonding enthalpies calculated according to Equation (9) and the experimental data confirms the consistency between the compensation relationship given by Equation (5) and Abraham's two-parameter equation (4). The acidity and basicity parameters of Equation (4) are readily available for more than 600 compounds [26], or 3.6·10^5 acid-base pairs. It is reasonable to expect that Equation (9) can be a useful tool for estimating $\Delta_{HB}H$ in numerous acid-base systems not studied before without measuring K_{HB}. Hydrogen bonding entropies can also be estimated from the calculated Gibbs energies and enthalpies.

One can recall the two- or multi-parameter models [6,7,29,30] for estimating complex formation enthalpies. They rely on the empirical acidity and basicity parameters correlated to the experimental enthalpic data. An important difference of the present study is that Equations (4), (5) and (9) do not follow from the experimental hydrogen bonding enthalpies at all, and their consistency with $\Delta_{HB}H$ in the literature is demonstrated independently.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/liquids4030034/s1, Table S1: Abraham's acidity parameters of the proton donors and basicity parameters of proton acceptors used in this research.

Author Contributions: Conceptualization, B.N.S.; methodology, B.N.S. and M.I.Y.; investigation, B.N.S., M.B.K. and M.I.Y.; writing—original draft preparation, B.N.S. and M.I.Y.; writing—review and editing, B.N.S. and M.I.Y. All authors have read and agreed to the published version of the manuscript.

Funding: The work was carried out in accordance with the Strategic Academic Leadership Program "Priority 2030" of the Kazan Federal University of the Government of the Russian Federation.

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Joesten, M.D.; Schaad, L. *Hydrogen Bonding*; Marcel Dekker: New York, NY, USA, 1974; p. 599.
2. Laurence, C.; Graton, J.; Berthelot, M.; Besseau, F.; Le Questel, J.-Y.; Luçon, M.; Ouvrard, C.; Planchat, A.; Renault, E. An enthalpic scale of hydrogen-bond basicity. 4. Carbon π bases, oxygen bases, and miscellaneous second-row, third-row, and fourth-row bases and a survey of the 4-fluorophenol affinity scale. *J. Org. Chem.* **2010**, *75*, 4105–4123. [CrossRef]
3. Laurence, C.; Gal, J. Thermodynamic and spectroscopic scales of hydrogen-bond basicity and affinity. In *Lewis Basicity and Affinity Scales: Data and Measurement*; John Wiley & Sons, Ltd.: New York, NY, USA, 2009; pp. 111–227.
4. Pimentel, G.C.; McClellan, A. Hydrogen bonding. *Annu. Rev. Phys. Chem.* **1971**, *22*, 347–385. [CrossRef]
5. Drago, R.S.; O'Bryan, N.; Vogel, G.C. A frequency shift-enthalpy correlation for a given donor with various hydrogen-bonding acids. *J. Am. Chem. Soc.* **1970**, *92*, 3924–3929. [CrossRef]
6. Raevsky, O.A.; Novikov, V.P. Unification of the donor-acceptor interaction characteristics to reveal structure-activity-relationships. *Pharm. Chem. J.* **1982**, *16*, 583–586.
7. Raevsky, O.A.; Grigor'ev, V.Y.; Kireev, D.B.; Zefirov, N.S. Complete thermodynamic description of H-bonding in the framework of multiplicative approach. *QSAR* **1992**, *11*, 49–63. [CrossRef]
8. Abraham, M.H.; Grellier, P.L.; Prior, D.V.; Taft, R.W.; Morris, J.J.; Taylor, P.J.; Laurence, C.; Berthelot, M.; Doherty, R.M. A general treatment of hydrogen bond complexation constants in tetrachloromethane. *J. Am. Chem. Soc.* **1988**, *110*, 8534–8536. [CrossRef]
9. Solomonov, B.N.; Yagofarov, M.I. Can the hydrogen bonding enthalpy be calculated from the binding constant at 298.15 K? *J. Mol. Liq.* **2024**, *409*, 125353. [CrossRef]
10. Solomonov, B.N.; Khisamiev, M.B.; Yagofarov, M.I. Calculation of the formation enthalpies of charge-transfer complexes with iodine from the binding constants at 298.15 K. *J. Mol. Liq.* **2024**, *411*, 125690. [CrossRef]
11. Arnett, E.M.; Joris, L.; Mitchell, E.; Murty, T.; Gorrie, T.; Schleyer, P.v.R. Hydrogen-bonded complex formation. III. Thermodynamics of complexing by infrared spectroscopy and calorimetry. *J. Am. Chem. Soc.* **1970**, *92*, 2365–2377. [CrossRef]
12. Epley, T.D.; Drago, R.S. Calorimetric studies on some hydrogen-bonded adducts. *J. Am. Chem. Soc.* **1967**, *89*, 5770–5773. [CrossRef]
13. Spencer, J.; Gleim, J.E.; Blevins, C.H.; Garrett, R.C.; Mayer, F.J. Enthalpies of solution and transfer enthalpies. An analysis of the pure base calorimetric method for the determination of hydrogen bond enthalpies. *J. Phys. Chem.* **1979**, *83*, 1249–1255. [CrossRef]
14. Abraham, M.H.; Grellier, P.L.; Prior, D.V.; Duce, P.P.; Morris, J.J.; Taylor, P.J. Hydrogen bonding. Part 7. A scale of solute hydrogen-bond acidity based on log K values for complexation in tetrachloromethane. *J. Chem. Soc. Perkin Trans. 2* **1989**, *6*, 699–711. [CrossRef]
15. Abraham, M.H.; Grellier, P.L.; Prior, D.V.; Morris, J.J.; Taylor, P.J. Hydrogen bonding. Part 10. A scale of solute hydrogen-bond basicity using log K values for complexation in tetrachloromethane. *J. Chem. Soc. Perkin Trans. 2* **1990**, *4*, 521–529. [CrossRef]
16. Abraham, M.H. Scales of solute hydrogen-bonding: Their construction and application to physicochemical and biochemical processes. *Chem. Soc. Rev.* **1993**, *22*, 73–83. [CrossRef]
17. Abraham, M.H.; Gola, J.M.R.; Cometto-Muñiz, J.E.; Acree, W.E., Jr. Hydrogen Bonding between Solutes in Solvents Octan-1-ol and Water. *J. Org. Chem.* **2010**, *75*, 7651–7658. [CrossRef]
18. Abraham, M.H.; Acree, W.E.; Earp, C.E.; Vladimirova, A.; Whaley, W.L. Studies on the hydrogen bond acidity, and other descriptors and properties for hydroxyflavones and hydroxyisoflavones. *J. Mol. Liq.* **2015**, *208*, 363–372. [CrossRef]

19. Abraham, M.H.; Acree, W.E. Descriptors for the hydrogen halides, their solution properties and hydrogen- bonding acidity and basicity: Comparison of the latter with gas phase data. *J. Mol. Liq.* **2019**, *275*, 667–673. [CrossRef]
20. Solomonov, B.N.; Yagofarov, M.I. Compensation relationship in Thermodynamics of solvation and vaporization: Features and applications. I. Non-hydrogen-bonded systems. *J. Mol. Liq.* **2022**, *368*, 120762. [CrossRef]
21. Solomonov, B.N.; Yagofarov, M.I. Compensation relationship in thermodynamics of solvation and vaporization: Features and applications. II. Hydrogen-bonded systems. *J. Mol. Liq.* **2023**, *372*, 121205. [CrossRef]
22. Solomonov, B.N.; Novikov, V.B.; Varfolomeev, M.A.; Mileshko, N.M. A new method for the extraction of specific interaction enthalpy from the enthalpy of solvation. *J. Phys. Org. Chem.* **2005**, *18*, 49–61. [CrossRef]
23. Gramstad, T. Studies of hydrogen bonding—Part VII: Hydrogen-bond association of phenol and pentachlorophenol with carbonyl compounds and ethers. *Spectrochim. Acta* **1963**, *19*, 497–508. [CrossRef]
24. Perelygin, I.S.; Ahunov, T.F. IR spectra and hydrogen bonds of hydroxyls of chlorine-substituted phenols. I. Complexes with acetonitrile. *Opt. Spektrosk.* **1971**, *30*, 679–683, Chem. Abst. 75: 27627.
25. Catalan, J.; Gomez, J.; Couto, A.; Laynez, J. Toward a solvent basicity scale: The calorimetry of the pyrrole probe. *J. Am. Chem. Soc.* **1990**, *112*, 1678–1681. [CrossRef]
26. Abraham, M.H.; Chadha, H.S.; Whiting, G.S.; Mitchell, R.C. Hydrogen bonding. 32. An analysis of water-octanol and water-alkane partitioning and the Δlog P parameter of Seiler. *J. Pharm. Sci.* **1994**, *83*, 1085–1100. [CrossRef]
27. Cebe, P.; Thomas, D.; Merfeld, J.; Partlow, B.P.; Kaplan, D.L.; Alamo, R.G.; Wurm, A.; Zhuravlev, E.; Schick, C. Heat of fusion of polymer crystals by fast scanning calorimetry. *Polymer* **2017**, *126*, 240–247. [CrossRef]
28. Bolmatenkov, D.N.; Yagofarov, M.I.; Valiakhmetov, T.F.; Rodionov, N.O.; Solomonov, B.N. Vaporization enthalpies of benzanthrone, 1-nitropyrene, and 4-methoxy-1-naphthonitrile: Prediction and experiment. *J. Chem. Thermodyn.* **2022**, *168*, 106744. [CrossRef]
29. Drago, R.S.; Wayland, B.B. A Double-Scale Equation for Correlating Enthalpies of Lewis Acid-Base Interactions. *J. Am. Chem. Soc.* **1965**, *87*, 3571–3577. [CrossRef]
30. Vogel, G.C.; Drago, R.S. The ECW Model. *J. Chem. Educ.* **1996**, *73*, 701. [CrossRef]