

# Manifestation of hydrogen bonds of aqueous ethanol solutions in the Raman scattering spectra

T.A. Dolenko, S.A. Burikov, S.V. Patsaeva, V.I. Yuzhakov

**Abstract.** Spectra of Raman scattering of light by aqueous ethanol solutions in the range of concentrations from pure water to 96 % alcohol are studied. For water, 25 %, and 40 % solutions of ethanol in water, as well as for 96 % alcohol the Raman spectra are measured at temperatures from the freezing point to nearly the boiling point. The changes in the shape of the stretching OH band are interpreted in terms of strengthening or weakening of hydrogen bonds between the molecules in the solution. The strongest hydrogen bonding of hydroxyl groups is observed at the ethanol content from 20 to 25 volume percent, which is explained by formation of ethanol hydrates of a definite type at the mentioned concentrations of alcohol. This is confirmed by means of the method of multivariate curve resolution, used to analyse the Raman spectra of aqueous ethanol solutions. With growing temperature the weakening of hydrogen bonding occurs in all studied systems, which consists in reducing the number of OH groups, linked by strong hydrogen bonds.

**Keywords:** Raman scattering, stretching vibrations, hydrogen bond, aqueous ethanol solutions, ethanol hydrates.

## 1. Introduction

The properties of aqueous ethanol solutions nonlinearly depend on their quantitative composition. The range of concentrations of ethanol in water from 22 % to 27 % is characterised by anomalous behaviour of many physical and chemical properties [1–6]. (In the present paper the concentration is expressed in volume percent.) Thus, in the paper by Mendeleyev [1] the dependence of the first derivative of the density of aqueous ethanol solutions on the concentration of ethanol had extremums at certain concentrations, including 22 %. The heat capacity of the mixture has a maximum at the concentration of alcohol about 27 % [3]. At a 25 % concentration of ethanol in the solution, the authors of Refs [4, 5] discovered the existence of sharp maxima of Rayleigh scattering of light, whose amplitudes decrease with increasing temperature. In

Ref. [6], based on the study of the absorption spectra of rhodamine 6G in aqueous ethanol solutions, the binding energy of associated rhodamine molecules was calculated, which appeared to be maximal at the ethanol content about 25 %.

The authors of Refs [7, 8] explained the properties of aqueous alcohol solutions in the framework of the concept of the solvent structure stabilisation by nonelectrolytes. However, in the literature there is no consentient opinion about the kind of complexes (water–water, water–alcohol, alcohol–alcohol) that dominate in the solution at different concentrations of alcohol. The authors of [9] developed the theory describing hydrophobic interaction of nonpolar molecules with water that produces clathrate-like structures around nonelectrolyte molecules, changing the network of hydrogen bonds between the water molecules. The experimental data on the differential thermal analysis (DTA) of water–ethanol systems confirm the production of water–alcohol hydrates of semi-clathrate nature, in which the hydroxyl group of the ethanol molecule participates in the formation of the water framework of the clathrate hydrate [10]. The study of low-frequency ( $60\text{--}185\text{ cm}^{-1}$ ) bands of the Raman spectrum at changing the solution concentration from pure water to pure alcohol [11] indicates incomplete mixing of water and alcohol: at any composition the associates of both water and ethanol molecules exist in the mixture. Using the methods of NMR and IR spectroscopy [12] it is shown that at low content of alcohol the bonds strengthen between water molecules that form the clathrate-like structure around the ethanol molecules in the solution, while the hydrogen bonds between the proton of the ethanol hydroxyl group and the oxygen atom of the water molecule do not arise. Differential scanning calorimetry and dielectric relaxation technique revealed the existence of alcohol hydrates of clathrate nature with the composition  $A \cdot 5\text{H}_2\text{O} - A \cdot 6\text{H}_2\text{O}$  in aqueous solutions of a number of alcohols, including ethanol [13]. Using the method of neutron diffraction it was shown [14] that the ethanol molecules form micelle-like structures in aqueous solutions.

The absence of common understanding of the processes, taking place in the course of mixing water and ethanol, in the literature and the existing controversies in explaining the anomalous properties of these solutions stimulate closer investigation of molecular interactions in aqueous ethanol solutions. Important information about the intra- and intermolecular interactions in water and aqueous solutions can be obtained from the Raman spectra [15–17]. In the present work we continue the studies of molecular inter-

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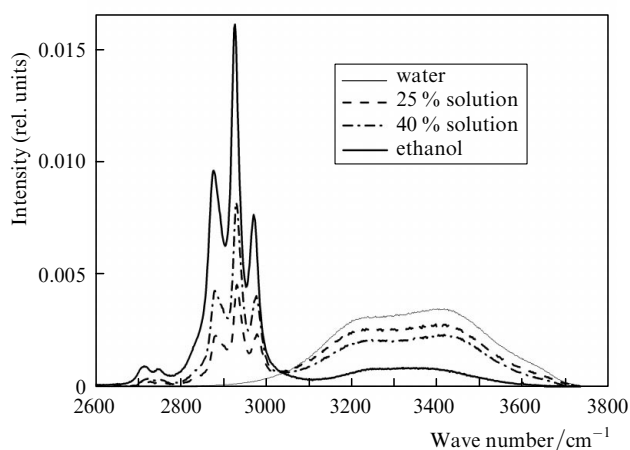
actions in the water–ethanol system with different content of alcohol using the Raman spectroscopy and the method of multivariate curve resolution for the analysis of the spectra [18].

## 2. Experimental technique

The laser Raman spectrometer is described in detail elsewhere [19]. The excitation of Raman spectra was accomplished using the radiation of the argon laser with the wavelength 488 nm and the power about 350 mW. The registration of the spectra was implemented using a CCD-camera; the actual resolution of the Raman spectrometer was  $2\text{ cm}^{-1}$ . The temperature of the samples during the concentration measurements was kept constant using the IRT-2 temperature meter-adjuster and equalled  $22.0 \pm 0.2\text{ }^\circ\text{C}$ . For water, aqueous solutions containing 25% and 40% of ethanol and for 96% ethanol the Raman spectra were measured at different temperatures from the freezing point to nearly the boiling point; the minimal temperature was  $-27\text{ }^\circ\text{C}$  and the maximal one reached  $90\text{ }^\circ\text{C}$ . To measure and keep the required temperature we used the liquid-based low-temperature Cryo-BT-01 thermostat that allowed fixing any temperature from  $-30\text{ }^\circ\text{C}$  to  $+100\text{ }^\circ\text{C}$  with an accuracy of  $0.3\text{ }^\circ\text{C}$ . The reservoirs with the studied solutions were placed inside the thermostat. The probing of samples and detection of the scattered light were implemented via the combined input-output light guide, whose central filament was used to transmit the laser radiation, while the peripheral ones were used to transmit the optical echo-signal to the detector of the spectrometer.

## 3. Dependence of Raman spectra in the region of stretching vibrations of CH and OH groups upon the alcohol concentration

Figure 1 represents the Raman spectra of aqueous alcohol solutions of different concentration at  $5\text{ }^\circ\text{C}$  in the region of wave numbers  $2600\text{--}3800\text{ cm}^{-1}$ . The intensity of the presented stretching bands is scaled to their total area. In this spectral region the stretching vibrations of CH groups of ethanol, as well as those of OH groups of water

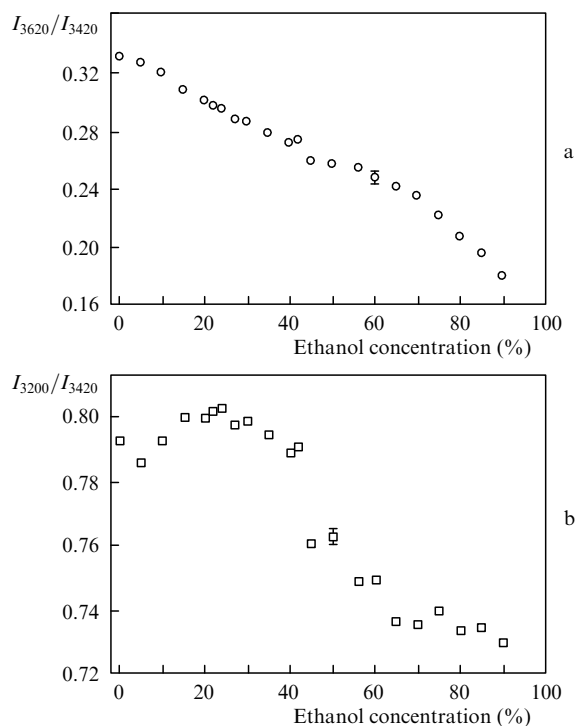


**Figure 1.** Raman spectra in the region of stretching vibrations of CH- and OH-groups for aqueous alcohol solutions with different concentration at the temperature  $5\text{ }^\circ\text{C}$ .

and ethanol, manifest themselves. The band of CH group stretching vibrations  $2800\text{--}3000\text{ cm}^{-1}$  has several distinct peaks, whose position, width and intensity depend on the ethanol concentration in the solution. The amplitudes of all peaks essentially and not synchronously increase with increasing ethanol content, while their position and width change insignificantly in the studied range of ethanol concentrations.

The integral intensity of the broad structureless band of stretching OH vibrations ( $3000\text{--}3700\text{ cm}^{-1}$ ) decreases with increasing ethanol content (Fig. 1), since the concentration of OH groups decreases. With the increase in the ethanol concentration the shape of the stretching vibration band of hydroxyl OH-groups of water and ethanol also exhibits essential changes. To estimate quantitatively the change in the shape of the stretching OH-band we introduced the intensity ratios at the frequencies  $3620$  and  $3420\text{ cm}^{-1}$  and also at  $3200$  and  $3420\text{ cm}^{-1}$  within this band. The positions of the mentioned frequency components were chosen using the singular points of the calculated second derivative of the spectral intensity of the OH-group stretching band. The low-frequency part of the stretching OH-band at  $3200\text{ cm}^{-1}$  is caused by the vibrations of OH groups with strong hydrogen bonds, the region of the stretching OH band in the vicinity of  $3420\text{ cm}^{-1}$  is due to the vibrations of OH oscillators with weak hydrogen bonds, and the higher frequency region of the stretching band (at  $3620\text{ cm}^{-1}$ ) is due to the vibrations of water molecules with broken hydrogen bonds [20]. Therefore, the intensity ratio  $I_{3200}/I_{3420}$  shows the relative number of OH groups with strong and weak hydrogen bonds, while the ratio  $I_{3620}/I_{3420}$  shows the relative number of OH groups with broken and weak hydrogen bonds.

The dependences of the intensity ratios  $I_{3620}/I_{3420}$  and

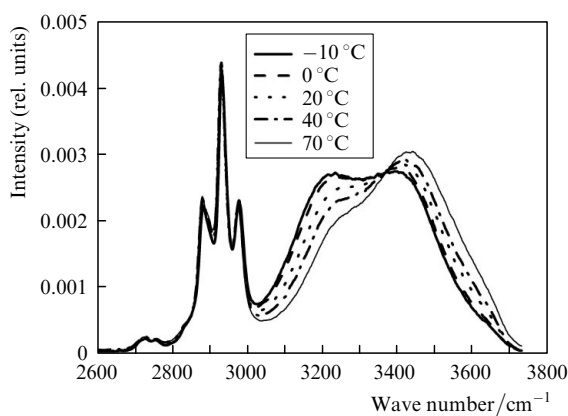


**Figure 2.** Intensity ratios  $I_{3620}/I_{3420}$  (a) and  $I_{3200}/I_{3420}$  (b) versus ethanol concentration in the solution (expressed in volume percent) at the temperature of solutions  $22\text{ }^\circ\text{C}$ .

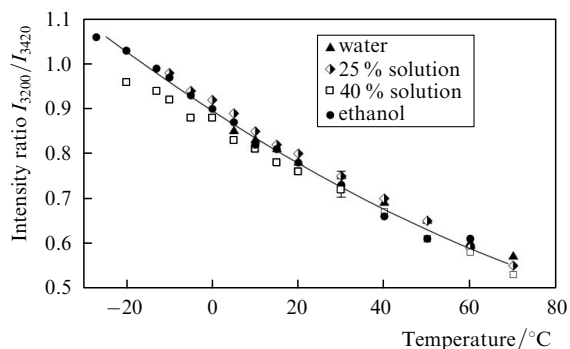
$I_{3200}/I_{3420}$  on the ethanol concentration in the solution are presented in Fig. 2. It is seen that the ratio  $I_{3620}/I_{3420}$  decreases monotonically with increasing ethanol concentration in the solution. This may be explained by the reduction of the fraction of free hydroxyl groups, not linked with a hydrogen bond (both in alcohol and in water molecules). The dependence of  $I_{3200}/I_{3420}$  on the ethanol concentration behaves in a more sophisticated way (Fig. 2b), namely, for diluted solutions it increases, at the ethanol concentrations from 20% to 25% has its maximum, and then decreases with increasing concentration. Such a behaviour of the curve means that at the ethanol concentrations 20% – 25% in the solution the fraction of strong hydrogen bonds is maximal in the studied concentration range. This result confirms the hypothesis that at the mentioned concentrations of alcohol in the water–ethanol systems the structure rearrangement is observed, as a result of which the stabilisation of water structure by ethanol molecules and the strengthening of hydrogen bonds between the hydroxyl groups occur. At further increasing the ethanol concentration the hydrogen bonds in the solution become weaker.

#### 4. Temperature dependence of Raman spectra of aqueous ethanol solutions in the region of stretching vibrations of CH and OH groups

The variations of Raman spectra of 25% solution of ethanol in water with the change in temperature are shown in Fig. 3. With the growth of temperature the band of stretching CH vibrations do not practically change both its shape and intensity. On the contrary, the band of stretching vibrations of hydroxyl groups essentially changes its shape: with the growth of temperature the intensity in the region  $3200\text{--}3300\text{ cm}^{-1}$  decreases and the intensity of scattering in the region of higher frequency vibrations ( $3400\text{--}3600\text{ cm}^{-1}$ ) increases. Similar behaviour of the Raman spectra is observed when the temperature changes from  $-27\div 5\text{ }^{\circ}\text{C}$  to  $50\div 90\text{ }^{\circ}\text{C}$  for water, 40% solution of ethanol in water, and 96% ethanol. For each sample the stretching CH band does not change its shape and intensity, but with growing temperature the intensity of the low-frequency region of the stretching OH band monotonously decreases and the intensity of the high-frequency region increases (Fig. 4 and Table 1).



**Figure 3.** Temperature dependence of the Raman spectra of 25% solution of ethanol in water.



**Figure 4.** Dependence of the intensity ratio  $I_{3200}/I_{3420}$  in the Raman spectra of water, ethanol, and aqueous alcohol solutions with concentrations 25% and 40% on the temperature of the samples. The approximating curve is drawn for the point, corresponding to the intensity ratio in the Raman spectrum of ethanol.

**Table 1.** Intensity ratios  $I_{3200}/I_{3420}$  at the frequencies  $3200 \pm 4$  and  $3420 \pm 4\text{ cm}^{-1}$  in the Raman spectra of water, aqueous alcohol solutions with concentrations 25% and 40%, and 96% ethanol, measured at different temperatures.

Temperature/ $^{\circ}\text{C}$	Water	25% solution	40% solution	96% ethanol
-27				1.06
-20			0.96	1.03
-10		0.98	0.92	0.97
0		0.92	0.88	0.90
5	0.85	0.89	0.83	0.87
10	0.83	0.85	0.81	0.82
15	0.81	0.82	0.78	0.81
20	0.78	0.80	0.76	0.78
30	0.75	0.75	0.72	0.73
40	0.69	0.70	0.67	0.66
50	0.65	0.65	0.61	0.61
60	0.60	0.59	0.58	0.61
77	0.54	0.54	0.50	
90	0.50			

Note: The intensities are averaged over the intervals  $8\text{ cm}^{-1}$  ( $\pm 4\text{ cm}^{-1}$ ).

Such behaviour of the stretching OH band is an evidence of monotonous weakening of hydrogen bonding in the solution with the temperature growth. The weakening of hydrogen bonding is understood as reduction of the fraction of OH groups with strong hydrogen bonds and increase in the fraction of OH groups with weak or broken hydrogen bonds. In this case it is possible to say that the mean energy of hydrogen bonding per a hydroxyl group (or per a molecule of water at small concentrations of ethanol in the solution) decreases.

#### 5. Analysis of the components of the concentration series of Raman spectra of aqueous alcohol solutions using the method of multivariate curve resolution

The essence of the Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS) method consists in searching for partial spectra and concentration profiles of the components basing on a set of spectra of the system, which is a mixture of components with different contents [18]. Consider a system, consisting of several components (e.g., substances or complexes), each having its spectrum  $S$

(the spectra may overlap, but should be different). Let the concentrations of the components regularly change in time, so that the mixture spectrum at any moment of time  $t$  is a linear superposition of the products of concentrations of the components by their partial spectra. Then the results of the experiment (the spectra of the mixture at different moments of time) may be presented in the form

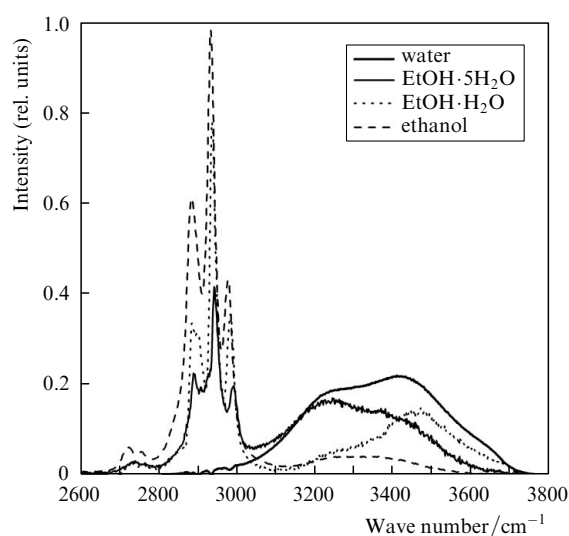
$$\mathbf{X} = \mathbf{CS}^t + \mathbf{E}.$$

Here, the matrices of data  $\mathbf{X}$  and error  $\mathbf{E}$  have the dimension  $I \times J$ , where  $I$  is the number of observations in time;  $t_1, \dots, t_I$ , and  $J$  is the number of wavelengths  $\lambda_1, \dots, \lambda_J$  in the spectrum. If  $A$  components are present in the system, then the concentration matrix  $\mathbf{C}$  has  $I$  rows and  $A$  columns. Each its column is a profile of the concentration change for the corresponding substance. The matrix of pure spectra  $\mathbf{S}^t$  (it is more convenient to present it in the transposed form) has  $A$  rows and  $J$  columns. Each row of this matrix is a pure spectrum of the corresponding component. The problem of curve resolution consists in determining the number of components  $A$  using the given data matrix  $\mathbf{X}$ , the concentration matrix  $\mathbf{C}$ , and the matrix of pure spectra  $\mathbf{S}$  (partial spectra of the components). It is assumed that we have no *a priori* knowledge about the matrices  $\mathbf{C}$  and  $\mathbf{S}$ , except the most general and natural limitations: non-negativity, continuity (in  $t$  and  $\lambda$ ), etc.

The MCR-ALS method found wide application in the spectroscopy of mixtures [18, 21–23]. In the papers [21–23] it was assumed that different types of molecular complexes (referred as components) are present in the mixture, and instead of measurements at different moments of time  $t$  the measurements at different concentrations of the mixture ingredients are considered. In Ref. [21] the MCR-ALS method was used to analyse the molecular association in aqueous solutions of methanol basing on the IR absorption spectra. Four components of the solution were found, namely, the methanol associates, the water associates and the water–methanol complexes of two types with the ratio of molecules 1:1 and 4:1, respectively. In Refs [22, 23], this method was applied to the analysis of the IR absorption spectra of aqueous ethanol solutions. Thus, the authors of [22] found four components, namely, the water associates, the ethanol associates and two types of water–ethanol complexes (or ethanol hydrates) with the composition  $\text{EtOH} \cdot 5.36\text{H}_2\text{O}$  and  $\text{EtOH} \cdot 1.28\text{H}_2\text{O}$ , where 5.36 and 1.28 are actually the hydrate numbers, showing the mean number of water molecules per one ethanol molecule. The composition of hydrates in [22, 23] was determined by means of comparing the area of partial MCR-components with that of the experimental spectra of IR absorption (searching for two solutions with the nearest areas of spectra and linear interpolation of the concentration). However, for the Raman spectra this approach is not applicable, since the measurement of absolute intensities of Raman scattering is a complicated experimental problem.

In the present paper the method of multivariate curve resolution is used to analyse the experimental Raman spectra of aqueous ethanol solutions in the whole range of possible concentrations of ethanol. In Fig. 5 the partial spectra are presented, i.e., the spectral curves in the region of CH and OH bands for four types of molecular complexes of the aqueous ethanol solution, obtained as a result of application of the MCR-ALS method. The spectrum of water associates is similar to that of the pure water, and the

spectrum of ethanol associates is similar to that of pure ethanol. However, it is not sufficient to have only two components, pure water and pure ethanol, to describe the series of Raman spectra of aqueous ethanol solutions of all concentrations by means of a linear combination of partial spectra. The use of MCR-ALS method demonstrated that there are two more components whose partial spectra strongly contribute to the Raman spectra of the solutions. We identify these components as complexes, consisting of water and ethanol molecules, i.e., ethanol hydrates, since in their partial spectra both CH and OH stretching bands are present. For the first-type hydrate the OH band is predominant in the spectrum, for the hydrate of the second type the CH band prevails. It should be noted that the spectra of both the first- and the second-type hydrates strongly differ from the Raman spectra of water, ethanol or their mixtures in the region of OH group stretching vibrations.



**Figure 5.** Spectra of molecular complexes of the aqueous ethanol solution, obtained using the MCR-ALS method from the concentration dependence of Raman spectra of aqueous ethanol solutions.

The approach we use in the present paper to determine the hydrate numbers of the ethanol–water complexes by means of MCR-ALS is different from that of Refs [22, 23]. The new method is based on the linear dependence of the ratio of the stretching CH or OH band intensity to the sum of these intensities, discovered by us earlier [19]. For partial spectra the same intensity ratio for CH and OH bands is calculated as for the experimental solutions with known concentrations of alcohol, and then the obtained linear calibration dependence is used to find the concentration of alcohol in the hydrate from the ratio of CH and OH bands in the MCR-spectrum. We applied this approach to analyse the Raman spectra of aqueous ethanol solutions described above. First, the linear calibration dependences of the integral intensities of the CH band  $I_{\text{CH}}$  and the OH band  $I_{\text{OH}}$ , normalised to their total intensity  $I_{\text{CH}} + I_{\text{OH}}$ , on the ethanol concentration were obtained. Then for the spectra of ethanol hydrates, found by means of the MCR-ALS method, the values of  $I_{\text{CH}}/(I_{\text{CH}} + I_{\text{OH}})$  and  $I_{\text{OH}}/(I_{\text{CH}} + I_{\text{OH}})$  were calculated and, using the calibration dependences, the concentrations of ethanol in the complexes were determined. This approach provides reliable estimation of

the composition of water–ethanol complexes, independent of the absolute intensity of Raman spectra, and is stable with respect to noises present in the experimental spectra.

The hydrate numbers, derived by us from the Raman spectra of the solutions, appeared to equal 5.05 for the ethanol hydrates of the first type and 2.40 for the hydrates of the second type. It is important to note, that the obtained values are in satisfactory agreement with the hydrate numbers 5.36 and 1.28, found for associates in aqueous ethanol solutions from IR absorption spectra [22, 23]. Thus, the averaged formulas for the hydrates may be written as  $\text{EtOH} \cdot 5\text{H}_2\text{O}$  and  $\text{EtOH} \cdot \text{H}_2\text{O} - \text{EtOH} \cdot 2\text{H}_2\text{O}$ .

## 6. Discussion of the obtained results

Based on the analysis of the concentration dependence of Raman spectra of aqueous ethanol solutions we conclude that the hydrogen bonds in the solution at the ethanol concentration 20 %–25 % are stronger than in pure water, i.e., that the number of OH groups, linked by strong hydrogen bonds with the adjacent water molecules, increases at these concentrations. The form of hydrate spectra, obtained by multivariate resolution of bands of CH and OH groups, also confirms this conclusion. For the hydrates of the first type with water/alcohol molecule number ratio 5:1 a specific feature of the spectrum is the intense peak in the low-frequency part of the stretching OH band (near  $3200 \text{ cm}^{-1}$ ), which is a signature of large number of strong hydrogen bonds between the OH groups of molecules in the solution as compared with the pure water. Since in this hydrate the water molecules are prevalent, we conclude that in the complexes with the composition  $\text{EtOH} \cdot 5\text{H}_2\text{O}$  the bonds between water molecules are just those that become stronger. Similar strengthening of hydrogen bonds between water molecules in the gaseous hydrate leads to the intensity increase of the stretching band low-frequency part (near  $3200 \text{ cm}^{-1}$ ) observed in the Raman spectra [24]. On the contrary, for the ethanol hydrates of the second type the weakening of hydrogen bonds occurs, which appears as the intensity reduction of the low-frequency part of the OH stretching vibration band. Such an interpretation of the hydrate spectra, obtained using the MCR-ALS method, corresponds to the conception of clathrate or clathrate-like structure of the first-type hydrates and the chain structure of the second-type ones.

At the ethanol concentration in the solution from 20 % to 25 % the number of alcohol molecules becomes large enough to disturb the spatial network of hydrogen bonds, typical for pure water. The penetration of alcohol molecules causes a rearrangement of the network of hydrogen bonds, because the alcohol molecules cannot fit into the cavities, formed by the network of hydrogen bonds, typical for pure water. The embedding of ethanol molecules occurs in such a way, that the polar OH groups of ethanol substitute water molecules in the spatial network of hydrogen bonds, while the more extensive hydrophobic groups of ethanol enter the cavities, formed by the water molecules, arranged 'in a new way', i.e., with new organisation of the network of hydrogen bonds between them. As a result the first-type hydrates are produced, or the 'guest–host'-type compounds (clathrates), where the ethanol molecule is hold fixed in the skeleton consisting of water molecules, between which the hydrogen bonds become stronger due to hydrophobic interaction. In

the liquid phase the hydrogen bonds between the molecules permanently break down and arise again, so that the structure, typical for clathrates in the solid phase, is eroded, and it is reasonable to speak only about 'clathrate-like' structures in the solution.

In the hydrates of the second type, i.e., chains consisting of water and alcohol molecules, the molecules of water can form two or three hydrogen bonds (unlike in pure water, where each molecule can form, at an average, four hydrogen bonds). The hydrogen bonds in water and solutions have cooperative character, which manifests itself in their strengthening at increasing the average number of bonds per one molecule of water. Therefore, in the second-type hydrates the hydrogen bonds become weaker as compared with pure water. The concentration of such hydrates begins to grow at the ethanol content in the solution higher than 25 %, therefore the hydrogen bonds in solutions with higher concentration become gradually weaker. In the Raman spectra this is seen as monotonous decrease of the ratio  $I_{3200}/I_{3420}$ .

With the growth of temperature from the freezing point to the temperature near the boiling point of the aqueous alcohol solution the gradual weakening of hydrogen bonding occurs. This is valid for all studied concentrations of the aqueous alcohol solutions. The weakening of hydrogen bonds manifests itself in the increase in the fraction of OH groups with weak or broken hydrogen bonds and in the decrease in the mean energy of hydrogen bond per one hydroxyl group.

## 7. Conclusions

The study of concentration dependences of Raman spectra of aqueous ethanol solutions from pure water to pure ethanol confirms the enhancement of hydrogen bonds in the solution at the ethanol concentration 20 %–25 % as compared with the pure water, i.e., the number of OH groups, linked with the adjacent water molecules by strong hydrogen bonds, increases. It is supposed that such a change in the hydrogen bonding in solutions is caused by its structure rearrangement, namely, by the appearance of clathrate-like formations at the mentioned alcohol content in the solution. In these clathrate-like structures the nonpolar part of the ethanol molecule is surrounded by a network of water molecules, linked by strong hydrogen bonds, and the hydroxyl OH-group of the ethanol molecule is embedded into this 3D network of water molecules via the hydrogen bonds. Using the multivariate curve resolution (MCR-ALS) method it is shown that at the ethanol concentrations 20 %–25 % in the solution the complexes of water and alcohol molecules having the stoichiometric composition  $\text{EtOH} \cdot 5\text{H}_2\text{O}$  (clathrate-type ethanol hydrates) prevail. Along with the hydrates  $\text{EtOH} \cdot 5\text{H}_2\text{O}$  in the solutions, the water associates, the alcohol associates, and the second-type ethanol hydrates are present, in which there are 1–2 water molecules per each ethanol molecule. Such hydrates have the structure of branched chains of water and alcohol molecules, the hydrogen bonds in them being weaker as compared to both clathrate-like hydrates and water. The hydrogen bonds monotonously weaken with increasing temperature of aqueous ethanol solutions (the increase of the fraction of OH groups with weak or broken hydrogen bonds occurs), and strengthen

with decreasing temperature (the fraction of OH groups with strong hydrogen bonds increases).

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