Thermodynamic functions of hydrogen bonding of amines in methanol derived from solution calorimetry data and headspace analysis

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ABSTRACT

Reactivity and equilibrium properties of organic molecules in self-associated liquids greatly depend on the hydrogen bonding with solvent. This work contains comprehensive thermodynamic analysis of hydrogen bonding of aliphatic and aromatic amines in self-associated solvent methanol. Enthalpies of solution at infinite dilution and limiting activity coefficients for the studied systems were measured experimentally. Enthalpies and Gibbs energies of hydrogen bonding of amines with neat methanol were determined. These values were found to be decreased compared with hydrogen bond energy in equimolar complexes "methanol–amine" determined in inert solvent or base media. A linear dependence between enthalpies and Gibbs energies of hydrogen bonding of amines with neat methanol was observed. It was firstly revealed that the entropy of specific interactions of amines with neat methanol can be about zero or positive. Disruption of solvent–solvent hydrogen bonds can be regarded as the most important step during dissolution of amine in methanol. It was found that the cooperative effect influences on the Gibbs energies of hydrogen bonding of amines in methanol, but in a lesser extent than in aqueous solutions. The new results show that the hydrogen bonding process in the self-associated solvents differs significantly from equimolar complexation in aprotic media.

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1. Introduction

The non-covalent interactions in condensed phase influence greatly on various physical, chemical and biological processes [1]. Among all non-covalent interactions, hydrogen bonding takes a special place [2]. H-bonds play a huge role in substrate–enzyme binding [3], and determine the specificity of DNA molecule [4]. They regulate the structure and reactivity of supramolecular assemblies [5] and control an association of molecules in condensed phase [6]. One of the most widely-spread examples of self-associated liquids by hydrogen bonds is methanol. This solvent is used in oil and chemical industry. Methanol is the most similar molecule to water. It presents a mixture of the complexes of varied structure (linear and cyclic) [7,8] and stoichiometry (dimer, trimer, . . ., polymer) [9,10]. Solute molecules can be completely H-bonded in methanol environment and their reactivity is largely determined by the thermodynamic parameters of hydrogen bonding. This makes

the estimation of hydrogen bonding thermodynamic functions of solutes with neat methanol a crucial problem.

Hydrogen bonding in equimolar complexes of methanol with organic substances is broadly investigated using various experimental methods. Solution calorimetry [11–16], FTIR-spectroscopy [16–18] and NMR-spectroscopy [16,19] measurements were applied to obtain extensive data on thermodynamic functions of equimolar complexation $CH_3OH\cdots B$ (B – proton acceptor) in inert or aprotic media [11,16,19–21]. Also empirical equations, such as Iogansen [22], Badger–Bauer [23], Raevsky [24], Abraham [25] and other relations [26,27] were created for estimating enthalpies and equilibrium constants in binary hydrogen bonded complexes. The complexation of solute molecules with neat methanol is on the other hand much less investigated. The application of spectral methods is hardened by the overlapping O—H bands related to various hetero- and self-associated species in methanol environment. Empirical equations also cannot be used in this case because they only deal with parameters for equimolecular complexes.

Problems in examination of hydrogen bonding between solute molecules and methanol are related to special properties of self-associated liquids, which are stipulated by the existing hydrogen bonded species of varied composition in their media. Thermodynamic function of hydrogen bonding process of solutes in

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self-associated solvent includes two interrelated terms. First term is the thermodynamic function of hydrogen bond formation of solute molecule with solvent associative species. The strength of H-bonds in such complexes depends on the size of the associative species and is obviously higher than in equimolar complexes $CH_3OH\cdots B$ due to cooperative effect [15,17,28]. The cooperativity phenomenon implies that the overall hydrogen bonding energy in multi-particle complex is not equal to the sum of hydrogen bond energies in pair complexes [6,17,29]. Second term is the thermodynamic function of reorganization of self-associated by H-bonds solvent (disruption of solvent–solvent hydrogen bonds) [13,30,31]. Because the association degree of aliphatic alcohols is near 100% [31,32], the interaction of dissolved molecules with alcohol leads to the equilibrium shift between various associative species of H-bonded solvent. Furthermore, the values of solvation thermodynamic functions in alcohols are influenced by the so-called solvophobic effect [33,34], which is similar to the hydrophobic effect in water [35].

All these peculiarities make the estimation of the thermodynamic functions of hydrogen bonding in methanol an ambiguous problem. Previously, we investigated the enthalpic contribution of cooperative strengthening in hydrogen bonding process of several tertiary amines in aliphatic alcohols [28,32,36]. In the current work we extended it to primary and secondary amines and identified the purpose of this study as a first entire thermodynamic analysis of hydrogen bonding of amines in methanol including the determination of Gibbs energies and entropies. We also analyzed the influence of amine structure on the magnitudes of enthalpies and Gibbs energies of hydrogen bonding with methanol.

2. Experimental part

All chemicals were supplied by Acros Organics (mass fraction min. 98%). They were dried and purified before use by standard methods [37]. The purity of chemicals was monitored by gas chromatography; the relative content of main substances in all cases was no less than 99.8%. The water content was determined by Karl Fischer titration and FTIR-spectroscopy. The mass fraction of water in amines and methanol does not exceed 0.1%.

Calorimetric measurements were carried out at 298.15 ± 0.01 K using a semi-adiabatic solution calorimeter constructed in Kazan University. Detailed description of apparatus is presented in Refs. [32,38]. The detection limit of the apparatus is about 10 µK, which corresponds approximately to 0.005 J if solvent is water. The reproducibility of calorimetric data regarding the electrical calibrations only was found to be about 0.15% for calibration heat range from 0.5 to 1.5 J. The calorimeter was tested by measuring the solution enthalpy of potassium chloride in water. For this system there are several literature values: $\Delta_{soln}H^{KCl/H_2O} = 17.25 \pm 0.04$ kJ mol^{-1} ($T = 298.15$ K) [39], $\Delta_{soln}H^{KCl/H_2O} = 15.72 \pm 0.04$ kJ mol^{-1} ($T = 313.15$ K, $m = 0.1994$ mol kg^{-1}) [40]. The standard value was found also in the report of the ICTAC (International Confederation for Thermal Analysis and Calorimetry) working group "thermochemistry" [41] ($T = 298.15$ K, $m = 0.02775$ mol kg^{-1}): $\Delta_{soln}H^{KCl/H_2O} = 17.47 \pm 0.07$ kJ mol^{-1}. In our own experiments water volume of 0.11 L with an accuracy of 0.0001 L and potassium chloride weighted samples of about 0.228 g were taken. Potassium chloride of 99.9% purity was recrystallized and dried according to Ref. [42]. The averaged value obtained is $\Delta_{soln}H^{KCl/H_2O} = 17.41 \pm 0.04$ kJ mol^{-1} ($T = 298.15$ K, $m = 0.02783$ mol kg^{-1}) that corresponds to the standard data [41]. Each value of the solution enthalpy was reproduced 6–8 times. All experimental data were statistically processed; they are shown in Table 1. In addition, the concentration measurements of

Table 1
The enthalpies of solution at infinite dilution obtained in this work ($\Delta_{soln}H^{A/S}$), $T = 298.15 \pm 0.01$ K, atmospheric pressure.

Solute (A)	Solvent (S)	$\Delta_{soln}H^{A/S}$(kJ mol^{-1})
n-Butylamine	Methanol	−15.81 ± 0.05
n-Butylamine	Cyclohexane	6.48 ± 0.05
n-Butylamine	Benzene	2.87 ± 0.10
sec-Butylamine	Methanol	−16.88 ± 0.09
sec-Butylamine	Cyclohexane	5.95 ± 0.14
sec-Butylamine	Benzene	1.55 ± 0.07
tert-Butylamine	Methanol	−18.99 ± 0.05
tert-Butylamine	Cyclohexane	5.15 ± 0.12
tert-Butylamine	Benzene	1.27 ± 0.03
n-Hexylamine	Methanol	−14.54 ± 0.19
n-Hexylamine	Cyclohexane	6.41 ± 0.09
n-Hexylamine	Benzene	2.30 ± 0.03
Cyclohexylamine	Methanol	−14.90 ± 0.11
Cyclohexylamine	Cyclohexane	4.98 ± 0.03
Cyclohexylamine	Benzene	2.05 ± 0.03
Diethylamine	Methanol	−16.30 ± 0.20
Diethylamine	Cyclohexane	3.50 ± 0.06
Diethylamine	Benzene	0.87 ± 0.03
Di-n-propylamine	Methanol	−15.20 ± 0.15
Di-n-propylamine	Cyclohexane	3.43 ± 0.12
Di-n-propylamine	Benzene	1.83 ± 0.03
Di-n-butylamine	Methanol	−13.80 ± 0.15
Di-n-butylamine	Cyclohexane	2.99 ± 0.08
Di-n-butylamine	Benzene	2.50 ± 0.05
4-Methylpyridine	Cyclohexane	7.82 ± 0.09
4-Methylpyridine	Benzene	−0.09 ± 0.03
Methanol	n-Butylamine	−11.68 ± 0.13
Methanol	sec-Butylamine	−11.67 ± 0.26
Methanol	tert-Butylamine	−12.00 ± 0.17
Methanol	n-Hexylamine	−11.12 ± 0.10
Methanol	Cyclohexylamine	−11.55 ± 0.16
Methanol	Diethylamine	−11.20 ± 0.03
Methanol	Di-n-propylamine	−8.44 ± 0.14

dissolution enthalpies were carried out. The absence of concentration dependence of solution enthalpies confirms the performance of dissolution experiments at infinite dilution conditions.

Measurements of limiting activity coefficients were carried out at 298.15 ± 0.01 K using gas chromatographic head space analysis (Chromatec Crystall-2000M gas chromatograph, quartz glass column with RTX-5 amine stationary phase). The limiting activity coefficient $\gamma^{A/S}$ can be calculated from the ratio of vapor pressure of solute A over its solution in S ($p_A^{A/S}$) to the saturated vapor pressure of pure A in bar (p_{sat}^A):

$$\gamma^{A/S} = p_A^{A/S}/p_{sat}^A x_A^{A/S}, \tag{1}$$

where $x_A^{A/S}$ is the mole fraction of A in the solution. The ratio $p_A^{A/S}/p_{sat}^A$ is proportional to the ratio of chromatographic peak areas in two appropriate headspace analyses of pure A and its solution. Design of the automatic electropneumatic dosing system used for headspace sampling was described elsewhere [43]. The gas phase samples were taken from 15 mL vials with 1 mL of solution or pure compound. The concentration of solutes was 1–3 vol %. Correction of initial concentration on the quantity of evaporated solute was made for calculating $\gamma^{A/S}$. Obtained limiting activity coefficients are related to the Gibbs energies of solvation through Eq. (2):

$$\Delta_{solv}G^{A/S} = RT \ln(\gamma^{A/S} p_{sat}^A). \tag{2}$$

For all studied systems, measurements were repeated 3 times. In all measurements, the values of activity coefficients for the same solute–solvent system did not differ more than 10%. The absence of significant concentration dependence of $\gamma^{A/S}$ was established by measurements at 3–4 different concentrations of A.

The solvation Gibbs energies were calculated using Eq. (2). Saturated vapor pressures of pure compounds needed for calculation were taken from the EPI Suite program database [44]. All

Table 2

The limiting activity coefficients ($\gamma^{A/S}$) measured in this work at $T = 298.15 \pm 0.01$ K and atmospheric pressure, the Gibbs energies of solvation ($\Delta_{solv}G^{A/S}$).

Solute (A)	Solvent (S)	$\gamma^{A/S}$	$\Delta_{solv}G^{A/S}$ kJ mol^{-1}
n-Butylamine	Methanol	0.46 ± 0.03	−7.1
sec-Butylamine	Methanol	0.75 ± 0.04	−4.3
sec-Butylamine	Benzene	1.15 ± 0.07	−1.4
tert-Butylamine	Methanol	0.36 ± 0.09	−4.3
tert-Butylamine	Benzene	1.26 ± 0.09	−1.2
n-Hexylamine	Methanol	13.70 ± 0.96	−4.5
n-Hexylamine	Benzene	16.20 ± 1.30	−4.1
Cyclohexylamine	Methanol	4.81 ± 0.19	−6.8
Cyclohexylamine	Benzene	6.43 ± 0.42	−6.1
Diethylamine	Methanol	0.40 ± 0.07	−5.1
Di-n-propylamine	Methanol	0.91 ± 0.05	−9.2
Di-n-propylamine	Benzene	1.48 ± 0.06	−8.0
Triethylamine	Benzene	1.28 ± 0.04, 1.30^a, 1.21^b, 1.24^b	−5.8
Tri-n-propylamine	Methanol	6.67 ± 0.15	−10.7
Tri-n-propylamine	Benzene	1.63 ± 0.08, 1.13^b	−14.2
Tri-n-propylamine	n-Hexadecane	0.94 ± 0.01	−15.6
Pyridine	Methanol	1.20 ± 0.08	−8.4
2-Methylpyridine	Methanol	0.75 ± 0.03	−11.1
3-Methylpyridine	Methanol	0.82 ± 0.03	−12.4
3-Methylpyridine	Benzene	0.96 ± 0.05	−12.0
4-Methylpyridine	Methanol	1.00 ± 0.05	−12.1
2,6-Dimethylpyridine	Methanol	0.94 ± 0.03	−12.3
Methanol	n-Butylamine	0.35 ± 0.03	−7.0
Methanol	sec-Butylamine	0.38 ± 0.02	−6.8
Methanol	tert-Butylamine	0.29 ± 0.02	−7.5
Methanol	n-Hexylamine	0.38 ± 0.02	−6.8
Methanol	Cyclohexylamine	0.33 ± 0.01	−7.2
Methanol	Diethylamine	0.51 ± 0.01	−6.1
Methanol	Di-n-propylamine	0.69 ± 0.02	−5.3
Methanol	2-Methylpyridine	0.79 ± 0.04	−5.0
Methanol	3-Methylpyridine	0.65 ± 0.02	−5.5
Methanol	4-Methylpyridine	0.68 ± 0.04	−5.4
Methanol	2,6-Dimethylpyridine	0.61 ± 0.04	−5.6

[a] Ref. [45].
[b] Ref. [46].

experimental data on limiting activity coefficients and calculated Gibbs energies of solvation are presented in Table 2.

3. Methodology

One of the main experimental quantities reflecting the non-covalent intermolecular interactions in the liquid state is a thermodynamic function of solvation, $\Delta_{solv}f^{A/S}$. It presents a thermodynamic function of isothermal transfer of solute A from the ideal gas state to an infinitely diluted solution of unit mole fraction in solvent S at temperature 298.15 K and pressure 0.1 MPa. In general, the solvation thermodynamic function of liquid solute A in solvent S can be found as follows:

$$\Delta_{solv}f^{A/S} = \Delta_{soln}f^{A/S} - \Delta_{vap}f^{A}, \tag{3}$$

where $\Delta_{soln}f^{A/S}$ is the thermodynamic function of solution of solute A in the studied solvent S at infinite dilution, $\Delta_{vap}f^{A}$ is the thermodynamic function of vaporization of A if it is a liquid at the standard state (Eq. (3)).

The thermodynamic function of solvation in an associated liquid can be regarded as a sum of three contributions: the thermodynamic function of non-specific solvation of solute A in solvent S (van der Waals interactions) ($\Delta_{solv(nonsp)}f^{A/S}$), thermodynamic function of specific interaction (hydrogen bonding) of A with solvent S ($\Delta_{int(sp)}f^{A/S}$)

and also the contribution of the solvophobic effect ($\Delta_{s.e.}f^{A/S}$) [33,47]:

$$\Delta_{solv}f^{A/S} = \Delta_{solv(nonsp)}f^{A/S} + \Delta_{s.e.}f^{A/S} + \Delta_{int(sp)}f^{A/S}. \tag{4}$$

The thermodynamic function of solvation is the experimental value. Therefore, to determine the thermodynamic function of hydrogen bonding of solute A with the self-associated solvent S one should estimate correctly the nonspecific solvation term ($\Delta_{solv}f^{A/S}$) and the solvophobic effect ($\Delta_{s.e.}f^{A/S}$).

The thermodynamic function of specific interaction ($\Delta_{int(sp)}f^{A/S}$) is a function of solute–solvent H-bonding only if the solvent is not self-associated through hydrogen bonds. Otherwise, the solute–solvent hydrogen bond formation may cause a disruption of hydrogen bonds within the associated solvent species. In this case the thermodynamic function of specific interaction ($\Delta_{int(sp)}f^{A/S}$) of solutes in methanol and other highly associated solvents may include two terms: the thermodynamic functions of H-complexation and of solvent reorganization.

Methods for the determination of Gibbs energy and enthalpy of non-specific solvation were proposed previously [11,48]. Thus, the Gibbs energy of non-specific solvation can be found from Eq. (5) [48]:

$$\Delta_{solv(nonsp)}G^{A/S} = \Delta_{solv}G^{A/S_0} + (\delta_{cav}g^{S} - \delta_{cav}g^{S_0}) \cdot V_x^{A}$$

$$+ (a + b\sqrt{\delta_{cav}g^{S}}) \cdot [(\Delta_{solv}G^{A/S_R} - \Delta_{solv}G^{A/S_0}) - (\delta_{cav}g^{S_R}$$

$$- \delta_{cav}g^{S_0}) \cdot V_x^{A}],$$

$$a = \frac{-\sqrt{\delta_{cav}g^{S_0}}}{\sqrt{\delta_{cav}g^{S_R}} - \sqrt{\delta_{cav}g^{S_0}}}$$

$$b = \frac{1}{\sqrt{\delta_{cav}g^{S_R}} - \sqrt{\delta_{cav}g^{S_0}}} \tag{5}$$

Here $\Delta_{solv}G^{A/S_0}$, $\Delta_{solv}G^{A/S_R}$ are the Gibbs energies of solvation of solute A in the standard solvents S_0 and S_R, which interact with A only non-specifically; $\delta_{cav}g^{S}$, $\delta_{cav}g^{S_0}$ and $\delta_{cav}g^{S_R}$ are the specific relative Gibbs energies of cavity formation for each solvent, and V_x^{A} is the characteristic volume of solute A [49], which can be determined by a simple additive scheme from atomic contributions. The parameter $\delta_{cav}g^{S}$ reflects the non-specific interactions with the studied solvent. It is determined from the Gibbs energy of solvation of n-octane in solvent S:

$$\delta_{cav}g^{S}(10^{-2} \text{ kJ cm}^{-3})$$

$$= \frac{(\Delta_{solv}G^{C_8H_{18}/S} - \Delta_{solv}G^{C_8H_{18}/C_{16}H_{34}})(\text{kJ mol}^{-1})}{V_x^{C_8H_{18}}(10^2 \text{ cm}^3 \text{ mol}^{-1})}. \tag{6}$$

Here $\Delta_{solv}G^{C_8H_{18}/C_{16}H_{34}}$ is the Gibbs solvation energy of n-octane in n-hexadecane. In the case of associated solvents (water and alcohols) there must be a correction for the solvophobicity of n-octane.

The Gibbs energy of the solvophobic effect ($\Delta_{s.e.}G^{A/S}$) refers to a special property of solvents highly associated through hydrogen bonds [35]. It was found before that the term $\Delta_{s.e.}G^{A/S}$ linearly depends on the McGowan characteristic volume of the solute [33]. The Gibbs energy of solvophobic effect ($\Delta_{s.e.}G^{A}$) in methanol can be obtained through Eq. (7) [33]:

$$\Delta_{s.e.}G^{A/S} = 5.17 \cdot V_x^{A} + 0.23. \tag{7}$$

According to Eqs. (4), (5) and (7) the Gibbs energy of specific interaction of solute A in methanol is equal to:

$$\Delta_{int(sp)}G^{A/S} = \Delta_{solv}G^{A/S} - \Delta_{solv}G^{A/S_0} - (\delta_{cav}g^{S} - \delta_{cav}g^{S_0}) \cdot V_x^{A}$$

$$- (a + b\sqrt{\delta_{cav}g^{S}}) \cdot [(\Delta_{solv}G^{A/S_R} - \Delta_{solv}G^{A/S_0})$$

$$- (\delta_{cav}g^{S_R} - \delta_{cav}g^{S_0}) \cdot V_x^{A}] - 5.17 \cdot V_x^{A} - 0.23. \tag{8}$$
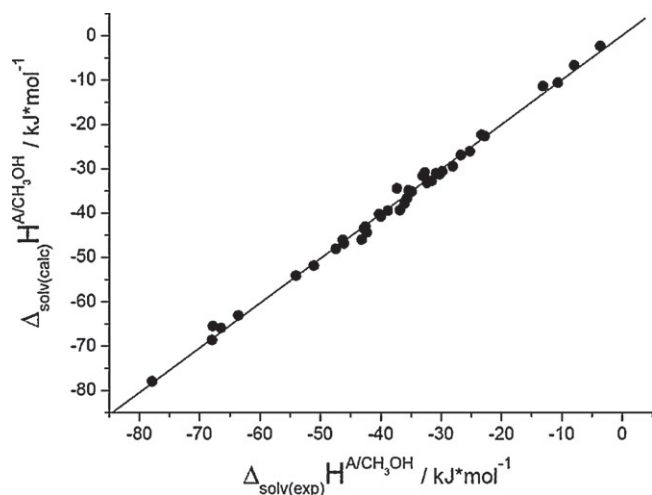
Fig. 1. Comparison of the enthalpies of the nonspecific solvation calculated by Eq. (9) with experimental enthalpies of solvation of organic compounds in methanol.

In Ref. [11] an equation for the determination of the non-specific solvation enthalpy ($\Delta_{solv(nonsp)}H^{A/S}$) was proposed:

$$\Delta_{solv(nonsp)}H^{A/S} = \Delta_{solv}H^{A/C_6H_{12}} + (\delta_{cav}h^S - \delta_{cav}h^{C_6H_{12}}) \cdot V_x^A$$
$$+ (a_R + b_R\sqrt{\delta_{cav}h^S}) \cdot [(\Delta_{solv}H^{A/S_R} - \Delta_{solv}H^{A/C_6H_{12}}) - (\delta_{cav}h^{S_R}$$
$$- \delta_{cav}h^{C_6H_{12}}) \cdot V_x^A]. \tag{9}$$

Here $\Delta_{solv}H^{A/S_R}$, $\Delta_{solv}H^{A/C_6H_{12}}$ are the solvation enthalpies of solute A in standard solvent S_R and in cyclohexane, respectively. $\delta_{cav}h^S$, $\delta_{cav}h^{S_R}$ and $\delta_{cav}h^{C_6H_{12}}$ are the specific relative cavity formation enthalpies for each solvent. The specific relative cavity formation enthalpy $\delta_{cav}h^S$ is the enthalpy of transfer of an alkane from imaginary solvent S_0, where the solution enthalpy of an alkane is zero ($\Delta_{soln}H^{C_nH_{2n+2}/S_0}$), to the solvent S, divided by alkane's characteristic volume $V_x^{C_nH_{2n+2}}$. Hence, the $\delta_{cav}h^S$ is given by:

$$\delta_{cav}h^S(10^{-2}\ kJ\ cm^{-3}) = \frac{\Delta_{soln}H^{C_nH_{2n+2}/S}(kJ\ mol^{-1})}{V_x^{C_nH_{2n+2}}(10^2\ cm^3\ mol^{-1})}. \tag{10}$$

Eq. (9) was verified on different solute–solvent systems [11,50]. For the determination of non-specific solvation enthalpy one should use benzene (a_R = 0.20, b_R = 0.38) as solvent S_R for proton acceptor solutes or carbon tetrachloride (a_R = 0.34, b_R = 0.61) for proton donor solutes.

One question arises about the quantity "solvophobic effect enthalpy". It was shown that the hydration enthalpy of alkanes and aromatic hydrocarbons includes the contribution of the hydrophobic effect [51], however, no dependence of this term on the characteristic volume was obtained. What is the magnitude of the solvophobic effect enthalpy in methanol? For answering this question we calculated the nonspecific solvation enthalpy of alkanes, aromatic hydrocarbons and their halogenated derivatives in methanol using Eq. (9). We compared calculated and experimental values of solvation enthalpies in methanol in Fig. 1. The experimental enthalpies of solvation and data needed for their calculation are presented in appendix (Table S1). One can see (Fig. 1), that between the values of solvation and non-specific solvation enthalpies a linear dependence with unit slope and zero intercept is obtained ($\Delta_{solv(nonsp)}H^{A/CH_3OH} = 1.0 \cdot \Delta_{solv}H^{A/CH_3OH}$, N = 41, SD = 1.3 kJ mol^{-1}, R = 0.997). This means that Eq. (4) for the enthalpy of solvation of alkanes, aromatic compounds and their halogenated derivatives in methanol includes only one term – the

enthalpy of non-specific solvation in methanol. Thus, the enthalpy of the solvophobic effect in methanol is close to zero.

See Supp Table S1 as supplementary file. Supplementary material related to this article found, in the online version, at doi:10.1016/j.tca.2012.02.005.

The specific interaction enthalpy of solute A in methanol can be derived from Eqs. (4) and (9) [11]:

$$\Delta_{int(sp)}H^{A/S} = \Delta_{soln}H^{A/S} - (\delta_{cav}h^S - \delta_{cav}h^{C_6H_{12}}) \cdot V_x^A$$
$$- \Delta_{soln}H^{A/C_6H_{12}} - (a_R + b_R \cdot \sqrt{\delta_{cav}h^S}) \cdot [(\Delta_{soln}H^{A/S_R}$$
$$- \Delta_{soln}H^{A/C_6H_{12}}) - (\delta_{cav}h^{S_R} - \delta_{cav}h^{C_6H_{12}}) \cdot V_x^A] \tag{11}$$

Eqs. (8) and (11) were used in present work to determine the enthalpy and Gibbs energy of specific interactions (hydrogen bonding) in methanol.

4. Results and discussion

The analysis of hydrogen bonding enthalpies and Gibbs energies of aliphatic and aromatic amines in methanol was performed. The enthalpies and Gibbs energies of solvation were obtained for this purpose. These values were determined through solution calorimetry and headspace gas chromatographic data.

4.1. Hydrogen bonding enthalpies of amines in methanol

The enthalpies of solvation of amines in methanol calculated using Eq. (3) are presented in Table 3. They were calculated using solution enthalpies, part of which were taken from literature, or otherwise measured in the current work (Table 1), and vaporization enthalpies. The solvation enthalpies of amines in benzene and cyclohexane required for the determination of specific interaction enthalpies are also collected in Table 3.

Benzene was used as the standard solvent S_R because carbon tetrachloride is capable to form donor–acceptor complexes with amines [55] and is therefore not suitable in this case. In Table 3, the characteristic volumes of amine molecules are also presented. The specific relative cavity formation enthalpies in benzene (5.02×10^2 kJ cm^{-3}), cyclohexane (1.42×10^2 kJ cm^{-3}) and methanol (5.1×10^2 kJ cm^{-3}) were taken from Ref. [56]. The calculated enthalpies of specific interaction of primary, secondary and tertiary aliphatic amines are presented in Table 4. This table also contains values of $\Delta_{int(sp)}H^{A/CH_3OH}$ for pyridine and its methyl derivatives.

The obtained enthalpies of specific interaction in methanol depend on the type of dissolved amine. Values of $\Delta_{int(sp)}H^{A/CH_3OH}$ for aliphatic amines are significantly larger than for pyridines. For the primary aliphatic amines with a butyl radical (n-butyl-, tert-butyl- and sec-butylamines) values are slightly larger than for secondary and tertiary aliphatic amines.

Specific interaction enthalpies of amines in methanol were compared with hydrogen bond enthalpies in equimolar complexes for these systems. The latter values measured by IR-spectroscopy in carbon tetrachloride or by solution calorimetry in pure base media were collected in Table 4. Some values of solution enthalpies of methanol in amines were measured in this work. Also, for the determination of hydrogen bonding enthalpies in methanol-in-amine systems using Eq. (11), the specific relative cavity formation enthalpies of some amines were calculated, which are also presented in Table 4. In this case, carbon tetrachloride is used as a standard solvent S_R. The enthalpies of solution of methanol in cyclohexane ($\Delta_{soln}H^{CH_3OH/C_6H_{12}}$ = 24.3 kJ mol^{-1}) and carbon tetrachloride ($\Delta_{soln}H^{CH_3OH/CCl_4}$ = 18.4 kJ mol^{-1}), and the characteristic volume of methanol ($V_x^{CH_3OH}$ = 0.3082 $\times$ 10^{-2} cm^3 mol^{-1}) were taken from Ref. [32]. The hydrogen bonding enthalpies of methanol

Table 3
Characteristic volumes (V_x^A) and vaporization enthalpy of amines ($\Delta_{vap}H^A$)[a], the solvation enthalpies of amines in methanol ($\Delta_{solv}H^{A/CH_3OH}$)[b], cyclohexane ($\Delta_{solv}H^{A/C_6H_{12}}$)[b] and benzene ($\Delta_{solv}H^{A/C_6H_6}$)[b] at $T = 298.15$ K.

Substance (A)	$V_x^A \times 10^{-2}$ (cm³ mol⁻¹)	$\Delta_{vap}H^A$ (kJ mol⁻¹)	$\Delta_{solv}H^{A/CH_3OH}$ (kJ mol⁻¹)	$\Delta_{solv}H^{A/C_6H_{12}}$ (kJ mol⁻¹)	$\Delta_{solv}H^{A/C_6H_6}$ (kJ mol⁻¹)
n-Butylamine	0.7720	35.6	−51.4[d]	−29.1[d]	−32.7[d]
sec-Butylamine	0.7720	32.6	−49.5[d]	−26.7[d]	−31.1[d]
$tert$-Butylamine	0.7720	30.5	−49.5[e]	−25.4[d]	−29.2[d]
n-Hexylamine	1.0538	45.0	−59.5[d]	−38.6[d]	−42.7[d]
Cyclohexylamine	0.9452	42.8	−57.7[d]	−37.8[d]	−40.8[d]
Diethylamine	0.7720	32.7	−49.0[d]	−29.2[d]	−31.8[d]
Di-n-propylamine	1.0538	41.6[c]	−56.8[d]	−38.2[d]	−39.8[d]
Di-n-butylamine	1.3356	49.5	−63.3[d]	−46.5[d]	−47.0[d]
Triethylamine	1.0538	35.4	−48.4[e]	−34.3[e]	−33.3[e]
Tri-n-propylamine	1.4765	46.2	−54.5[f]	−44.5[f]	−41.5[f]
Pyridine	0.6753	40.5	−44.6[g]	−32.3[g]	−40.5[g]
2-Methylpyridine	0.8162	42.5	−50.1[f]	−35.9[f]	−43.0[f]
3-Methylpyridine	0.8162	44.5	−49.8[f]	−36.1[f]	−44.1[f]
4-Methylpyridine	0.8162	44.9	−50.0[h]	−37.1[d]	−45.0[d]
2,6-Dimethylpyridine	0.9571	46.1	−53.5[h]	−40.6[i]	−45.7[i]

[a] Ref. [52].
[b] The solvation enthalpies were calculated using Eq. (2).
[c] Vaporization enthalpy calculated in this work.
[d] Values measured in this work.
[e] Ref. [36].
[f] Ref. [32].
[g] Ref. [28].
[h] Ref. [53].
[i] Ref. [54].

in amine also depend on the structure of amines (Table 4). Among amines with one type of substituents (n-, di- or trialkyl radicals) hydrogen bonding enthalpies decrease with increasing alkyl radical length (Table 4). Hydrogen bonding enthalpies for aromatic amines are smaller than for aliphatic amines. It is also clear from Table 4 that values of $\Delta_{HB}H^{CH_3OH/A}$ are significantly larger than enthalpies of specific interaction ($\Delta_{int(sp)}H^{A/CH_3OH}$) in methanol media. This fact can be explained by reorganization of solvent. The dissolution of solute molecules in self-associated solvents leads to the breaking of a part of the solvent–solvent hydrogen bonds and the equilibrium shift between the associative species of methanol. Consequently, thermodynamic data for complexes 1:1 cannot be used for quantitative characterization of specific interaction of solute with neat associated solvent.

Aliphatic amines dissolved in methanol can principally form two types of hydrogen bonds. The first one is a N—H···O hydrogen bond, where amine interacts as a proton donor, and the second

one is an O—H···N hydrogen bond, where amine interacts as a proton acceptor. Interactions of the second type predominate in the case of hydrogen bonding in neat methanol. The enthalpies of specific interaction of primary amines in methanol would be greater than for the secondary amines if amine acted as a proton donor, but the values are practically equal (Table 4). It can also be seen from Table 4 that the difference between enthalpies of specific interaction of triethylamine and primary amines in methanol is less than 3 kJ mol⁻¹. Consequently, N—H···O hydrogen bonds are not formed in methanol solutions or their enthalpy of formation is lower than 3 kJ mol⁻¹. Similar conclusions can be found in literature [57].

4.2. Hydrogen bonding Gibbs energies of amines in methanol

Measured data on the solvation Gibbs energies in methanol, benzene and n-hexadecane, along with literature data, were used to calculate the Gibbs energies of specific interaction of amines with

Table 4
Specific cavity formation enthalpies in amines ($\delta_{cav}h^S$), the enthalpies of specific interaction of amines in methanol ($\Delta_{int(sp)}H^{A/CH_3OH}$) and the hydrogen bonding enthalpies for amine–methanol complexes ($\Delta_{HB}H^{CH_3OH/A}$).

Substance (A)	$\Delta_{int(sp)}H^{A/CH_3OH}$ (kJ mol⁻¹)	$\delta_{cav}h^S \times 10^2$ (kJ cm⁻³)	$\Delta_{HB}H^{CH_3OH/A}$ (kJ mol⁻¹)
n-Butylamine	−18.4[a]	4.05[a]	−27.3[a]
sec-Butylamine	−18.1[a]	5.06[a]	−26.7[a]
$tert$-Butylamine	−19.9[a]	5.40[a]	−26.9[a]
n-Hexylamine	−16.5[a]	2.53[a]	−27.8[a]
Cyclohexylamine	−16.7[a]	3.87[a]	−27.3[a]
Diethylamine	−16.9[a]	3.39[a]	−27.3[a]
Di-n-propylamine	−16.8[a]	1.80[a]	−25.9[a]
Di-n-butylamine	−16.1[a]	0.65[a]	−26.1[a]
Triethylamine	−15.6[b]	0.43[e]	−24.2[b]
Tri-n-propylamine	−12.8[c]	0.02[c]	−22.7[c]
Pyridine	−3.6[d]	6.66[e]	−16.2[d]
2-Methylpyridine	−6.6[c]	4.66[c]	−19.0[c]
3-Methylpyridine	−5.2[c]	4.96[c]	−17.9[c]
4-Methylpyridine	−4.4[a]	4.58[a]	−18.3[c]
2,6-Dimethylpyridine	−7.5[a]		−21.0[f]

[a] Obtained in this work.
[b] Ref. [36].
[c] Ref. [32].
[d] Ref. [28].
[e] Ref. [11].
[f] Ref. [16].

Table 5

The Gibbs energies of solvation of amines in methanol ($\Delta_{solv}G^{A/CH_3OH}$), n-hexadecane ($\Delta_{solv}G^{A/n-C_6H_{34}}$) and benzene ($\Delta_{solv}G^{A/C_6H_6}$); the solvophobic effect Gibbs energy of amines ($\Delta_{s.e.}G^{A/CH_3OH}$); the Gibbs energies of specific interaction of amines in methanol ($\Delta_{int(sp)}G^{A/CH_3OH}$), specific relative cavity formation Gibbs energies in amines ($\delta_{cav}g^S$) and the Gibbs energies of complexes methanol–amine ($\Delta_{HB}G^{CH_3OH/A}$).

Substance(A)	$\Delta_{solv}G^{A/CH_3OH}$ (kJ mol^{-1})	$\Delta_{solv}G^{A/n-C_6H_{34}}$ (kJ mol^{-1})	$\Delta_{solv}G^{A/C_6H_6}$ (kJ mol^{-1})	$\Delta_{s.e.}G^{A/CH_3OH}$ (kJ mol^{-1})	$\Delta_{int(sp)}G^{A/CH_3OH}$ (kJ mol^{-1})	$\Delta_{HB}G^{CH_3OH/A}$ (kJ mol^{-1})	$\delta_{cav}g^S \times 10^2$ (kJ cm^{-3})
n-Butylamine	−7.1[a]	−3.9[c]	−3.6[c]	4.2	−8.1	−10.5	6.05
sec-Butylamine	−4.3[a]	−3.3[a]	−1.4[a]	4.2	−8.0	−10.3	6.38
$tert$-Butylamine	−4.3[a]	−3.3[c]	−1.2[a]	4.2	−8.2	−11.0	6.29
n-Hexylamine	−4.5[a]	−9.3[c]	−4.1[a]	5.7	−7.9	−10.7	2.18
Cyclohexylamine	−6.8[a]	−9.4[c]	−6.1[a]	5.1	−7.1	−10.9	2.57
Diethylamine	−5.1[a]	−2.7[c]	−2.7[c]	4.2	−7.0	−10.0	1.81
Di-n-propylamine	−9.2[a]	−8.3[c]	−8.0[a]	5.7	−7.4	−9.1	2.70
Triethylamine	−6.0[b]	−6.6[c]	−5.8[a]	5.7	−6.6	−10.5[c]	-
Tri-n-propylamine	−10.7[a]	−15.6[c]	−14.2[a]	7.9	−5.4	−10.5[d]	-
Pyridine	−8.4[a]	−6.2[c]	−8.0[c]	3.7	−4.0	−8.7	4.50
2-Methylpyridine	−11.1[a]	−8.5[c]	−10.6[c]	4.5	−4.8	−8.7	2.83
3-Methylpyridine	−12.4[a]	−9.7[c]	−12.0[a]	4.5	−4.6	−9.1	3.60
4-Methylpyridine	−12.1[a]	−9.8[c]	−11.9[c]	4.5	−4.5	−8.9	4.54
2,6-Dimethylpyridine	−12.3[a]	−10.5[c]	−12.7[c]	5.2	−4.7	−9.5	2.02

[a] Values obtained in this work.
[b] Ref. [58].
[c] Ref. [59].
[d] Value calculated using Abraham correlation relationships for 1:1 complexes in carbon tetrachloride medium [25].

methanol (Table 2 and Table 6). The last values were obtained using Eq. (8). Benzene was used as a standard solvent S_R ($\delta_{cav}g^{S_R} = 1.7 \times 10^{-2}$ kJ cm^{-3}; $a = 0$ and $b = 0.78$). n-Hexadecane was taken as a standard solvent S_0 since it can not interact specifically (H-bond formation) with solutes and hundreds of solvation Gibbs energy values for various solutes can be calculated from the available data on Ostwald solubility coefficient L^{16}. Specific relative cavity formation Gibbs energies of n-hexadecane (S_0) ($\delta_{cav}g^{S_0} = 0.0 \times 10^{-2}$ kJ cm^{-3} [48]) and methanol ($\delta_{cav}g^{CH_3OH} = 2.6 \times 10^{-2}$ kJ cm^{-3} [33]) were used for calculations. The calculated Gibbs energies of specific interaction of amines in methanol are presented in Table 5.

It can be seen from Table 5 that Gibbs energies of specific interaction of aliphatic amines in methanol are practically equal: the average value of $\Delta_{int(sp)}G^{A/CH_3OH}$ is about -7.5 ± 0.6 kJ mol^{-1} for all studied amines. Gibbs energies of specific interaction for pyridines are less negative and lay in a range of -4.5 ± 0.2 kJ mol^{-1}. Analogously with enthalpies, Gibbs energies of specific interaction in methanol environment were compared with the Gibbs energies for complexes amine–methanol of 1:1 stoichiometry. Eqs. (4) ($\Delta_{s.e.}G^{A/S} = 0$) and (5) were applied for determination of $\Delta_{HB}H^{CH_3OH/A}$ values. Carbon tetrachloride was used as a standard solvent S_R ($\delta_{cav}g^{S_R} = 0.8 \times 10^{-2}$ kJ cm^{-3}; $a = 0$ and $b = 1.12$ [60]). The Gibbs energy of solvation of methanol in carbon tetrachloride is $\Delta_{solv}G^{CH_3OH/CCl_4} = 4.3$ kJ mol^{-1} [60], and the solvation Gibbs energy of methanol in n-hexadecane is $\Delta_{solv}G^{CH_3OH/C_{16}H_{34}} = 5.5$ kJ mol^{-1} [60]. The calculated values are presented in Table 5. It is evident from Table 5 that the difference between Gibbs energies of specific interaction of amines in methanol and Gibbs energies of hydrogen bonding for methanol–amine complexation is about 2.8 kJ mol^{-1} for aliphatic amines and about 4.3 kJ mol^{-1} for pyridines. This difference can be ascribed to the breaking of methanol–methanol hydrogen bonds during amine dissolution (endothermic term) and also to the cooperative strengthening of hydrogen bonding of solutes with methanol clusters (exothermic term). We have found, using Eq. (8), that the contribution of solvent–solvent hydrogen bond reorganization in methanol solution is about 11.4 kJ mol^{-1}. So, if the difference between Gibbs energies of hydrogen bonding in methanol and amine environment was only due to reorganization effect, the values of specific interaction Gibbs energies of amines in methanol would be about zero or positive. Consequently, the cooperative effect has a great impact on the Gibbs energies of specific interaction of amines in methanol.

Gibbs energies of specific interaction of amines in methanol with the same data for water solutions, obtained in Ref. [59] were also compared. The Gibbs energies of hydrogen bonding for equimolar complexes 1:1 in methanol–amine systems (-9.8 ± 0.8 kJ mol^{-1}) and water–amine (averaged -9.6 ± 0.5 kJ mol^{-1} [59]) have quite similar values. Consequently, the proton-donating ability of free water and methanol molecules in the absence of self-association is approximately equal. At the same time, the Gibbs energies of specific interaction of amines with neat water (-13.3 ± 0.5 kJ mol^{-1} for pyridines and -18.8 ± 0.5 kJ mol^{-1} for aliphatic amines [59]) are much increased comparing with data for methanol (Table 5). Consequently, cooperative effects have a significantly greater influence on the solvation Gibbs energy of amines in water medium than in methanol. Similar conclusions were obtained in Ref. [61]. Authors have shown that the co-operative nature of hydrogen bonds and the propensity of water to association are the main factors that determine the properties of aqueous systems [61]. Obtained results prove that the thermodynamics of hydrogen bonding in inert or aprotic solvents differs significantly from the thermodynamics of specific interaction in self-associated through hydrogen bonds liquids.

4.3. Validation of enthalpies and Gibbs energies of specific interactions of amines with neat methanol

Data obtained in this work on Gibbs energies and enthalpies of specific interaction of amine with neat methanol are novel. We therefore decided to validate them using another method. The values of $\Delta_{int(sp)}G^{A/CH_3OH}$ and $\Delta_{int(sp)}H^{A/CH_3OH}$ can also be estimated by the "non hydrogen bonding baseline" (NHBB) method, proposed in Ref. [62]. For this purpose one must find a model M structurally suitable to the studied molecule, A. In the case of Gibbs energy, model M should have the same value of the solvophobic effect energy. Thus, one should take the enthalpies (or Gibbs energies) of solvation of A and M in series of non-hydrogen bonded solvents (S_i). The difference between enthalpies (or Gibbs energies) of solvation of studied solute A and its model M in these solvents (S_i) ($\Delta_{solv}f^{A/S_i} - \Delta_{solv}f^{M/S_i}$) should be linear by related with solvents π^*-parameter [63]. The deviation of ($\Delta_{solv}f^{A/S_i} - \Delta_{solv}f^{M/S_i}$) from the "non-hydrogen-bonding baseline" is supposed to be the enthalpy (or Gibbs energy) of specific interaction of solute A with the studied solvent. Let us consider the determination of $\Delta_{int(sp)}H^{A/ROH}$ of n-butylamine in methanol. The molecule of n-pentane was taken as a model compound for n-butylamine.

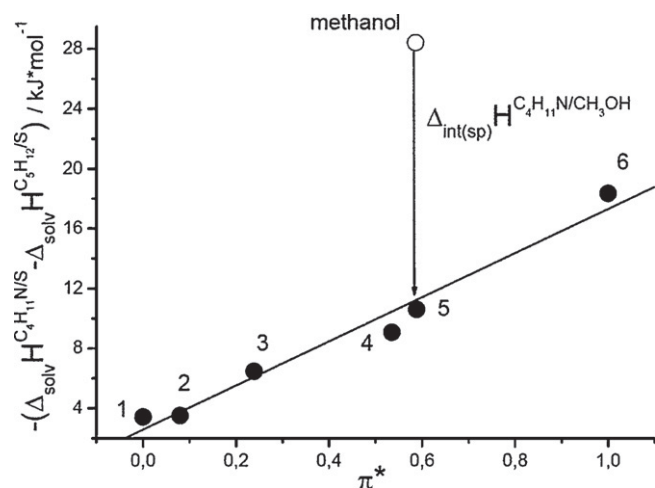**Fig. 2.** Application of NHBB method to the determination of the enthalpy of specific interaction of n-butylamine in methanol (model compound is n-pentane): 1 – cyclohexane, 2 – n-hexadecane, 3 – butyl ether, 4 – toluene, 5 – benzene, 6 – dimethylsulfoxide.

Both of them are acyclic substances and have similar characteristic volumes. A plot of $\Delta_{solv}H^{C_4H_{11}N/S_i} - \Delta_{solv}H^{C_5H_{12}/S_i}$ (experimental values of solution enthalpies were taken from [64–68], enthalpy of vaporization of n-pentane is -26.7 kJ mol^{-1} [52]) versus π^*-parameter is shown in Fig. 2.

The linearity in Fig. 2 is described by equation $-(\Delta_{solv}H^{C_4H_{11}N/S_i} - \Delta_{solv}H^{C_5H_{12}/S_i}) = 2.6 + 14.7 \cdot \pi^* (R = 0.986, SD = 1.0$ kJ mol^{-1}). The enthalpy of specific interaction of n-butylamine in methanol (-17.3 kJ mol^{-1}) obtained by NHBB method corresponds to the value calculated by Eq. (11) (-18.4 kJ mol^{-1}).

For estimating the Gibbs energy of specific interaction in methanol we chose triethylamine (model molecule – n-heptane). The values of solvation Gibbs energies of triethylamine and n-heptane were taken from [58,59,69–71]. A plot of the difference between Gibbs energies of triethylamine and n-heptane in series of solvents versus π^*-parameters of solvents is presented in Fig. 3. The obtained linear dependence
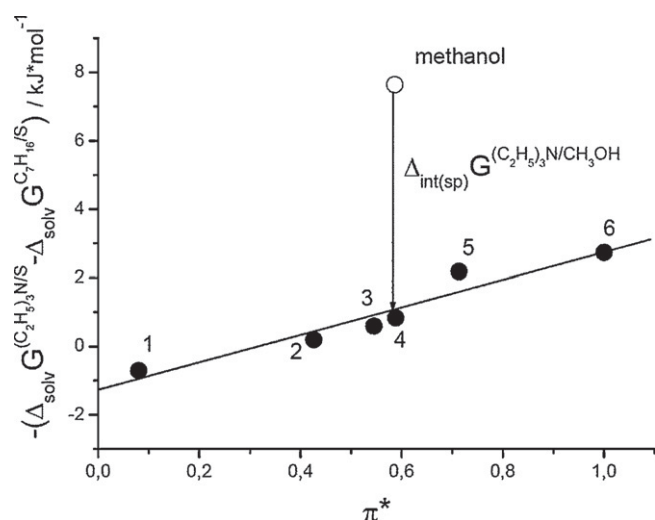

Fig. 3. Application of NHBB method to the determination of the Gibbs energy of specific interaction of triethylamine in methanol (model compound is n-heptane): 1 – n-hexadecane, 2 – p-xylene, 3 – ethyl acetate, 4 – benzene, 5 – acetonitrile, 6 – dimethylsulfoxide.
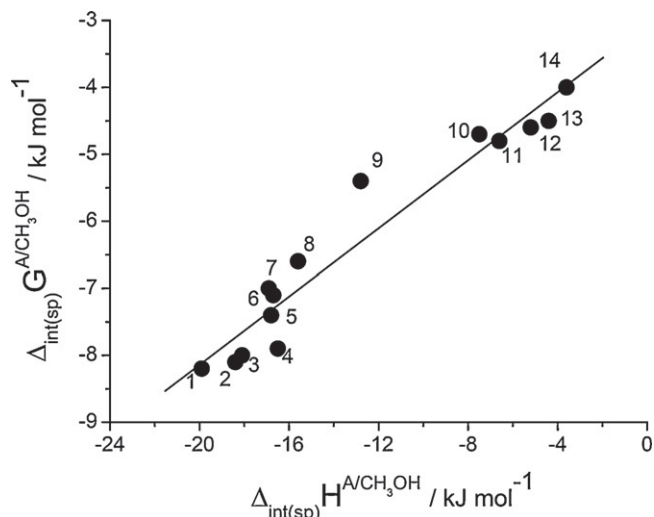

Fig. 4. Enthalpy-energy plot for the process of specific interaction of amines in methanol: 1 – tert-butylamine, 2 – n-butylamine, 3 – sec-butylamine, 4 – n-hexylamine, 5 – di-n-propylamine, 6 – diethylamine, 7 – cyclohexylamine, 8 – triethylamine, 9 – tri-n-propylamine, 10 – 2,6-dimethylpyridine, 11 – 2-methylpyridine, 12 – 3-methylpyridine, 13 – 4-methylpyridine, 14 – pyridine.

is described by equation $-(\Delta_{solv}G^{(C_2H_5)_3N/S_i} - \Delta_{solv}G^{n-C_7H_{16}/S_i}) = -1.3 + 4 \cdot \pi^* (R = 0.960, SD = 0.4$ kJ mol^{-1}).

The value of $\Delta_{int(sp)}G^{(C_2H_5)_3N/CH_3OH}$ obtained from NHBB method is -6.6 ± 0.4 kJ mol^{-1} which coincides with Gibbs energy calculated using Eq. (8) (-6.6 kJ mol^{-1}).

4.4. Isoequilibrium relation. Hydrogen bonding entropy of amines in methanol

The isoequilibrium relationship was obtained using the enthalpies and Gibbs energies of specific interaction of amines in methanol. Earlier existence of linearity between enthalpy and Gibbs energy was shown for the thermodynamic functions of solvation [72]. The enthalpy–energy relation is shown in Fig. 4. Its parameters are $\Delta_{int(sp)}G^{A/CH_3OH} = 0.3\Delta_{int(sp)}H^{A/CH_3OH} - 3.1$, $N = 14$, $SD = 0.4$ kJ mol^{-1}, $R = 0.967$. The intercept in this equation reflects an entropy term in the hydrogen bonding process. Consequently, entropy plays an important role in the specific interaction process of solute with self-associated by hydrogen bonds methanol.

The values of entropies of specific interaction of amines in methanol were found using Eq. (12):

$$\Delta S = \frac{\Delta H - \Delta G}{T} \qquad (12)$$

Table 6
The entropies of specific interaction of amines in methanol and "amine–methanol" complexation.

Substance (A)	$\Delta_{int(sp)}S^{A/CH_3OH}$(J mol^{-1} K^{-1})	$\Delta_{HB}S^{CH_3OH/A}$(J mol^{-1} K^{-1})
n-Butylamine	−34.6	−56.4
sec-Butylamine	−33.9	−54.7
tert-Butylamine	−39.3	−53.3
n-Hexylamine	−28.9	−57.4
Cyclohexylamine	−32.2	−55.0
Diethylamine	−33.2	−57.9
Di-n-propylamine	−31.5	−58.5
Triethylamine	−30.2	−46.3
Tri-n-propylamine	−27.2	−40.9
Pyridine	1.3	−25.2
2-Methylpyridine	−6.0	−34.6
3-Methylpyridine	−2.0	−29.5
4-Methylpyridine	0.3	−31.5

We also determined the entropies of hydrogen bonding for complexation of methanol in amine. Values of $\Delta_{int(sp)}G^{A/CH_3OH}$ and $\Delta_{HB}S^{CH_3OH/A}$ are shown in Table 6.

It is seen from Table 6 that the entropies of specific interaction in methanol are less negative than for hydrogen bonding in complexes 1:1. In two cases entropies of specific interactions of amines in methanol are close to zero or positive. Dissolution of solutes in associated solvent methanol causes the disruption of the associated chain of hydrogen bonds and leads to the increase in the amount of smaller species in solution. This process explains the increase in the entropy of hydrogen bonding process.

5. Conclusion

In the present work an investigation of the specific interactions of strong bases (primary, secondary and tertiary amines, pyridines) with methanol was carried out. The experimental values of enthalpies of solution and Gibbs energies of solvation were measured using solution calorimetry and headspace gas chromatography. The calculated specific interaction enthalpies and Gibbs energies were analyzed in terms of influence of amines' structure. They were also compared with the enthalpies and Gibbs energies of hydrogen bonding in equimolar "methanol–amine"complexes. The difference in their magnitudes is ascribed to the reorganization of methanol associates. The contribution of cooperativity to the Gibbs energies of specific interaction of amines in methanol is also demonstrated, but its value is significantly smaller than in water. A linear relationship is observed between the Gibbs energies and enthalpies of specific interaction. The entropies of specific interaction of amines in methanol were estimated. It was shown that $\Delta_{int(sp)}S^{A/CH_3OH}$ can be positive. Such behavior is observed due to the breaking of part of methanol associates.The results obtained give a correct view on the thermodynamics of hydrogen bond formation of amines with aliphatic alcohols. They show that the specific interactions in the self-associated solvents can not be quantitatively described using thermodynamic functions of hydrogen bonding in the 1:1 complexes formed in aprotic solvents.

Acknowledgment

References

[1] D.H. Williams, E. Stephens, D.P. O'Brian, M. Zhou, Understanding noncovalent interactions: ligand binding energy and catalytic efficiency from ligand-induced reductions in motion within receptors and enzymes, Angew. Chem. Int. Ed. Engl. 43 (2004) 6596–6616.

[2] G.A. Jeffrey, W. Saenger, Hydrogen Bonding in Biological Structures, Springer-Verlag, New York, 1991.

[3] W.W. Cleland, M.M. Kreevoy, Low-barrier hydrogen bonds and enzymic catalysis, Science 264 (1994) 1887–1890.

[4] N.M. Luscombe, R.A. Laskowski, J.M. Thornton, Amino acid–base interactions: a three-dimensional analysis of protein–DNA interactions at an atomic level, Nucleic Acids Res. 29 (2001) 2860–2874.

[5] L.J. Prins, D.N. Reinhoudt, P. Timmerman, Noncovalent synthesis using hydrogen bonding, Angew. Chem. Int. Ed. Engl. 40 (2001) 2382–2426.

[6] T. Steiner, The hydrogen bond in the solid state, Angew. Chem. Int. Ed. 41 (2002) 48–76;
A. Karpfen, Cooperative effects in hydrogen bonding, Adv. Chem. Phys. 123 (2002) 469–510.

[7] V.A. Durov, I.Yu. Shilov, Supramolecular structure and physicochemical properties of the mixture tetrachloromethane–methanol, J. Mol. Liq. 92 (2001) 165–184.

[8] R.A. Provencal, J.B. Paul, K. Roth, C. Chapo, R.N. Casaes, R.J. Saykally, G.S. Tschumper, H.F. Schaefer III, Infrared cavity ringdown spectroscopy of methanol clusters: single donor hydrogen bonding, J. Chem. Phys. 110 (1999) 4258–4267.

[9] J.Q. Deng, R.H. Lipson, NMR study of hydrogen bonding in methanol – carbon tetrachloride solutions, Can. J. Chem. 84 (2006) 886–892.

[10] K. Ohno, T. Shimoaka, N. Akai, Y. Katsumoto, Relationship between the broad OH stretching band of methanol and hydrogen-bonding patterns in the liquid phase, J. Phys. Chem. A 112 (2008) 7342–7348.

[11] B.N. Solomonov, V.B. Novikov, M.A. Varfolomeev, N.M. Mileshko, A new method for the extraction of specific interaction enthalpy from the enthalpy of solvation, J. Phys. Org. Chem. 18 (2005) 49–61.

[12] J.A. González, I. Mozo, I. García De La Fuente, J.C. Cobos, V.A. Durov, Thermodynamics of 1-alkanol + cyclic ether mixtures, Fluid Phase Equilib. 245 (2006) 168–184.

[13] W. Marczak, A. Heintz, M. Bucek, Calorimetric investigations of hydrogen bonding in binary mixtures containing pyridine and its methyl-substituted derivatives. II. The dilute solutions of methanol and 2-methyl-2-propanol, J. Chem. Thermodyn. 36 (2004) 575–582.

[14] N. Deenadayalu, T.M. Letcher, Application of the extended real associated solution theory to excess molar enthalpies and excess molar volumes of binary mixtures of (benzene or 1-alkanol + quinoline), J. Mol. Liq. 121 (2005) 143–147;
W. Marczak, A. Chowanska, B. Piwowarska, Acoustic and volumetric studies of intermolecular interactions in dilute solutions of methanol in aromatic amines, J. Phys. IV France. 129 (2005) 69–71;
T.M. Letcher, B.C. Bricknell, Calorimetric investigation of the interactions of some hydrogen-bonded systems at 298.15 K, J. Chem. Eng. Data 41 (1996) 166–169;
M. Reis, L. Moreira, N. Nunes, R. Leitão, F. Martins, Solution enthalpies of hydroxylic compounds Study of solvent effects through quantitative structure property relationships, J. Therm. Anal. Calorim. (2011), doi:10.1007/s10973-011-1975-x;
F. Martins, N. Nunes, M.L. Moita, R.E. Leitão, Solution enthalpies of 1-bromoadamantane in monoalcohols at 298.15 K, Thermochim. Acta 444 (2006) 83–85.

[15] E. Bich, M. Dzida, T. Vasiltsova, A. Heintz, Experimental and theoretical study of thermodynamic excess properties of associating liquid alkanol + 4-picoline mixtures based on quantum mechanical ab initio calculations, J. Mol. Liq. 136 (2007) 94–103.

[16] M. Joesten, L. Schaad, Hydrogen Bonding, Marcel Dekker, New York, 1974.

[17] H. Kleeberg, D. Klein, W.A.P. Luck, Quantitative infrared spectroscopic investigations of hydrogen-bond cooperativity, J. Phys. Chem. 91 (1987) 3200–3203.

[18] E. Kamieńska-Piotrowicz, K. Dziewulska, J. Stangret, An effective method for studying intermolecular interactions in binary liquids with hydrogen bonds; FTIR spectra and ab initio calculations in the N-methylformamide-methanol system, J. Phys. Chem. B 114 (2010) 5810–5818;
N. Borho, M.A. Suhm, K. Le Barbu-Debus, A. Zehnacker, Intra- vs. intermolecular hydrogen bonding: dimers of alpha-hydroxyesters with methanol, Phys. Chem. Chem. Phys. 8 (2006) 4449–4460.

[19] J.S. Lomas, F. Maurel, Water and alcohol(s): what's the difference? A proton NMR and DFT study of hetero-association with pyridine, J. Phys. Org. Chem. 21 (2008) 464–471;
J.S. Lomas, F. Maurel, A. Adenier, 1H NMR study of the hetero-association of non-symmetrical diols with pyridine; GIAO/DFT calculations on diols, J. Phys. Org. Chem. 24 (2011) 798–808.

[20] S. Villa, N. Riesco, I. García De La Fuente, J.A. González, J.C. Cobos, Thermodynamics of mixtures with strongly negative deviations from Raoult's law. Part 8. Excess molar volumes at 298.15 K for 1-alkanol + isomeric amine ($C_6H_{15}N$) systems: characterization in terms of the ERAS model, Fluid Phase Equilib. 216 (2004) 123–133.

[21] H. Ratajczak, W.J. Orville Thomas, C.N.R. Rao, Charge transfer theory of hydrogen bonds: relations between vibrational spectra and energy of hydrogen bonds, Chem. Phys. 17 (1976) 197–216.

[22] A.V. Iogansen, Direct proportionality of the hydrogen bonding energy and the intensification of the stretching ν (XH) vibration in infrared spectra, Spectrochim. Acta A 55 (1999) 1585–1612.

[23] R.M. Badger, S.H. Bauer, Spectroscopic studies of the hydrogen bond. II. The shift of the O—H vibrational frequency in the formation of the hydrogen bond, J. Chem. Phys. 5 (1937) 839–851.

[24] O.A. Raevsky, V.Yu. Grigor'ev, D.B. Kireev, N.S. Zefirov, Complete thermodynamic description of H-bonding in the framework of multiplicative approach, Quant. Struct.–Act. Relat. 11 (1992) 49–63.

[25] M.H. Abraham, P.L. Grellier, D.V. Prior, P.P. Duce, J.J. Morris, P.J. Taylor, 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 6 (1989) 699–711.

[26] J.L. Cook, C.A. Hunter, C.M.R. Low, A. Perez-Velasco, J.G. Vinter, Solvent effects on hydrogen bonding, Angew. Chem. Int. Ed. 46 (2007) 3706–3709.

[27] C.A. Hunter, Quantifying intermolecular interactions: guidelines for the molecular recognition toolbox, Angew. Chem. Int. Ed. 43 (2004) 5310–5324.

[28] B.N. Solomonov, M.A. Varfolomeev, V.B. Novikov, A new method for the determination of cooperative hydrogen bonding enthalpy of proton acceptors with associated species of alcohols, J. Phys. Org. Chem. 19 (2006) 263–268.

[29] E.E. Tucker, S.D. Christian, Hydrogen bond cooperativity. The methanol-tri-n-octylamine system in n-hexadecane, J. Am. Chem. Soc. 97 (1975) 1269–1271;
E.E. Tucker, S.D. Christian, Suprabinary hydrogen bonded complexes. The methanol-N,N-diethyldodecanamide system in n-hexadecane, J. Phys. Chem. 79 (1975) 2484–2488.

[30] M.D. Borisover, B.N. Solomonov, A.I. Konovalov, Analysis of enthalpies of specific interaction of non-electrolytes in associated solvents, Russ. J. Gen. Chem. 61 (1991) 329–337.

[31] M.C.R. Symons, V.K. Thomas, N.J. Fletcher, N.G. Pay, Infrared and proton magnetic resonance studies of the structures of methanol + aprotic solvent systems, J. Chem. Soc. Faraday Trans. 1 77 (1981) 1899–1911;
M.C.R. Symons, H.L. Robinson, A near infrared and NMR spectroscopic study of the solvation of basic aprotic solvents and anions in tert-butanol, Phys. Chem. Chem. Phys. 3 (2001) 535–541.

[32] K.V. Zaitseva, M.A. Varfolomeev, V.B. Novikov, B.N. Solomonov, Enthalpy of cooperative hydrogen bonding in complexes of tertiary amines with aliphatic alcohols: calorimetric study, J. Chem. Thermodyn. 43 (2011) 1083–1090.

[33] I.A. Sedov, M.A. Stolov, B.N. Solomonov, Solvophobic effects and relationships between the Gibbs energy and enthalpy for the solvation process, J. Phys. Org. Chem. 24 (2011) 1088–1094.

[34] P. Ruelle, U.W. Kesselring, The hydrophobic effect. 1. A consequence of the mobile order in H-bonded liquids, J. Pharm. Sci. 87 (1998) 987–997.

[35] N.T. Southall, K.A. Dill, A.D.J. Haymet, A view of the hydrophobic effect, J. Phys. Chem. B 106 (2002) 521–533.

[36] M.A. Varfolomeev, I.T. Rakipov, B.N. Solomonov, Enthalpy of cooperative hydrogen bonding in the complexes of triethyl- and tri-n-butylamines with alcohols: effect of the alkyl chain length, Russ. J. Gen. Chem. 80 (2010) 402–407.

[37] D.D. Perrin, W.L.F. Armarego, D.R. Perrin, Purification of Laboratory Chemicals, second ed., Pergamon Press, Oxford, 1980.

[38] M.A. Varfolomeev, D.I. Abaidullina, B.N. Solomonov, S.P. Verevkin, V.N. Emel'Yanenko, Pairwise substitution effects, inter- and intramolecular hydrogen bonds in methoxyphenols and dimethoxybenzenes. Thermochemistry, calorimetry, and first-principles calculations, J. Phys. Chem. B 114 (2010) 16503–16516.

[39] A.V. Kustov, O.A. Antonova, V.P. Korolev, Enthalpies of 1,4-dioxane, 1,2 dimethoxyethane, and ethylacetate solvation in the water-1-propanol and water-glycerol binary mixtures, J. Solut. Chem. 31 (2002) 671–680.

[40] M. Woldan, Enthalpy of solution of some electrolytes in water–acetamide mixtures at 313.15 K, Thermochim. Acta 105 (1986) 41–49.

[41] R. Sabbah, X.W. An, J.S. Chickos, M.L.P. Leitao, M.V. Roux, L.A. Torres, Reference materials for calorimetry and differential thermal analysis, Thermochim. Acta 331 (1999) 93–204.

[42] G.T. Armstrong, D. Garvin, M.V. Kilday, Standard Reference Material 1655, Potassium Chloride KCl(cr) for Solution Calorimetry, National Bureau of Standards Certificate, Washington, 1981.

[43] V.V. Gorbatchuk, A.G. Tsifarkin, I.S. Antipin, B.N. Solomonov, A.I. Konovalov, J. Seidel, F.D. Baitalov, Thermodynamic comparison of molecular recognition of vaporous guests by solid calixarene and diol hosts, J. Chem. Soc. Perkin Trans. 2 11 (2000) 2287–2294.

[44] EPI Suite, Version 3.20 2007, US Environment Protection Agency, http://www.epa.gov/oppt/exposure/pubs/episuite.htm, 27.10.2011.

[45] M.H. Abraham, P.L. Grellier, J. Mana, Limiting activity coefficients of triethylamine in 30 solvents by a simple gas-liquid chromatographic method, J. Chem. Thermodyn. 6 (1974) 1175–1179.

[46] E.R. Thomas, B.A. Newman, G.L. Nicolaides, C.A. Eckert, Limiting activity coefficients from differential ebulliometry, J. Chem. Eng. Data 27 (1982) 233–240.

[47] M.D. Borisover, F.D. Baitalov, B.N. Solomonov, Evaluation of the contribution to hydration of nonelectrolytes from the hydrophobic effect, J. Solut. Chem. 24 (1995) 579–586.

[48] B.N. Solomonov, I.A. Sedov, The hydrophobic effect Gibbs energy, J. Mol. Liq. 139 (2008) 89–97.

[49] M.H. Abraham, J.C. McGowan, The use of characteristic volumes to measure cavity terms in reversed phase liquid chromatography, Chromatographia 23 (1987) 243–246.

[50] N. Nunes, L. Moreira, R.E. Leitao, F. Martins, Determination of solvation and specific interaction enthalpies of adamantane derivatives in aprotic solvents, J. Chem. Thermodyn. 39 (2007) 1201–1205.

[51] B.N. Solomonov, I.A. Sedov, M.A. Varfolomeev, A method for calculating the enthalpy of hydrophobic effect, Russ. J. Phys. Chem. 80 (2006) 659–662.

[52] W. Acree Jr., J.S. Chickos, Phase transition enthalpy measurements of organic and organometallic compounds. sublimation, vaporization and fusion enthalpies from 1880 to 2010, J. Phys. Chem. Ref. Data 39 (2010), art. no 043101.

[53] C.H. Rochester, J.A. Waters, Thermodynamic study of the transfer of pyridines from the gas phase to solution in methanol, J. Chem. Soc. Faraday Trans. 1 78 (1982) 631–640.

[54] I. Uruska, H. Inerowicz, Calorimetric investigations of the solvent effect on complex formation between pyridine derivatives and molecular iodine, J. Solut. Chem. 9 (1980) 97–108.

[55] R.S. Drago, L.B. Parr, C.S. Chamberlain, Solvent effects and their relationship to the E and C equation, J. Am. Chem. Soc. 99 (1977) 3203–3210.

[56] B.N. Solomonov, V.B. Novikov, M.A. Varfolomeev, A.E. Klimovitskii, Calorimetric determination of hydrogen-bonding enthalpy for neat aliphatic alcohols, J. Phys. Org. Chem. 18 (2005) 1132–1137.

[57] J.N. Spencer, W.S. Wolbach, J.W. Hovick, L. Ansel, K.J. Modaress, Hydrogen bonding by alcohols and amines, J. Solut. Chem. 14 (1985) 805–814.

[58] M.H. Abraham, G.S. Whiting, P.W. Carr, H. Ouyang, Hydrogen bonding. Part 45. The solubility of gases and vapours in methanol at 298 K: an LFER analysis, J. Chem. Soc. Perkin Trans. 2. 6 (1998) 1385–1390.

[59] B.N. Solomonov, I.A. Sedov, A.A. Akhmadiyarov, Gibbs energy of cooperative hydrogen-bonding interactions in aqueous solutions of amines and pyridines, J. Phys. Org. Chem. 22 (2009) 1142–1147.

[60] I.A. Sedov, B.N. Solomonov, A method to determine the Gibbs energy of specific interactions in solutions. Hydrogen bonding of proton donating solutes in basic solvents, Fluid Phase Equilib. 276 (2009) 108–115.

[61] W. Marczak, B. Czech, L. Almasy, D. Lairez, Molecular clusters in aqueous solutions of pyridine and its methyl derivatives, Phys. Chem. Chem. Phys. 13 (2011) 6260–6269.

[62] W.K. Stephenson, R. Fuchs, Enthalpies of hydrogen bond formation of 1-octanol with aprotic organic solvents. A comparison of the solvation enthalpy, pure base, and non-hydrogen-bonding baseline methods, Can. J. Chem. 63 (1985) 342–348.

[63] M.J. Kamlet, J.L. Abboud, R.W. Taft, The solvatochromic comparison method. 6. The π scale of solvent polarities, J. Am. Chem. Soc. 99 (1977) 6027–6038.

[64] C. Mintz, M. Clark, K. Burton, W.E. Acree Jr., M.H. Abraham, Enthalpy of solvation correlations for gaseous solutes dissolved in benzene and in alkane solvents based on the Abraham model, QSAR Comb. Sci. 26 (2007) 881–888.

[65] C. Mintz, M. Clark, K. Burton, W.E. Acree Jr., M.H. Abraham, Enthalpy of solvation correlations for gaseous solutes dissolved in toluene and carbon tetrachloride based on the Abraham model, J. Solut. Chem. 36 (2007) 947–966.

[66] C. Mintz, T. Ladlie, K. Burton, M. Clark, W.E. Acree Jr., M.H. Abraham, Enthalpy of solvation correlations for gaseous solutes dissolved in alcohol solvents based on the Abraham model, QSAR Comb. Sci. 27 (2008) 627–635.

[67] C. Mintz, K. Burton, W.E. Acree Jr., M.H. Abraham, Enthalpy of solvation correlations for gaseous solutes dissolved in dimethyl sulfoxide and propylene carbonate based on the Abraham model, Thermochim. Acta 459 (2007) 17–25.

[68] C. Mintz, K. Burton, T. Ladlie, M. Clark, W.E. Acree Jr., M.H. Abraham, Enthalpy of solvation correlations for gaseous solutes dissolved in dibutyl ether and ethyl acetate, Thermochim. Acta 470 (2008) 67–76.

[69] M.H. Abraham, Free energies, enthalpies, and entropies of solution of gaseous nonpolar nonelectrolytes in water and nonaqueous solvents. The hydrophobic effect, J. Am. Chem. Soc. 104 (1982) 2085–2094.

[70] E.R. Thomas, B.A. Newman, T.C. Long, D.A. Wood, C.A. Eckert, Limiting activity coefficients of nonpolar and polar solutes in both volatile and nonvolatile solvents by gas chromatography, J. Chem. Eng. Data 27 (1982) 399–405.

[71] M.H. Abraham, J. Andonianhaftvan, G.S. Whiting, A. Leo, R.W. Taft, Hydrogen bonding. Part 34. The factors that influence the solubility of gases and vapours in water at 298 K, and a new method for its determination, J. Chem. Soc. Perkin Trans. 2. 8 (1994) 1777–1791.

[72] I.M. Barclay, J.A.V. Butler, The entropy of solution, Trans. Faraday Soc. 34 (1938) 1445–1454.