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Thermodynamics of Specific Interactions of Pyridines in Aliphatic Alcohols: Gibbs Energy, Entropy, and Degree of Binding

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Abstract—The activity coefficients at infinite dilution (T = 298.15 K) and Gibbs energy of solvation of pyridines in aliphatic alcohols were determined. The thermodynamic functions of specific interactions in these systems were calculated.

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Hydrogen bonds are of great importance in various physicochemical and biological processes. In particular, they have a great influence on the molecular recognition of receptors, the stability of nucleic acids, and the enzymatic catalysis [1]. Various experimental [2–5] and theoretical methods [6–8] are used for the study of hydrogen bonding.

Hydrogen bonding of organic molecules in equimolar complexes has been studied quite well. In the literature a large number of complex formation constants and enthalpies AH···B for various organic molecules was collected, usually in inert solvents [2]. The scales of basicity and acidity of organic compounds [9–11] and the equations by which it is possible to estimate the parameters of the hydrogen bond on the basis of spectral characteristics of molecules [12, 13] were developed. In [11, 14–17] various empirical relations were suggested allowing a prediction of the thermodynamic parameters of hydrogen bonds with fairly good accuracy.

In turn, the hydrogen bonds of organic molecules in the environment of associated solvents, where multicomponent complexes may form, have been studied much worse, despite the wide application of such fluids in various fields of science and technology. An example of the solvents associated through hydrogen bonding is aliphatic alcohols. Their physicochemical properties are determined by the presence in them of the hydrogen-bonded clusters which are in equilibrium with each other [18]. Hydrogen bonding of the dissolved molecules with the alcohol clusters can affect their reactivity and the occurrence of various processes in the alcohol medium. Therefore, quantitative determination of the thermodynamic functions of hydrogen bonding of solutes with alcohols is of practical interest.

A difficulty in determining the parameters of the hydrogen bonding in the medium of aliphatic alcohols is associated with the peculiarities of the interaction of solutes with the associated fluid. Dissolving of molecules in an aliphatic alcohol can result in the formation of hydrogen bonds with the alcohol clusters rather than with the monomeric alcohol. The strength of such complexes increases in comparison with the 1:1 complexes (ROH···B) due to increasing polarity of the OH groups involved in the complex formation [19, 20]. At the same time, since the degree of self-association of alcohol is close to 100% [21], the hetero association requires breaking the hydrogen bonds in the alcohol associates. This process is known as reorganization [19, 22, 23], which is defined as the displacement of equilibrium between the alcohol associates under the influence of the proton acceptors. The cleavage of the alcohol clusters is disadvantageous in terms of enthalpy, however, it can be characterized by an increase in the number of microstates of the system. Furthermore, the determination of the thermodynamic functions of hydrogen bonding in associated solvents is complicated by the existence of solvophobic effect [24, 25].

We have previously investigated the enthalpy component of hydrogen bonding of pyridines in aliphatic alcohols [20, 26]. Since the probability of the process under standard conditions (T = 298.15 K, p = 0.1 MPa) is characterized by the Gibbs energy, we have determined in the present study the free energies of solvation and specific interaction of pyridine and its methylated derivatives in a series of aliphatic alcohols. Activity coefficients of pyridines in alcohols at infinite dilution were measured by gas chromatographic analysis of the equilibrium vapor. The Gibbs energy of specific interactions in the medium of the associated fluid was compared with the Gibbs energy of hydrogen bonding in equimolar complexes formed by dissolving the alcohols in pyridine media. The entropy of specific interaction of pyridines in alcohols was derived.

An approach to the study of intermolecular interactions is based on the analysis of the thermodynamic functions of solvation. Solvation means the transfer of molecules from an ideal gas to an extremely dilute solution at constant temperature and pressure (T = 298.15 K and p = 0.1 MPa). Gibbs energy of solvation can be defined as Eq. (1):

$$\Delta_{\mathrm{solv}}G^{\mathrm{A/S}} = \Delta_{\mathrm{soln}}G^{\mathrm{A/S}} - \Delta_{\mathrm{vap}}G^{\mathrm{A}}. \tag{1}$$

where $\Delta_{\mathrm{solv}}G^{\mathrm{A/S}}$ is the Gibbs energy of solvation of substance A in solvent S; $\Delta_{\mathrm{soln}}G^{\mathrm{A/S}}$ is the Gibbs energy of dissolution of a substance A in solvent S; $\Delta_{\mathrm{vap}}G^{\mathrm{A/S}}$ is the Gibbs energy of vaporization of the liquid substance A. Gibbs energy of dissolution can be calculated from activity coefficients at infinite dilution ($\gamma_\infty^{\mathrm{A/S}}$) Eq. (2):

$$\Delta_{\mathrm{soln}}G^{\mathrm{A/S}} = RT\ln \gamma_\infty^{\mathrm{A/S}}. \tag{2}$$

The Gibbs energy of solvation in the environment of aliphatic alcohols includes the nonspecific solvation Gibbs energy [$\Delta_{\mathrm{solv(nonsp)}}G^{\mathrm{A/S}}$], the contribution of solvophobic effect ($\Delta_{\mathrm{s.e.}}G^{\mathrm{A/S}}$), and the Gibbs energy of specific interaction between the solute and the solvent [$\Delta_{\mathrm{int(sp)}}G^{\mathrm{A/S}}$]:

$$\begin{aligned}\Delta_{\mathrm{solv}}G^{\mathrm{A/S}} = \Delta_{\mathrm{solv(nonsp)}}G^{\mathrm{A/S}} + \Delta_{\mathrm{s.e.}}G^{\mathrm{A/S}} \\ + \Delta_{\mathrm{int(sp)}}G^{\mathrm{A/S}}.\end{aligned} \tag{3}$$

The Gibbs energy of nonspecific solvation corresponds to the van der Waals interactions between the molecules of the solute and the solvent. The contribution of solvophobic effect characterizes the special property of the associated systems as compared to nonassociated solvents. The Gibbs energy of specific interactions related to a localized donor–acceptor interaction is the difference between the Gibbs energies of all existing associates in the solution of a solute A with the solvent and the free form of the substance A.

It was shown in [24] that $\Delta_{\mathrm{s.e.}}G^{\mathrm{A/S}}$ linearly depends on the size of the solute molecules. So the Gibbs energy of specific interactions can be found [32, 33] as Eq. (4)

$$\begin{aligned}\Delta_{\mathrm{int(sp)}}G^{\mathrm{A/S}} = \Delta_{\mathrm{solv}}G^{\mathrm{A/S}} - \Delta_{\mathrm{solv}}G^{\mathrm{A/C_{16}H_{34}}} - (\delta_{\mathrm{cav}}g^{\mathrm{S}} \\ - \delta_{\mathrm{cav}}g^{\mathrm{C_{16}H_{34}}})\gamma_{\mathrm{X}}^{\mathrm{A}} - (a + b\sqrt{\delta_{\mathrm{cav}}g^{\mathrm{S}}})[(\Delta_{\mathrm{solv}}G^{\mathrm{A/R}} \\ - \Delta_{\mathrm{solv}}G^{\mathrm{A/C_{16}H_{34}}}) - (\delta_{\mathrm{cav}}g^{\mathrm{R}} - \delta_{\mathrm{cav}}g^{\mathrm{C_{16}H_{34}}})V_{\mathrm{x}}^{\mathrm{A}}] - cV_{\mathrm{x}}^{\mathrm{A}} - d,\end{aligned} \tag{4}$$

where $\Delta_{\mathrm{solv}}G^{\mathrm{A/S}}$, $\Delta_{\mathrm{solv}}G^{\mathrm{A/R}}$, $\Delta_{\mathrm{solv}}G^{\mathrm{A/C_{16}H_{34}}}$ are the Gibbs energies of solvation of A in the test solvent S and in two standard solvents (benzene and *n*-hexadecane); $\delta_{\mathrm{cav}}g^{\mathrm{S}}$, $\delta_{\mathrm{cav}}g^{\mathrm{R}}$ and $\delta_{\mathrm{cav}}g^{\mathrm{C_{16}H_{34}}}$ are the specific relative Gibbs energies of formation of a cavity in each solvent. This parameter corresponds to the nonspecific interactions with the solvent and depends on the difference in the Gibbs energies of solvation of *n*-octane in a solvent S ($\Delta_{\mathrm{solv}}G^{\mathrm{C_8H_{18}/S}}$) and in *n*-hexadecane ($\Delta_{\mathrm{solv}}G^{\mathrm{C_8H_{18}/C_{16}H_{34}}}$):

$$\delta_{\mathrm{cav}}g^{\mathrm{S}} = (\Delta_{\mathrm{solv}}G^{\mathrm{C_8H_{18}/S}} - \Delta_{\mathrm{solv}}G^{\mathrm{C_8H_{18}/C_{16}H_{34}}})/V_{\mathrm{x}}^{\mathrm{C_8H_{18}}}. \tag{5}$$

$V_{\mathrm{x}}^{\mathrm{A}}$ is the characteristic volume of the molecule by McGowan [34]; a = 0, b = 0.78 when the reference solvent R is benzene, and a = 0, b = 1.12, when R is carbon tetrachloride. Term ($c\ V_{\mathrm{x}}^{\mathrm{A}}$–$d$) corresponds to the contribution of the solvophobic effect of the alcohols. The values of c and d were evaluated previously [24] and are as follows: for methanol c = 5.17, d = 0.23; for ethanol c = 3.98, d = 0.83, for propanol-1 c = 3.94, d = 0.36, for butanol-1 c = 3.06, d = 0.50, for octanol-1 c = 1.78, d = 0.60.

We used Eq. (4) to determine the Gibbs energy of specific interaction of pyridines in the environment of aliphatic alcohols. The Gibbs energy of solvation of pyridine, 2- and 3-methylpyridines in aliphatic alcohols ($\Delta_{\mathrm{solv}}G^{\mathrm{A/ROH}}$) are listed in Table 2. A part of these data we have taken from the literature, and in this case for the calculation of Gibbs energies of solvation Eqs. (1), (2) and (6) were used:

$$\Delta_{\mathrm{solv}}G^{\mathrm{A/S}} = RT\ln\left(\frac{RT}{Lp^0V_{\mathrm{m}}^{\mathrm{S}}}\right), \tag{6}$$

where $V_{\mathrm{m}}^{\mathrm{S}}$ is the molar volume of solvent; p^0 is the standard pressure. The experimental Gibbs solvation

Table 1. Gibbs energies of solvation of pyridine, 2-methylpyridine, and 3-methylpyridine in a series of aliphatic alcohols, as well as the data for the calculation with the Eq. (4)[a] (kJ mol^{-1}), the specific relative Gibbs energies of the cavity formation in the solvents (kJ cm^{-3})

Base (A)	$\Delta_{solv}G^{A/CH_3OH}$	$\Delta_{solv}G^{A/C_2H_5OH}$	$\Delta_{solv}G^{A/C_3H_7OH}$	$\Delta_{solv}G^{A/C_4H_9OH}$	$\Delta_{solv}G^{A/C_8H_{17}OH}$	$\Delta_{solv}G^{A/C_{16}H_{34}}$	$\Delta_{solv}G^{A/C_6H_6}$
Pyridine	–8.4	–8.9 [30]	–8.4 [30]	–8.5 (–8.7) [30]	–9.8 [32, 33]	–6.2 [34]	–8.0 [35]
2-Methylpyridine	–11.2	–10.9	–11.2	–11.7	–13.2 [32, 33]	–8.5 [34]	–10.6 [35]
3-Methylpyridine	–12.5	–12.5	–12.2 [30]	–13.1 (–12.9) [30]	–14.2 [32, 33]	–9.7 [34]	–12.0
$\delta_{cav}g^S$	2.6	1.1	0.9	0.7	0.2	0.0	1.7

[a] All Gibbs energies are presented here in the mole fraction scale.

Table 2. Gibbs energies of specific interaction of aliphatic alcohols in pyridine (kJ mol^{-1})

Base (A)	$\Delta_{int(sp)}G^{A/CH_3OH}$	$\Delta_{int(sp)}G^{A/C_2H_5OH}$	$\Delta_{int(sp)}G^{A/C_3H_7OH}$	$\Delta_{int(sp)}G^{A/C_4H_9OH}$	$\Delta_{int(sp)}G^{A/C_8H_{17}OH}$
Pyridine	–4.0	–4.6	–3.6	–3.5	–4.5
2-Methylpyridine	–4.9	–4.5	–4.4	–4.6	–5.7
3-Methylpyridine	–4.8	–4.8	–4.1	–4.6	–5.4

energies obtained in this study from the activity coefficients are in good agreement with those calculated from the distribution coefficients [30] (Table 1). The Gibbs energies of solvation of pyridines in alcohols are almost independent of the length of the alcohol alkyl chain (Table 2), and only slightly increase with the introduction of a methyl group in the molecule of the base. Table 2 includes the Gibbs energies of the pyridine solvation in *n*-hexadecane and benzene required for the calculation. The relative values of the specific Gibbs energies of formation of a cavity in *n*-hexadecane and benzene were taken from [31], in alcohol, from [24]. All of them are listed in Table 2. The values of characteristic volumes V_x^A are equal to: 0.6753×10^{-2} cm^3 mol^{-1} for pyridine and 0.8162×10^{-2} cm^3 mol^{-1} for methylpyridines.

Table 2 lists the calculated Gibbs energies of specific interaction of pyridine in alcohol [$\Delta_{int(sp)}G^{A/ROH}$]. The Gibbs energy of specific interactions practically does not depend on the length of the alkyl radical of the alcohol and structure of the pyridines. The average value of $\Delta_{int(sp)}G^{A/ROH}$ is –4.6±0.4 kJ mol^{-1}.

Since the mole fraction scale is used for the Gibbs energy of specific interactions (a solution with the solute mole fraction $x = 1$ is taken for the standard state), the equilibrium constant of the hydrogen bond formation is introduced by Eq. (7) [31]:

$$\Delta\Delta_{int(sp)}G^{A/S} = -RT\ln(1 + K). \tag{7}$$

Since $K = [A\cdots S_n]_{bond}/[A]_{free}$, Eq. (7) can be transformed into Eq. (8):

$$\Delta_{int(sp)}G^{A/S} = RT\ln\alpha, \tag{8}$$

where α is a fraction of free solute molecules in solution. Using the values of the Gibbs energy of specific interaction from Table 2 we calculated the fraction of free molecules of the base, as well as the degree of binding pyridines in the aliphatic alcohol environment. It turned out that only 80–90% of the pyridines molecules are in bound state in solutions of aliphatic alcohols.

We have already mentioned that the evaluation of thermodynamic functions of the specific interaction in the associated media is a difficult task because of the existence of different clusters in equilibrium with each other. To demonstrate the difference in the thermodynamic functions of the specific interaction of pyridines with alcohol in the transition from an aprotic solvent to alcohol the derived Gibbs energy of specific interactions in the alcohol medium were compared with the Gibbs energies of formation of equimolar complexes pyridine–alcohol calculated from the free energies of solvation in the pyridines medium. Some of the $\Delta_{HB}G^{ROH/A}$ values are taken from [36], and other are calculated according to Eq. (5). At the dissolution

Table 3. Characteristic volumes of alcohol molecules by McGowan (cm^3 mol^{-1}), the Gibbs energies of solvation of aliphatic alcohols in pyridine, and the Gibbs energies of formation of equimolar complexes pyridine–alcohol (kJ mol^{-1})

Alcohol (ROH)	$V_x^A \times 10^{-2}$	$\Delta_{solv}G^{ROH/C_5H_5N}$	$\Delta_{solv}G^{ROH/2–C_6H_7N}$	$\Delta_{solv}G^{ROH/3–C_6H_7N}$	$\Delta_{HB}G^{ROH/C_5H_5N}$	$\Delta_{HB}G^{ROH/2–C_6H_7N}$	$\Delta_{HB}G^{ROH/3–C_6H_7N}$
Methanol	0.3082	–5.1 [31]	–5.0	–5.5	–8.7 [31]	–8.0	–8.3
Ethanol	0.4491	–6.8 [31]	–7.0 [31]	–7.3	–7.7 [31]	–7.9 [31]	–7.6
Propanol-1	0.5900	–9.2 [31]	–9.3	–9.5	–8.0 [31]	–7.2	–7.4
Butanol-1	0.7309	–11.9	–12.1	–11.5	–9.6	–9.0	–8.8
Octanol-1	1.2950	–20.6[a]	–21.3[a]	–18.6[a]	–9.7 (–8.1[b])	–8.5 (–8.3[b])	–8.6 (–8.1[b])

[a] The value was estimated based on the linear dependence of the Gibbs energies of solvation of alcohols in pyridines on their characteristic sizes. [b] The values are derived from the constants of the complex formation.

Table 4. Entropies of specific interaction of pyridines in aliphatic alcohols, as well as the entropies of formation of equimolar pyridine–alcohol complexes (J mol^{-1} K^{-1})

Alcohol (ROH)	$\Delta_{int(sp)}S^{C_5H_5N/ROH}$	$\Delta_{int(sp)}S^{2–CH_3C_5H_4N/ROH}$	$\Delta_{int(sp)}S^{3–CH_3C_5H_4N/ROH}$	$\Delta_{HB}S^{ROH/C_5H_5N}$	$\Delta_{HB}S^{ROH/2–CH_3C_5H_4N}$	$\Delta_{HB}S^{ROH/3–CH_3C_5H_4N}$
Methanol	1.3	–5.7	–1.3	–25.2	–36.9	–32.2
Ethanol	4.7	–2.0	2.3	–27.5	–35.2	–31.9
Propanol-1	5.0	0.0	2.7	–25.2	–35.9	–30.9
Butanol-1	5.4	3.0	6.0	–20.5	–31.5	–27.2
Octanol-1	11.7	8.1	9.1	–19.8	–33.6	–27.5

of an alcohol in the medium of a base the solvophobic effect is absent, therefore the term ($cV_x^A – d$) is zero. The Gibbs energies of solvation of alcohols in the pyridines are shown in Table 3. The Gibbs energies of octanol-1 solvation in pyridines were evaluated based on the linear dependence of Gibbs energies of solvation of alcohols in pyridines on their characteristic sizes (see figure). The equations of these relationships were used in the calculations.

$$\Delta_{solv}G^{ROH/C_5H_5N} = –16.18V_x^{ROH} + 0.18, \quad (9)$$

$$\Delta_{solv}G^{ROH/2–C_6H_7N} = –16.75V_x^{ROH} + 0.35, \quad (10)$$

$$\Delta_{solv}G^{ROH/3–C_6H_7N} = –14.34V_x^{ROH} + 1.00. \quad (11)$$

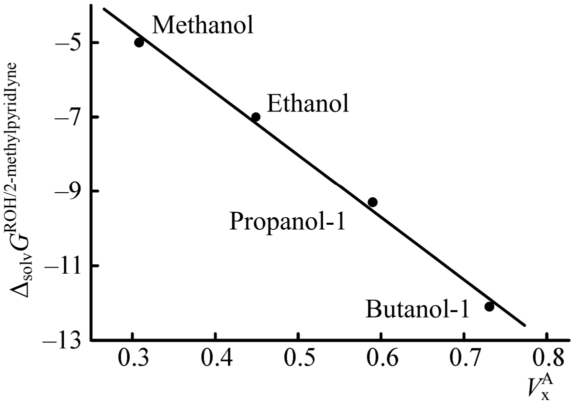
To calculate the Gibbs energies of hydrogen bonding of alcohols in pyridine and methylpyridines, carbon tetrachloride ($\delta_{cav}g^{S}R = 0.8\times10^{-2}$ kJ cm^{-3}, $a = 0$, $b = 1.39$) was used as a reference solvent R since the alcohols are capable of forming weak hydrogen bonds with the benzene molecule [36]. The Gibbs energies of solvation of alcohols in carbon tetrachloride and *n*-hexadecane are taken from [31]. The relative values of the specific Gibbs energies of formation of a cavity in a pyridine, which are used in the calculation according to Eq. (5), are as follows: pyridine, $\delta_{cav}g^R = 4.5\times10^{-2}$ kJ cm^{-3}, 2-methylpyridine, $\delta_{cav}g^R = 2.8\times10^{-2}$ kJ cm^{-3}, 3-methylpyridine: $\delta_{cav}g^R = 3.4\times10^{-2}$ kJ cm^{-3}.

The complexation constants of octanol-1 with pyridines in the carbon tetrachloride medium can also be estimated with the Abraham's equation (12) [11]:

$$\log K^{A\cdots B} = 7.354\alpha_2^H\beta_2^H – 1.094, \quad (12)$$

where α_2^H and β_2^H are acidity parameter of the proton-donor [11] and basicity parameter of the proton-acceptor [10] involved in the complex formation. The values of the Gibbs energies of the hydrogen bond calculated using the constants of complex formation in the mole fraction scale are shown in Table 3 in parentheses.

The values of $\Delta_{HB}G^{ROH/A}$ correspond to the free energy of formation of 1:1 complexes between the molecules of an alcohol and a pyridine. It is interesting to note that their values are also insignificantly changed with increasing alkyl chain of the alcohol. As seen in Tables 3 and 4, the Gibbs energies of specific interaction of pyridine and picolines in alcohols [$\Delta_{int(sp)}G^{A/ROH}$] are more endothermic than the Gibbs



Comparison of Gibbs energies of solvation of aliphatic alcohols in 2-methylpyridine with characteristic molecular volumes of the alcohols.

energies of the formation of equimolar heterocomplexes ($\Delta_{HB}G^{ROH/A}$) in the medium of the bases. It is evidently caused by the effect of the reorganization of the associated solvent. This process can be represented as a shift in equilibrium between different forms of alcohol associates due to the dissolution in it of the molecules of proton acceptor [2, 23, 37, 38]. The specific interaction of a proton acceptor with the associated solvent is a complex process. On the one hand, this interaction involves the formation of cooperative hydrogen bonds of the pyridine molecule with the alcohol cluster. On the other hand, the specific interaction is accompanied by the rupture of hydrogen bonds in the alcohol–alcohol clusters

$$(ROH)_n + B \rightleftarrows (ROH)_m\cdots B + (ROH)_k,\ m + k = n. \quad (13)$$

Table 5. Activity coefficients at the infinite dilution at 298.15 K

Solute (A)	Solvent	$\gamma_\infty^{A/S}$
Pyridine	Methanol	1.20±0.08
″	Butanol-1	1.18±0.08
2-Methylpyridine	Methanol	0.72±0.05
″	Ethanol	0.81±0.02
″	Propanol-1	0.73±0.02
″	Butanol-1	0.60±0.02
3-Methylpyridine	Methanol	0.79±0.02
″	Ethanol	0.80±0.02
″	Butanol-1	0.62±0.02
Methanol	3-Methylpyridine	0.65±0.02
Ethanol	″	0.66±0.08
Propanol-1	″	0.77±0.05
Butanol-1	″	1.08±0.06
Methanol	2-Methylpyridine	0.78±0.03
Propanol-1	″	0.83±0.08
Butanol-1	″	0.85±0.03
″	Pyridine	0.93±0.03

It is noteworthy that the difference in Gibbs energies of hydrogen bonding in the alcohol medium and in the 1:1 complexes are less in absolute value than the same for enthalpies. Thus, the enthalpy of complexation of 2-methylpyridine with ethanol is –18.4 kJ mol^{-1}, the enthalpy of specific interaction of 2-methylpyridine in ethanol is –5.1 kJ mol^{-1} [26].

The obtained Gibbs energies of the specific interaction of the pyridines in the alcohol, as well as published data on the enthalpies of specific interactions in these systems [26], allowed us to calculate the entropy of the specific interaction of pyridines in the aliphatic alcohols media:

$$\Delta_{int(sp)}S^{A/S} = [\Delta_{int(sp)}H^{A/S} - \Delta_{int(sp)}G^{A/S}]/T. \quad (14)$$

Table 5 lists the obtained values of $\Delta_{int(sp)}S^{A/ROH}$ and also shows the entropies of formation of equimolar pyridine–alcohol complexes in the media of the bases. The entropies of specific interaction between pyridines in the alcohol media are less in absolute value compared to the entropies of 1:1 complexation (ROH···A) in the medium of a base. The values of $\Delta_{int(sp)}S^{A/ROH}$ are close to zero, and in some cases, even positive. This fact is not trivial, since the published values of the complexation entropy are negative [12]. The absolute value of the entropies of specific interaction of pyridines in the aliphatic alcohols increases with the alkyl chain in the molecule of the solvent, while the entropy of complexation of pyridines with one molecule of alcohol in an aprotic solvent is about the same. Apparently, the entropy favorable process of breaking up the alcohol associates compensates the heat expenditure for the formation of a free hydroxy group due to the rupture of the alcohol–alcohol hydrogen bonds.

Thus, we carried out a comprehensive study of the thermodynamics of specific interaction of pyridines in aliphatic alcohols. Limiting activity coefficients of pyridine, 2-methylpyridine, and 3-methylpyridine in methanol, ethanol, propanol-1, and butanol-1 were measured by means of the gas chromatographic analysis. The calculated Gibbs energies of the specific interaction in the studied systems were found to be independent of the molecular structure of the solvent and solute. These values allowed us to determine the fraction of free molecules of pyridines in the environment of aliphatic alcohols, which unexpectedly turned out to be different from zero. We also calculated the entropies of a specific interaction of pyridines in aliphatic alcohols. For all the systems studied, obtained values are close to zero. The Gibbs energies and the entropies of the specific interaction of pyridines in the aliphatic alcohols are more positive than the thermodynamic functions of the 1:1 complexes formed in an aprotic solvent. This is due to the reorganization of the solvent–solvent hydrogen bonding in the associated liquid at the dissolution of molecules of a proton-acceptor. These data demonstrate the complex nature of specific interactions in the associated solvent medium. The data obtained can be used to analyze the effect of an associated solvent on the thermodynamics of the various processes.

EXPERIMENTAL

We used the reagents from Acros Organics (mass fraction no less than 0.98), which were further purified by usual methods [39]. Methanol was refluxed over magnesium methanolate in the presence of iodine, and then fractionally distilled over calcium hydride. Ethanol was subjected to prolonged boiling with calcium oxide, and then successively distilled over calcium hydride and an excess of sodium. 1-Propanol and 1-butanol were kept over alkali, and then fractionally distilled from sodium. Pyridine was dried over calcium hydride. Water content was determined by Karl Fischer titration and by IR-spectroscopy.

Activity coefficients were measured by the static gas chromatographic analysis of the equilibrium vapor (Chromatec Crystall-2000M gas chromatograph, quartz glass column with RTX-5 Amine stationary phase). The determination procedure is described in [40]. The calibration was performed by measuring the activity coefficients in the systems: benzene, toluene (the measured value 0.95, published 0.95 [41]), and diethylamine in *n*-hexadecane (the measured value 1.05, published 1.08 [42]). To measure the activity coefficients, 1 ml of a solution or pure substance was placed in a sealed thermostated 15 ml ampule (T = 298.15 K). The concentration of solutions was 1 vol %. The area of the peak in the chromatogram is proportional to the volume of the sample and the vapor pressure of the substance over the solution in the ampule. The sample volume depends on the flow rate of carrier gas, so during the entire experiment it is kept constant. The activity coefficient is calculated by Eq. (15):

$$\gamma_{\infty}^{\mathrm{A/S}} = \frac{p_{\mathrm{A}}^{\mathrm{A/S}}}{p_{\mathrm{sat}}^{\mathrm{A}} x_{\mathrm{A}}^{\mathrm{A/S}}}, \qquad (15)$$

where $x_{\mathrm{A}}^{\mathrm{A/S}}$ is the mole fraction of solute A in solvent S, $p_{\mathrm{sat}}^{\mathrm{A}}$ is the vapor pressure of pure substance A, $p_{\mathrm{A}}^{\mathrm{A/S}}$ is vapor A pressure over solution of the substance in a solvent S. Vapor pressure of pure substances $p_{\mathrm{sat}}^{\mathrm{A}}$ was taken from the database of the EPI Suite software [43]. The values of $\gamma_{\infty}^{\mathrm{A/S}}$ obtained are listed in Table 5. For each system 3 to 4 measurements were carried out, which were then averaged across all measurements, the measurement error did not exceed 10%. The resulting activity coefficients for solutions of various pyridines in the environment of aliphatic alcohols are practically independent of the length of the alkyl chain of the alcohol and are close to each other.

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