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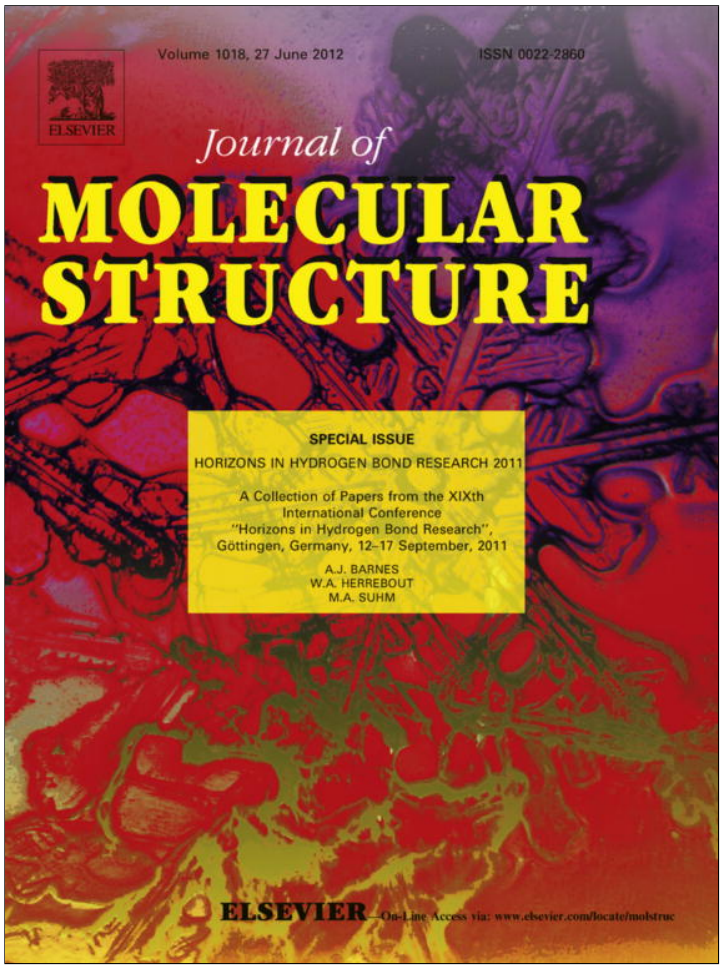

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Thermodynamics of hydrogen bonding of weak bases in alcohol solutions: Calorimetry of solution, IR-spectroscopy and vapor pressure analysis

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ABSTRACT

The properties of solutes and their reactivity in aliphatic alcohols significantly depend on the formation of hydrogen bonds. In this work, calorimetric, FTIR-spectroscopic and gas chromatographic vapor pressure studies of hydrogen bonds of weak bases in solution of aliphatic alcohols were carried out. Enthalpies of solutions at infinite dilution of ketones, nitriles and acetates in methanol and octan-1-ol were measured. Obtained from the calorimetric data, the enthalpies of specific interaction of weak bases in aliphatic alcohols unexpectedly found to be positive. IR spectra of solutions of ketones in aliphatic alcohols at infinite dilution were measured at different temperatures. Enthalpies of specific interaction in studied systems obtained from the spectroscopic data confirmed the endothermic process and are in good agreement with calorimetric results. Gibbs energies and entropies of specific interaction of weak bases in aliphatic alcohols were determined.

Obtained results show, that the hydrogen bonding process of weak bases in aliphatic alcohols differs substantially from the formation of complexes 1:1 ROH···B (B – weak proton acceptor) in aprotic media. The complicated process of hydrogen bonding of weak bases in aliphatic alcohols apparently is controlled by the entropy factor, because these values are above zero.

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1. Introduction

Aliphatic alcohols present an example of self-associated liquids, which physical and chemical properties are greatly affected by forming of hydrogen bonded complexes [1]. Hydrogen bonded clusters in alcohol medium can be varied by structure (linear, branched, cyclic) and composition (monomer, dimer, tetramer, etc.), and are in equilibrium with each other [1]. Various processes, realized in aliphatic alcohols, as well as the reactivity of the solute molecules in their medium, greatly depend on the hydrogen bonding with the solvent. Since aliphatic alcohols are widely used in various branches of science and technology, quantification of thermodynamic parameters of hydrogen bonding of them with various solutes induces a great practical interest.

Different experimental techniques, such as NMR [2] and infrared [3–5] spectroscopy, vapor pressure measurements [6,7] and solution calorimetry [8–13] were applied for investigation of the hydrogen bonding of various molecules with aliphatic alcohols. However, studies of hydrogen bonding of solute molecules with alcohol clusters in alcohol medium were rather poorly distributed. This task is greatly hampered by some peculiarities of self-associated solvents.

First, the net of hydrogen bonds in associated solvents may be broken while dissolution of some organic molecules in them. This process was discussed in works [3,11–14] and was called reorganization [15]. It was shown that reorganization depends on the solute and solvent molecules structure [12,16,17]. Comparing the number of lone electron pairs capable to hydrogen bonding with a number of active hydrogen atoms in solvent molecule, one may predict the presence (or absence) of reorganization process in it [12]. The type of hydrogen bonding centers (active hydrogen atoms or lone electron pairs) presented in excess determines the type of solute causing the reorganization. Alcohol molecule has two lone electron pairs and one active hydrogen atom. Almost all alcohol molecules are hydrogen bonded with its complexation degree close to 100% [18]. Regardless of association type (open, linear, branched or cyclic) there is a lack of free hydrogen atoms of O—H groups. Consequently, alcohol molecule cannot interact with solute as a proton donor without disruption of alcohol–alcohol hydrogen bonds. However, alcohol molecule possesses a lone electron pair for interacting as a proton acceptor.

Another feature of associated liquids is cooperativity phenomenon [19–22]. Solutes capable to specific interaction form hydrogen bonds with alcohol associates. The energy of such interaction is higher than in equimolar complexes due to cooperative effects [5,7,21,22]. Studies on the hydrogen bonding of amines with alcohols solutions have shown that the cooperative strengthening in complexes of pyridine and its methyl derivatives with alcohols

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clusters are approximately equal [9,16,23]. For complexes of trialkylamines cooperativity factor decreases going from triethylamine to tri-*n*-butylamine [16]. Thus, the cooperativity implies the change in strength of intermolecular contacts in the multi-particle complexes comparing with equimolar complexes due to mutual influence of the molecules. The contribution of cooperativity in complexes of alcohols depends on proton acceptor and proton donor ability of interacting molecules [24,25].

Unlike the solvation of strong proton acceptors, which complexation degree in alcohol environment is close to 100%, the solvation of weak proton acceptors probably has some peculiarities. Symons and Eaton [26] have studied IR-spectra of acetone–methanol solution in acetone C=O group stretching vibration absorbance region. Two bands (1707.5 cm^{-1} and 1717 cm^{-1}) in C=O group stretching vibration region were observed at infinite dilution of acetone in methanol, which authors attributed to hydrogen bonded acetone with methanol associates and non-hydrogen bonded acetone. The existence of free acetone molecules in alcoholic solution is much unexpected result. Authors of [27] have used factor analysis of acetone C=O and methanol O—H bands in IR spectra of acetone–methanol solution to reveal that only 54.3% of acetone in methanol–acetone mixture is hydrogen bonded. Evidently, such situation can be observed not only for acetone, but for other ketones and weak bases. At the same time there is not enough information on the hydrogen bonding thermodynamics for such systems in the literature. Moreover, no approaches were proposed for quantification of such interactions. In order to review the peculiarities of intermolecular interaction in systems "weak base-alcohol" we investigated the thermodynamics of hydrogen bonding in such systems. The solution calorimetry method was used to obtain enthalpies of solution of proton acceptors in methanol and octan-1-ol. Also IR-spectroscopy was applied for examining unusual results on hydrogen bonding thermodynamics in studied systems.

2. Experimental part

All chemicals were supplied by Acros Organics (mass fraction min. 0.98). They were additionally dried and fractionally distilled before use by standard methods [28]. The purity of chemicals was monitored by gas chromatographic analysis; the content of main substances in all cases was no less than 0.998. The residual water content was checked by Karl Fischer titration. It did not exceed 1×10^{-2} vol.% for alcohols and 5×10^{-3} vol.% for the other chemicals.

Calorimetric measurements were carried out using a semi-adiabatic solution calorimeter constructed in Kazan University. Detailed description of apparatus is presented in [16,29]. The reproducibility of calorimetric data regarding the electrical calibrations only was found to be about 0.15% for the range of calibration heat from 0.5 to 1.5 J. The apparatus was tested by the dissolution of potassium chloride in water. 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 [30]. Each value of the solution enthalpy was reproduced 6–8 times. All experimental data were statistically processed. In addition, the concentration measurements of solution enthalpies were carried out. The absence of concentration dependence of solution enthalpies confirms the performance of dissolution experiments at infinite dilution conditions.

FTIR spectra were recorded using Vector-22 Bruker spectrometer. 64 scans with a set resolution of 1 cm^{-1} were accumulated for each spectrum. A CaF_2 cell of 0.1 mm path length was utilized. Spectra were analyzed in the C=O stretching vibration region (~1700 cm^{-1}). Concentration of ketones in solutions of alcohols was about 1 vol.%. Spectra of pure solvents were subtracted from spectra of solutions for processing obtained data. The curve fitting was made by Peak Feat program package. Fitting was proved by coincidence of theoretical and experimental band contours (see example of fitting in Fig. S1 of Supporting material). Spectra were recorded in temperature range 293–333 K every 5 K with accuracy ±0.05 K.

The limiting activity coefficient ($\gamma^{A/S}$) of propionitrile in benzene was measured using gas chromatographic head space analysis (Chromatec Crystall-2000M gas chromatograph, quartz glass column with RTX-5 Amine stationary phase), for details see [31]. $\gamma^{A/S}$ can be calculated from the ratio of vapor pressure of solute A over its solution in S ($p^{A/S}$) to p^{A}_{sat}:

$$\gamma^{A/S} = p^{A/S}_{A}/p^{A}_{sat}x^{A/S}_{A}, \quad (1)$$

where $x^{A/S}_{A}$ is a mole fraction of A in solution.

3. Results and discussion

The aim of current work was to investigate the hydrogen bonding process in systems consisting of weak bases and self-associated liquids – aliphatic alcohols. As weak bases ketones, nitriles and acetates were chosen. We used solvation thermodynamic approach for determination of thermodynamic functions of hydrogen bonding in systems studied. Thermodynamic function of solvation $\Delta_{solv}f^{A/S}$ (enthalpy, Gibbs energy or others) of solute A in solvent S, which refers to isothermal transfer of solute A from the ideal gas state to an infinitely diluted solution in solvent S at temperature 298.15 K and pressure 0.1 MPa, can be found from experimental values:

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

where $\Delta_{soln}f^{A/S}$ is the thermodynamic function of solution of solute A in solvent S, $\Delta_{vap}f^{A}$ is the thermodynamic function of vaporization of solute A if it is a liquid, for solids we need to take sublimation thermodynamic function ($\Delta_{sub}f^{A}$). Value $\Delta_{solv}f^{A/S}$ reflects intermolecular interactions in solution. It consists of two contributions:

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

Here $\Delta_{solv(nonsp)}f^{A/S}$ is the thermodynamic function of non-specific solvation, $\Delta_{int(sp)}f^{A/S}$ is the thermodynamic function of specific interaction of solute A in solvent S. In general specific interaction can be understood as localized donor–acceptor interaction. In our case it was hydrogen bonding. The magnitude of specific interaction thermodynamic function of proton acceptor solute A in self-associated solvent – aliphatic alcohol – is of complex nature. On the one hand it characterizes the hydrogen bonding of solute A with associative species of solvent molecules (Eq. (4)). Therefore, the energy of hydrogen bond in this case is not equal to the complexation energy in binary complex A···S [5,7,21,22]. On the other hand the solute–solvent hydrogen bonding may cause a disruption of hydrogen bonds between solvent molecules (Eq. (5)) [3,11–14]. The summarized value of the specific interaction enthalpy ($\Delta_{int(sp)}H^{A/S}$) of proton acceptor solutes in aliphatic alcohol includes both enthalpies of the H-complexation and the solvent reorganization [11,16] (Eq. (7)):

$$(ROH)_m + A \rightleftarrows (ROH)_m\cdots A + \Delta_{HB}H^{A\cdots(ROH)_m} \quad (4)$$

$$(ROH)_n \rightleftarrows (ROH)_m + (ROH)_k + \Delta_{reorg}H^{ROH}, m + k = n \quad (5)$$

$$(ROH)_n + A \rightleftarrows (ROH)_m\cdots A + (ROH)_k + \Delta_{int(sp)}H^{A/ROH}, m + k = n \quad (6)$$

$$\Delta_{int(sp)}H^{A/ROH} = \alpha\cdot\Delta_{HB}H^{A\cdots(ROH)_m} + \Delta_{reorg}H^{ROH}, \quad (7)$$

where α – complexation degree.

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3.1. Calorimetric determination of the enthalpy of specific interaction of weak bases in solutions of alcohols

The enthalpies of solution of ketones, nitriles and acetates in methanol and octan-1-ol were measured at infinite dilution at 298.15 K and atmospheric pressure. They are presented in Tables 1 and 2 together with literature data. Enthalpies of solution of proton acceptors in alcohols have unexpectedly positive values for solutes which seem to form hydrogen bonds with solvent molecules. Despite the hydrogen bonding process, the solution enthalpies of bases in octan-1-ol are more positive than solution enthalpies of alkanes in octan-1-ol ($\Delta_{soln}H^{A/S}$ = 1.21 kJ mol^{-1} for *n*-hexane [32], $\Delta_{soln}H^{A/S}$ = 1.25 kJ mol^{-1} for *n*-heptane [32], $\Delta_{soln}H^{A/S}$ = 1.42 kJ mol^{-1} for *n*-octane [32]).

For the determination of specific interaction enthalpies from the solvation enthalpies various approaches were proposed earlier [33–35,9]. In current work method from [36] was used. This method is based on following equation [36]:

$$\Delta_{int(sp)}H^{A/S} = \Delta_{soln}H^{A/S} - \Delta_{soln}H^{A/C_6H_{12}} - \left(\delta_{cav}h^S - \delta_{cav}h^{C_6H_{12}}\right)\cdot V_x^A - \left(a_R + b_R\sqrt{\delta_{cav}h^S}\right)\cdot\left[\left(\Delta_{soln}H^{A/R} - \Delta_{soln}H^{A/C_6H_{12}}\right) - \left(\delta_{cav}h^R - \delta_{cav}h^{C_6H_{12}}\right)\cdot V_x^A\right]. \quad (8)$$

Here $\Delta_{soln}H^{A/S}$, $\Delta_{soln}H^{A/R}$, $\Delta_{soln}H^{A/C_6H_{12}}$ are the solution enthalpies of solute A in studied solvent S, in standard solvent R and in cyclohexane, respectively, $\delta_{cav}h^S$, $\delta_{cav}h^R$ and $\delta_{cav}h^{C_6H_{12}}$ are the specific relative cavity formation enthalpies for each solvent and V_x^A is characteristic volume of solute A [37]. 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 the characteristic volume $V_x^{C_nH_{2n+2}}$ of alkane. Hence, the $\delta_{cav}h^S$ is given by:

$$\delta_{cav}h^S/(10^{-2}\ \text{kJ cm}^{-3}) = \frac{\Delta_{soln}H^{C_nH_{2n+2}/S}/(\text{kJ mol}^{-1})}{V_x^{C_nH_{2n+2}}/(10^2\ \text{cm}^3\ \text{mol}^{-1})}. \quad (9)$$

For the determination of specific interaction enthalpy one should use benzene (a_R = 0.20, b_R = 0.38) as a solvent R, because benzene is not able to interact specifically with proton acceptor solutes.

The enthalpies of specific interaction of weak proton acceptors in methanol and octan-1-ol were calculated via Eq. (8) using experimental and literature solution enthalpies at infinite dilution. Required data for calculation of enthalpies of specific interaction according with Eq. (8) are presented in Table 1.

The specific relative cavity formation enthalpies in cyclohexane (1.42×10^2 kJ cm^{-3}), benzene (5.02×10^2 kJ cm^{-3}), methanol (5.1×10^2 kJ cm^{-3}) and octan-1-ol (1.1×10^2 kJ cm^{-3}) were taken from works [19,36]. Obtained using Eq. (8) enthalpies of specific interaction of weak bases in methanol and octan-1-ol are above zero (Table 2). Moreover, specific interaction enthalpies in octan-1-ol are more positive than in methanol. This fact is much unusual due to absence analogous data in literature. At the same time almost all published data on the enthalpies of hydrogen bonding of alcohols with weak bases obtained in aprotic solvents have negative values (for nitriles its value is equal to −7.9 ± 1.1 kJ mol^{-1}, for ketones an average value of $\Delta_{HB}H^{A\cdots CH_3OH}$ is −9.8 ± 0.6 kJ mol^{-1}, for acetates −9.1 ± 0.6 kJ mol^{-1} [36,44,45]).

The obtained positive values of specific interaction enthalpies can be explained in the following way. Enthalpy of specific interaction of weak proton acceptors with aliphatic alcohols decreases due to reorganization process. When the second term – the enthalpy of reorganization – in Eq. (7) exceeds the enthalpy of cooperative hydrogen bonding with alcohol associates, the total value of $\Delta_{int(sp)}H^{A/S}$ can be near zero or even positive. Last situation is observed while dilution of weak proton acceptors in liquid alcohols. At the same time for aliphatic and aromatic amines the enthalpy of cooperative hydrogen bonding exceeds the enthalpy of reorganization and total enthalpy of specific interaction has negative value. For example, $\Delta_{int(sp)}H^{A/C_8H_{17}OH} = -3.1$ kJ mol^{-1} in case of tri-*n*-propylamine [16].

Table 1
Characteristic volumes of proton acceptors (V_x^A), the solution enthalpies of proton acceptors in cyclohexane ($\Delta_{soln}H^{A/C_6H_{12}}$) and benzene ($\Delta_{soln}H^{A/C_6H_6}$) at 298.15 K.

Substance (A)	$V_x^A \times 10^{-2}$ (cm^3 mol^{-1})	$\Delta_{soln}H^{A/C_6H_{12}}$ (kJ mol^{-1})	$\Delta_{soln}H^{A/C_6H_6}$ (kJ mol^{-1})
Acetone	0.5470	9.74 ± 0.42[a]	1.13 ± 0.08[g]
Butanone	0.6879	8.20 ± 0.50[a]	0.42 ± 0.08[b]
Pentanone-2	0.8288	7.11 ± 0.09[a]	0.71 ± 0.05[b]
Pentanone-3	0.8288	7.53 ± 0.08[a]	0.08 ± 0.05[b]
Hexanone-2	0.9676	6.75 ± 0.10[a]	0.79 ± 0.05[b]
Heptanone-2	1.1106	6.80 ± 0.09[a]	1.00 ± 0.08[b]
Heptanone-4	1.1106	7.06 ± 0.40[b]	0.67 ± 0.20[b]
Nonanone-2	1.3924	6.60 ± 0.10[c]	1.63 ± 0.20[b]
Nonanone-5	1.3924	6.00 ± 0.10[c]	1.55 ± 0.08[b]
Cyclopentanone	0.7202	9.08 ± 0.01[b]	−1.05 ± 0.05[b]
Acetophenone	1.0139	10.73 ± 0.22[c]	1.51 ± 0.21[h]
Acetonitrile	0.4042	15.00 ± 0.30[d]	1.66 ± 0.12[g]
Propionitrile	0.5451	12.60 ± 0.10[d]	0.70 ± 0.05[f]
Butyronitrile	0.6860	10.20 ± 0.20[d]	0.21 ± 0.03[f]
Benzonitrile	0.8711	11.53 ± 0.32[c]	0.39 ± 0.03[f]
Methyl acetate	0.6057	8.62 ± 0.09[a]	1.02 ± 0.05[f]
Ethyl acetate	0.7466	7.28 ± 0.17[e]	0.46 ± 0.04[e]
Propyl acetate	0.8875	6.21 ± 0.10[f]	0.56 ± 0.04[f]
Butyl acetate	1.0284	6.19 ± 0.07[f]	0.51 ± 0.03[f]

[a] Ref. [38].
[b] Ref. [39].
[c] Ref. [36].
[d] Ref. [40].
[e] Ref. [41].
[f] Values measured in present work.
[g] Ref. [42].
[h] Ref. [43].

3.2. IR-spectroscopic determination of the enthalpy of specific interaction of weak bases in solutions of alcohols

We decided to verify obtained positive values of specific interaction enthalpies using IR-spectroscopy. It is a standard method for hydrogen bonding study, but it is less applicable to investigation of solute–solvent interactions in self-associated liquids. IR-spectra of acetone, butanone, pentanone-2, heptanone-2, nonanone-2 in methanol and octan-1-ol at infinite dilution were recorded at different temperatures. Hydrogen bonding of ketones in alcohol solutions were studied in the C=O group stretching vibration region. Figs 1 and 2 show selected IR-spectra of butanone-in-methanol and octan-1-ol in temperature range 293–328 K.

It is evident (Fig. 1) that C=O band of acetone in methanol has two components (1720 cm^{-1} and 1707 cm^{-1}), which in accordance with [26] are related to unbonded and H-bonded C=O groups. These overlapping bands were decomposed into individuals and integral intensities of H-bonded and "free" C=O groups were calculated. Supporting material contains an example of theoretical decomposition of C=O bands along with theoretical peaks (Fig. S1).

Integral intensities of free and H-bonded C=O bands correlate with concentration of these species in solution through Bouguer–Lambert–Beer law:

$$I_{bond} = \varepsilon_{bond}c_{bond}l$$
$$I_{free} = \varepsilon_{free}c_{free}l, \quad (10)$$

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Table 2
Solution enthalpies of studied bases in methanol ($\Delta_{soln}H^{A/CH_3OH}$) and octan-1-ol ($\Delta_{soln}H^{A/C_8H_{17}OH}$) at 298.15 K, enthalpies of specific interaction of bases in alcohols ($\Delta_{int(sp)}H^{A/CH_3OH}$ and $\Delta_{int(sp)}H^{A/C_8H_{17}OH}$).

Substance (A)	$\Delta_{soln}H^{A/CH_3OH}$ (kJ mol^{-1})	$\Delta_{soln}H^{A/C_8H_{17}OH}$ (kJ mol^{-1})	$\Delta_{int(sp)}H^{A/CH_3OH}$ (kJ mol^{-1})	$\Delta_{int(sp)}H^{A/C_8H_{17}OH}$ (kJ mol^{-1})
Acetone	2.51 ± 0.13[a]	8.91 ± 0.06[f]	2.0	5.7
Butanone	2.42 ± 0.13[a]	7.53 ± 0.06[f]	2.5	5.7
Pentanone-2	2.50 ± 0.10[a]	7.22 ± 0.06[f]	2.3	6.0
Pentanone-3	2.63 ± 0.10[a]	6.92 ± 0.04[f]	3.1	5.9
Hexanone-2	2.84 ± 0.10[a]	6.77 ± 0.07[f]	2.5	6.0
Heptanone-2	3.14 ± 0.13[a]	6.69 ± 0.13[g]	2.6	6.1
Heptanone-4	3.22 ± 0.13[a]	6.22 ± 0.06[f]	3.1	5.7
Nonanone-2	4.73 ± 0.13[a]	6.15 ± 0.34[g]	3.6	6.0
Nonanone-5	3.93 ± 0.13[a]	6.11 ± 0.21[g]	2.8	6.2
Cyclopentanone	3.40 ± 0.10[a]	8.38 ± 0.06[h]	5.1	7.1
Acetophenone	5.02 ± 0.42[b]	7.15 ± 0.07[e]	4.2	4.5
Acetonitrile	4.34 ± 0.05[c]	10.53 ± 0.15[e]	3.5	4.5
Propionitrile	3.99 ± 0.03[c]	9.62 ± 0.11[e]	4.1	5.5
Butyronitrile	3.81 ± 0.02[c]	8.02[i]	4.3	5.5
Benzonitrile	3.59 ± 0.02[b]	8.05 ± 0.10[e]	4.0	5.3
Methyl acetate	3.84 ± 0.02[d]	7.88[i]	3.3	5.3
Ethyl acetate	3.17 ± 0.19[e]	7.63 ± 0.05[e]	3.2	6.3
Propyl acetate	3.37 ± 0.20[e]	6.80[i]	3.3	6.2
Butyl acetate	3.65 ± 0.01[e]	6.76[i]	3.6	6.5

[a] Ref. [39].
[b] Ref. [46].
[c] Ref. [40].
[d] Ref. [47].
[e] Values measured in present work.
[f] Ref. [48].
[g] Ref. [49].
[h] Ref. [50].
[i] Ref. [51].

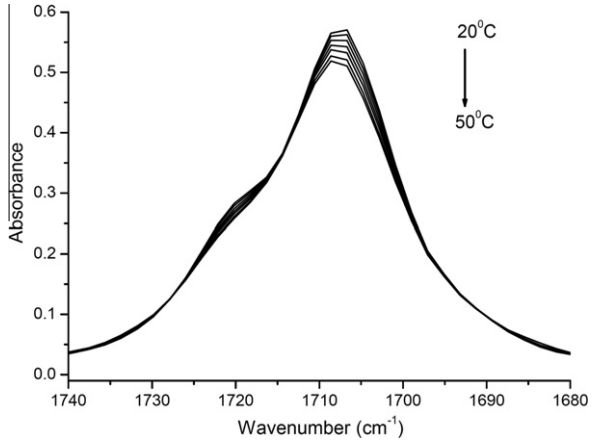

Fig. 1. Spectra of infinitely diluted butanone-in-methanol solution in C=O stretching vibration region.

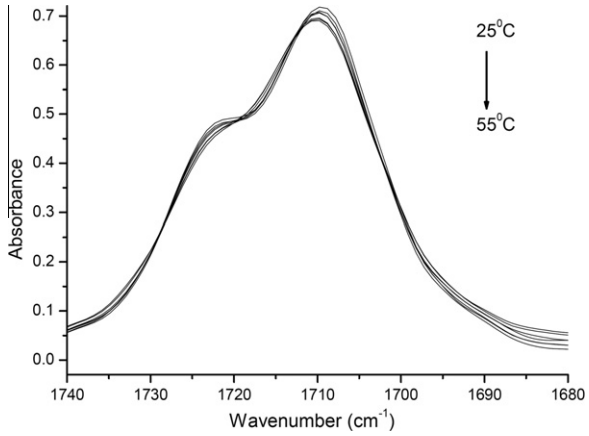

Fig. 2. Spectra of infinitely diluted butanone-in-octan-1-ol solution in C=O stretching vibration region.

where I_{bond} and I_{free} are the integral intensities of H-bonded and "free" C=O groups (absorbance units), ε_{bond} and ε_{free} are the molar extinction coefficients of H-bonded and "free" C=O groups, c_{bond} and c_{free} are the concentrations of H-bonded and free base species (mol L^{-1}), l is the cell length (mm). Assuming that extinction coefficients of "free" and H-bonded C=O groups vary with temperature in the same way and the specific interaction enthalpy does not change significantly in narrow temperature interval, we can estimate enthalpy of specific interaction by the Van't Hoff equation:

$$-\frac{\Delta_{int(sp)}H^{A/ROH}}{R} = \partial\left(\frac{I_{bond}}{I_{free}}\right) \Big/ \partial\left(\frac{1}{T}\right), \quad (11)$$

where T is the temperature, $\Delta_{int(sp)}H^{A/ROH}$ is the enthalpy of specific interaction of ketones in alcohol solutions. Figs. 3 and 4 demonstrate the dependence of $\ln I_{bond}/I_{free}$ of "free" and H-bonded C=O groups of butanone-in-methanol and octan-1-ol on $1/T$.

As it can be seen from Figs. 3 and 4 the ratio of integral intensities of H-bonded and unbonded C=O groups grows with temperature increasing. This result justifies the endothermic values of specific interaction enthalpy. The enthalpies of specific interaction in studied systems were calculated using dependencies analogous to that in Figs. 3 and 4. All obtained data are presented in Table 3. It can be noted that all calculated enthalpies of specific interaction have positive values. IR-spectroscopic investigation of ketone–alcohol solution has revealed that the enthalpy of specific interaction in such systems can be above zero. This result completely confirms calorimetric data.

The additional experiments were performed to verify an assumption about the same influence of the temperature on the extinction coefficients of H-bonded and "free" C=O groups. Temperature IR-spectroscopic investigation of ketones in *n*-hexane

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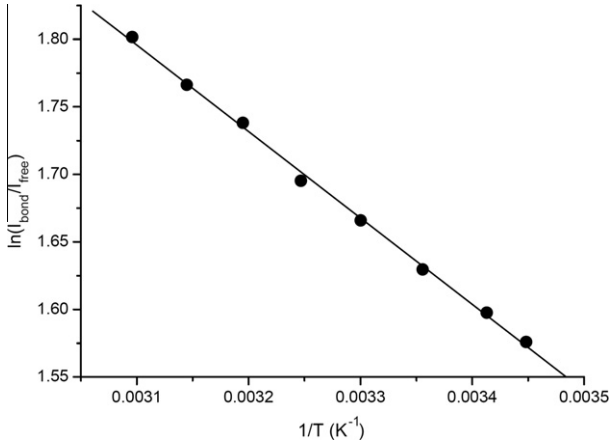

Fig. 3. Temperature dependence of logarithmic relation between integral intensities of H-bonded and "free" C=O group bands $\left(\frac{I_{bond}}{I_{free}}\right)$ (butanone-in-methanol system).

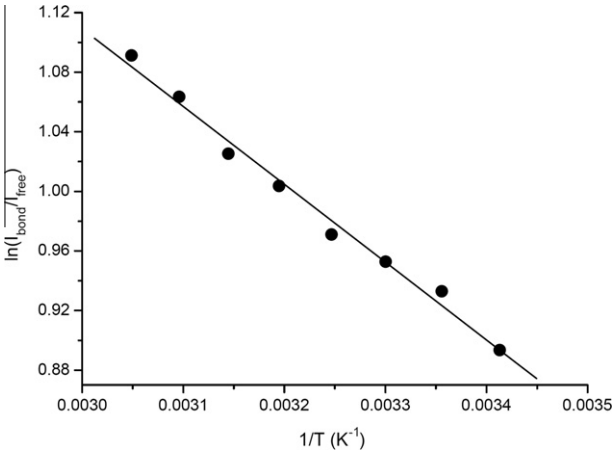

Fig. 4. Temperature dependence of logarithmic relation between integral intensities of H-bonded and "free" C=O group bands $\left(\frac{I_{bond}}{I_{free}}\right)$ (butanone-in-octan-1-ol system).

and chloroform was made. The first solution models the temperature behavior of "free" C=O group, the second one – the temperature behavior of H-bonded C=O group. It was shown that the temperature slightly influences on ε-coefficients of "free" and H-bonded C=O groups (Figs. S2 and S3). Consequently, if we took into account real temperature dependence of extinction coefficients we would probably obtain even more positive enthalpies.

3.3. Gibbs energies and entropies of specific interaction of weak bases in solutions of alcohols

How the process of specific interaction is realized? In order to answer this question we calculated the Gibbs energies of specific interaction of ketones, nitriles and acetates in methanol and octan-1-ol. For this purpose Eq. (12) analogous that for the enthalpy of specific interaction was used [52]:

$$\begin{aligned}\Delta_{int(sp)}G^{A/S} &= \Delta_{solv}G^{A/S} - \Delta_{solv}G^{A/S_0} - \left(\delta_{cav}g^{S} - \delta_{cav}g^{S_0}\right) \cdot V_x^A \\ &\quad - \left(a + b\sqrt{\delta_{cav}g^{S}}\right) \cdot \left[\left(\Delta_{solv}G^{A/S_R} - \Delta_{solv}G^{A/S_0}\right)\right. \\ &\quad \left. - \left(\delta_{cav}g^{S_R} - \delta_{cav}g^{S_0}\right) \cdot V_x^A\right] - c \cdot V_x^A - d, \\ a &= -\sqrt{\delta_{cav}g^{S_0}} \Big/ \left(\sqrt{\delta_{cav}g^{S_R}} - \sqrt{\delta_{cav}g^{S_0}}\right) \\ b &= 1/\left(\sqrt{\delta_{cav}g^{S_R}} - \sqrt{\delta_{cav}g^{S_0}}\right) \end{aligned} \quad (12)$$

Table 3
The enthalpies of specific interaction of ketones in methanol and octan-1-ol solutions, obtained by IR-spectroscopy.

Substance (A)	$\Delta_{HB}H^{A/CH_3OH}$ (kJ mol^{-1})	$\Delta_{HB}H^{A/C_8H_{17}OH}$ (kJ mol^{-1})
Acetone	3.5 ± 1.0	6.3 ± 1.0
Butanone	2.8 ± 1.0	4.3 ± 1.0
Pentanone-2	3.8 ± 1.0	7.1 ± 1.0
Heptanone-2	2.5 ± 1.0	7.4 ± 1.0
Nonanone-2	4.4 ± 1.0	6.3 ± 1.0

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, contribution $(c \cdot V_x^A - d)$ reflects solvophobic effect of alcohols as solvents ($c = 5.17$, $d = 0.23$ for methanol [53], $c = 1.78$, $d = 0.60$ for octan-1-nol [53]). Parameter $\delta_{cav}g^{S}$ is responsible for non-specific interactions with studied solvent and can be determined from Gibbs energies of solvation of *n*-octane in solvent S $(\Delta_{solv}G^{C_8H_{18}/S})$ and *n*-hexadecane $(\Delta_{solv}G^{C_8H_{18}/C_{16}H_{34}})$:

$$\delta_{cav}g^{S}/(10^{-2}\,\mathrm{kJ\,cm^{-3}}) = \frac{\left(\Delta_{solv}G^{C_8H_{18}/S} - \Delta_{solv}G^{C_8H_{18}/C_{16}H_{34}}\right) \Big/ \left(\mathrm{kJ\,mol^{-1}}\right)}{V_x^{C_8H_{18}} \Big/ \left(10^2\,\mathrm{cm^3\,mol^{-1}}\right)}. \quad (13)$$

All required Gibbs energies of solvation in alcohols, *n*-hexadecane and benzene are presented in Table 4. Gibbs energies of solvation in alcohols were calculated using gas–liquid partition coefficients *L* [54,55] via equation:

$$\Delta_{solv}G^{A/S} = RT\ln\left(\frac{RT}{LP^{\circ}V_m^S}\right), \quad (14)$$

where V_m^S is the molar volume of solvent S, P° is the standard pressure. Other data were taken from literature. The Gibbs energy of propionitrile in benzene was calculated from equation:

$$\Delta_{solv}G^{A/S} = RT\ln\left(\gamma^{A/S}p_{sat}^{A}\right), \quad (15)$$

where $\gamma^{A/S}$ is the limiting activity coefficient 298.15 K, p_{sat}^{A} is the saturated vapor pressure of pure A in bar.

As a standard solvent S_R we used benzene ($\delta_{cav}g^{S_R} = 1.7 \times 10^{-2}$ kJ cm^{-3} [52]; $a = 0$ and $b = 0.78$). Specific relative cavity formation Gibbs energies of *n*-hexadecane (S_0) ($\delta_{cav}g^{S_0} = 0.0 \times 10^{-2} kJ\ cm^{-3}$ [52]), methanol ($\delta_{cav}g^{CH_3OH} = 2.6 \times 10^{-2}$ kJ cm^{-3} [53]) and octan-1-ol ($\delta_{cav}g^{C_8H_{17}OH} = 0.2 \times 10^{-2}$ kJ cm^{-3} [53]) were taken for calculations.

As it is shown in Table 3 obtained magnitudes $\Delta_{int(sp)}G^{A/CH_3OH}$ and $\Delta_{int(sp)}G^{A/C_8H_{17}OH}$ have negative values. At the same time they are close to each other for the same proton acceptor within the error of calculations.

Using values of the enthalpies and Gibbs energies of specific interaction presented in Tables 2 and 4 we calculated the entropies of specific interaction of weak proton acceptors in methanol and octan-1-ol:

$$\Delta_{int(sp)}S^{A/S} = \left(\Delta_{int(sp)}H^{A/S} - \Delta_{int(sp)}G^{A/S}\right)/T \quad (16)$$

The values of $\Delta_{int(sp)}S^{A/S}$ are shown in Table 5. From this table one can see that all entropies of specific interaction of ketones and acetates are positive, their values increase when going from methanol to octan-1-ol. This result is rather unexpected. Most often the literature data on entropies of hydrogen bonding in complexes of alcohols with bases of 1:1 composition have negative values (−32.6 kJ mol^{-1} K^{-1} for complex methanol–methyl acetate, −30.5 kJ mol^{-1} K^{-1} for

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Table 4
Solvation Gibbs energies of proton acceptors in methanol and octan-1-ol, *n*-hexadecane and benzene, specific interaction Gibbs energies for studied systems.

Substance (A)	$\Delta_{solv}G^{A/CH_3OH}$ [a] (kJ mol^{-1})	$\Delta_{solv}G^{A/C_8H_{17}OH}$ [b] (kJ mol^{-1})	$\Delta_{solv}G^{A/n-C_{16}H_{34}}$ (kJ mol^{-1})	$\Delta_{solv}G^{A/C_6H_6}$ (kJ mol^{-1})	$\Delta_{int(sp)}G^{A/CH_3OH}$ (kJ mol^{-1})	$\Delta_{int(sp)}G^{A/C_8H_{17}OH}$ (kJ mol^{-1})
Acetone	−0.6	−0.6	1.4[c]	−1.9[c]	−1.2	−2.2
Butanone	−3.2	−3.3	−2.1[c]	−4.7[c]	−1.9	−1.9
Pentanone-2	−4.5	−5.7	−4.8[c]	−7.6[c]	−1.2	−1.7
Hexanone-2	−5.9	−8.5	−7.6[c]	−10.1[c]	−0.9	−1.9
Heptanone-2	−9.1	−11.1	−10.5[c]	−12.6[c]	−2.5	−2.1
Acetonitrile	−1.0	−0.6	1.1[c]	−2.2[c]	−0.5	−1.7
Propionitrile	−4.7	−2.8	−0.9[d]	−5.3[e]	−1.6	−1.8
Methyl acetate	−0.8	−0.6	−0.2[c]	−2.9[c]	−0.8	−1.0
Propyl acetate	−4.2	−5.6	−5.4[c]	−7.8[c]	−1.1	−1.1
Butyl acetate	−6.5	−8.3	−8.3[c]	−10.2[c]	−1.9	−1.4

[a] Gibbs energies of solvation were calculated via Eq. (14) using data from [54].
[b] Gibbs energies of solvation were calculated via Eq. (14) using data from [55].
[c] Ref. [56].
[d] Ref. [57].
[e] Values measured in present work.

Table 5
Entropies of specific interaction of proton acceptors in methanol and octan-1-ol.

Substance (A)	$\Delta_{int(sp)}S^{A/CH_3OH}$ [a] ($\times 10^3$ kJ mol^{-1} K^{-1})	$\Delta_{int(sp)}S^{A/C_8H_{17}OH}$ [a] ($\times 10^3$ kJ mol^{-1} K^{-1})
Acetone	10.7	26.5
Butanone	14.8	25.5
Pentanone-2	11.7	25.8
Hexanone-2	11.4	26.5
Heptanone-2	17.1	27.5
Acetonitrile	13.4	21.1
Propionitrile	19.1	24.5
Methyl acetate	13.8	21.1
Propyl acetate	14.8	24.5
Butyl acetate	18.5	26.5

[a] Calculated via Eq. (16).

complex methanol–acetone, −30.5 kJ mol^{-1} K^{-1} for complex octan-1-ol–hexyl hexanoate [44]). The increasing in entropy values can be explained in following way. Since the entropy can be expressed as a measure of randomness or disorder, its increasing indicates the growth of possible microscopic configurations of molecules in system. It may be an indirect proof of assumption that dissolution of weak proton acceptors in alcohols causes the disruption of associate chain of hydrogen bonds.

4. Conclusion

This work presents new and unexpected information on the thermodynamics of hydrogen bonding of weak bases in solution of aliphatic alcohols. It was shown that the enthalpies of specific interaction of weak bases in solution of aliphatic alcohols are positive. They are determined using two different experimental methods, namely, the solution calorimetry and IR spectroscopy. Part of the solute molecules is not H-bonded in the environment of alcohol. This is due to the influence of self-association of solvent molecules. The enthalpy of specific interaction of weak bases in solutions of alcohols consists of two contributions: formation of solute–solvent hydrogen bonds (exothermic value) and the breaking of solvent–solvent hydrogen bonds (endothermic value). The relationship between these contributions determines the magnitude and sign of the enthalpy of specific interaction in the systems studied. The Gibbs energy of hydrogen bonding of weak bases in solution of aliphatic alcohols are negative (spontaneous process) despite the positive enthalpy values. The process of specific interaction in systems studied is accompanied by an increase in entropy. The results show that the thermodynamics of hydrogen bonding of weak bases in solution of aliphatic alcohols differs from the usual thermodynamics of complexation between alcohol and base molecules in aprotic solvents (pure base or inert media).

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2012.01.020.

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