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INVITED ARTICLE

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In this study, an investigation of the behaviour of stretching bands of CH and OH groups of water–ethanol solutions at alcohol concentrations ranging from 0 to 96% by volume has been performed. A new approach to decomposition of the wide structureless water Raman band into spectral components based on modern mathematical methods of solution of inverse multi-parameter problems – combination of Genetic Algorithm and the method of Generalized Reduced Gradient – has been demonstrated. Application of this approach to decomposition of Raman stretching bands of water–ethanol solutions allowed obtaining new interesting results practically without *a priori* information. The behaviour of resolved spectral components of Raman stretching OH band in binary mixture with rising ethanol concentration is in a good agreement with the concept of clathrate-like structure of water–ethanol solutions. The results presented in this paper confirm existence of essential structural rearrangement in water–ethanol solutions at ethanol concentrations 20–30% by volume.

Keywords: Raman spectra; stretching bands structure; genetic algorithms; generalized reduced gradient; clathrate structure; hydrogen bonding; water; ethanol; alcohol solution

1. Introduction

Spectrum of Raman scattering of light by liquid water molecules consists of multiple vibrational bands caused by intra- and intermolecular interactions, by resonances among different vibrations and overtones of vibrations, and by vibrations at combination frequencies [1]. Up to the present time, the forming mechanisms of water Raman are not fully revealed, including those of the most intense and widest one – the stretching band (2800–3800 cm^{-1}). Numerous attempts to determine the contributions of intra- and inter-molecular interactions and of Fermi resonance to the stretching Raman band of water did not result in definite conclusions. The Raman stretching band of water is difficult to investigate due to the fact that its contour is a wide and practically structureless curve. Such bands *per se* have low information. For this reason, researchers study the behaviour of spectra under the influence of different factors, e.g. under changing temperature or when different substances are dissolved in water.

In this study, an investigation of the stretching bands of CH and OH groups in water–ethanol solutions and their behaviour with alcohol concentrations ranging from 0 to 96% by volume, has been performed. Water–ethanol solution is non-ideal and is a complex system whose properties have a non-linear dependence on the proportions of the components. Each alcohol molecule can form two hydrogen bonds, and each water molecule can form four hydrogen bonds. It is supposed that in pure water and in dilute solutions there exists a continuous three-dimensional random network of hydrogen bonds [2]. In binary water–ethanol systems a hydrogen bond can connect water molecules with each other, or ethanol molecules with each other (forming linear chain associates [3]), and also ethanol molecules with water molecules. In scientific literature there is no common opinion regarding what kind of complexes (water–water, water–ethanol, or ethanol–ethanol) dominate in the solution at different ethanol concentrations, and what is the proportion of their bond energies.

For example, in [4], the theoretically calculated energy of ethanol–ethanol hydrogen bond turned out to be close in value to the energy of the water–ethanol hydrogen bond. In [5], based on the results of NMR and IR-spectroscopy of water–ethanol solutions, it was

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shown that in dilute water–ethanol solutions the bonds between water molecules strengthen; water molecules form clathrate-like structures around ethanol molecules in the solution, and hydrogen bonds between the proton of the hydroxyl group of ethanol and the oxygen atom of water molecule are not formed. In [6], experimental data on differential-thermal analysis of ethanol–water system are explained by formation of ethanol hydrates and of ethanol–water compounds of semi-clathrate nature, when the ethanol hydroxyl group participates in formation of the clathrate hydrate framework.

Important information about intra- and intermolecular interactions in water and aqueous solutions is contained in their spectroscopic characteristics, in particular, in water Raman spectra [7–14]. In spite of the fact that investigation of the properties of water–ethanol solutions by Raman spectroscopy has been the subject of several studies [10–14], the question about structural peculiarities of water–ethanol solutions still remains far from being solved.

This study is devoted to investigation of properties of water–ethanol solutions with different alcohol content using Raman scattering spectroscopy. Raman spectra of water–ethanol solutions in the wavenumber range of $2500\ldots3800\,cm^{-1}$ with ethanol content in the solution from 0 to 96% by volume were obtained. The structure of stretching CH- and OH- bands was studied using decomposition of their contours into Gauss-shaped components. The behaviour of the resolved spectral components was studied as a function of ethanol concentration.

2. Experiment

Water–ethanol solutions were prepared from purified 96% ethyl alcohol and water. The purity of alcohol and water was controlled by absence of fluorescence excited by UV light. The ethanol concentration in the prepared solutions was changed from 0 to 96% with 2–5% steps, and it was expressed in volume per cent.

Excitation of Raman scattering in samples was performed by radiation of argon laser with wavelength 488 nm and power about 500 mWt. To suppress elastic scattering signal, an interference edge filter (Semrock) was used, which allowed approaching the Raman shift down to $100\,cm^{-1}$. Spectra registration was performed by a CCD camera (Jobin Yvon, Synapse1024*128 BIUV-SYN). Prior to registration, the scattered radiation passed a monochromator (Acton 2500i, grating 900 lines/mm, focus distance 500 mm). Practical resolution of the Raman spectrometer was $2\,cm^{-1}$. The temperature of the samples during the experiment was

maintained at a constant equal to $(22.0 \pm 0.2)^{\circ}C$. The spectra were normalized to the power of laser radiation and to spectrum accumulation time. Subsequent mathematical treatment for CH and OH stretching bands of Raman spectra included subtraction of the pedestal caused by light scattering in the cuvette with the sample, and normalization of the obtained spectra to their area.

3. Stretching Raman bands of OH and CH groups of water–ethanol solutions

In Figure 1, Raman spectra of water, ethanol and water–ethanol solutions in the wavenumber region $2500–3800\,cm^{-1}$ are presented. The band of stretching vibrations of hydroxyl groups of water and ethanol in the region $3100–3800\,cm^{-1}$ is wide with a maximum around $3420\,cm^{-1}$ and a less pronounced shoulder around $3200\,cm^{-1}$. The band of stretching vibrations of CH groups has several clear-cut peaks: the peak with maximum at frequency $2884\,cm^{-1}$ is caused by stretching symmetric vibrations of CH_2; the peak with maximum at frequency $2932\,cm^{-1}$ is caused by stretching symmetric vibrations of CH_3; the peak with maximum at frequency $2980\,cm^{-1}$ is caused by stretching asymmetric vibrations of CH_3.

Under increasing ethanol concentration, the position of the stretching band of OH vibrations remains practically unchanged, while its half-width and amplitude decrease monotonously. In contrast to the intensities of OH vibrations the intensities of stretching bands of CH groups are rising with increase of ethanol concentration. However, this rise happens not synchronously for different peaks. The most pronounced one is the increase in the intensity of the band of
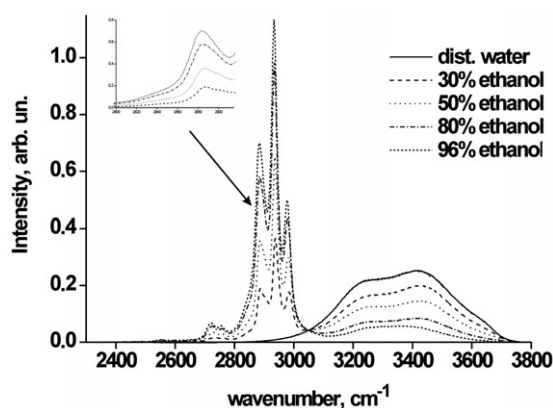

Figure 1. Raman stretching bands of water, ethanol and water–ethanol solutions at several ethanol concentrations: 30, 50, 80%.

symmetric stretching vibrations of CH_2 groups (with maximum at $2884\,cm^{-1}$). This may be explained by the fact that this peak is composed of two spectral components with close frequencies (see the inset at Figure 1), which become closer under increasing ethanol concentration. The positions of the bands of symmetric stretching vibrations of CH_2 and CH_3 groups remain unchanged in the whole range of concentration change, while the band of stretching asymmetric vibrations of CH_3 groups (with maximum $2980\,cm^{-1}$) suffers insignificant shift towards low frequencies at ethanol concentrations exceeding 15% (under ethanol concentration changing from 15 to 96%, this shift is $8\,cm^{-1}$). Such shift of this peak in concentrated solutions may be caused by reinforcement of Hydrogen bonds between ethanol molecules.

4. Decomposition of Raman stretching bands of CH and OH groups into components

To obtain information about connexity of different molecular groups in solutions and about dynamics of hydrogen bonds in water, the behaviour of spectral components of water and ethanol Raman stretching bands was investigated. The structure of Raman stretching bands of water–ethanol solutions was studied by decomposition of spectra into Gauss-shaped components. Decomposition of water and ethanol stretching bands in the region from 2500 up to $3800\,cm^{-1}$ into Gauss-shaped curves was performed using optimization methods by means of minimization of residual functional equal to the sum of squared differences between the intensity of the decomposed spectrum and the sum of intensities of the obtained components in each point of spectrum.

Two optimization methods were used: Genetic Algorithm (GA) [15] and the method of Generalized Reduced Gradient (GRG2) [16]. Necessity for simultaneous use of two powerful mathematical methods is connected with the fact that decomposition of such a wide structureless contour as water stretching band into components is an essentially incorrect inverse problem. If traditional methods are used, a large volume of *a priori* information is required for regularization of such a problem. The combination of powerful methods used in this study allows solving the named inverse problem without using *a priori* information about the number of decomposition components and without using preliminary models of intra- and intermolecular interactions.

From reasonable considerations, the maximal number of components for decomposition of bands in the region from 2500 up to $3800\,cm^{-1}$ was set to 15.

Each of the components was characterized by three parameters: the position of the component maximum, the component contour half-width, and the area under the component contour. The optimization problem was stated in such a way that the optimal values of all 45 parameters (for 15 Gauss-shaped components) were sought. However, if the area of any component contour during optimization became less than the pre-defined threshold value, the corresponding component was switched off completely. Therefore, the number of components required to describe the given spectral band was determined automatically during optimization, by the algorithm itself.

It should be pointed that for the given optimization problem in 45-dimensional space, the number of local extrema with essentially different values of the residual functional is very large. This fact makes using gradient methods without any preliminary determination of the starting point extremely ineffective. In such an unfavourable situation, even multiple launches of gradient descent from randomly chosen starting points do not guarantee finding global extremum, or even finding an extremum with the value of residual functional close to its value in the point of global extremum.

For this reason, at the first stage the stated problem was solved by means of Genetic Algorithm (GeneHunter® add-on for Microsoft® Excel from Ward Systems Group®, Inc. [17]). Due to high visibility inherent for Genetic Algorithms, it was possible to determine the region of the global extremum of the residual functional (or the region of a local extremum with optimal value of the functional close to that in the point of global extremum). To increase the probability of finding the global extremum, the GA was launched three times. One of the found points characterized by minimal value of residual functional was chosen as a starting point for further optimization.

At the second stage, the method of Generalized Reduced Gradient (GRG2) [16] implemented in Microsoft® Excel was used to refine the results of optimization, i.e. to perform quick convergence to the point of the extremum (the region of this extremum was found by GA at the first stage).

As a result of the solution of the stated inverse problem, it was shown that the stretching bands of CH and OH groups are described with good precision by 12 Gauss-shaped components. Seven components describe the stretching bands of CH groups, and five Gauss-shaped components describe the stretching bands of OH groups (Figure 2). As the problem stated in this study was an incorrect inverse problem, always suffering from non-uniqueness and instability
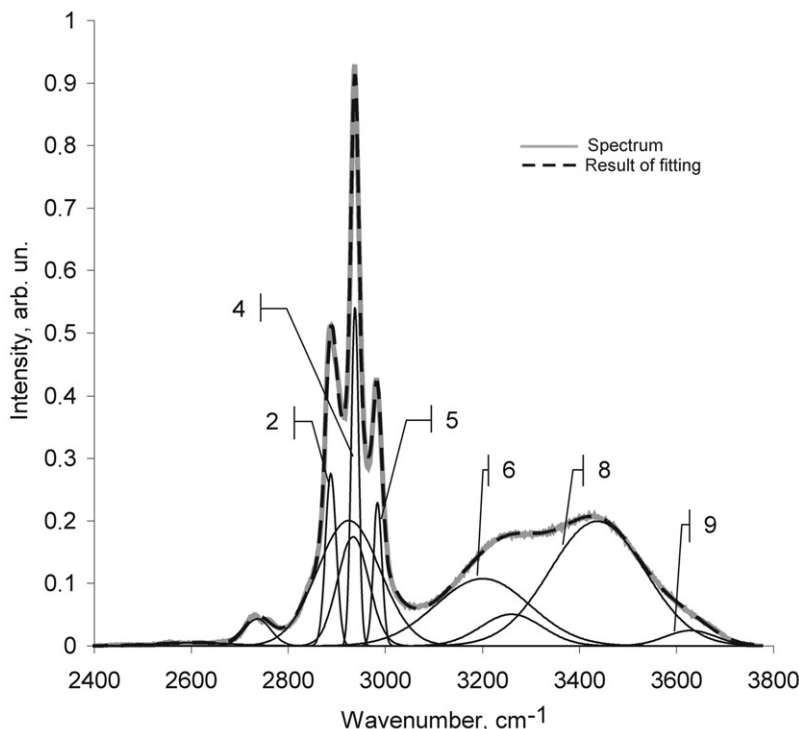
Figure 2. Raman stretching bands of water and ethanol decomposed into 12 Gauss-shaped curves. 2, 4, 5, 6, 8, 9 – the numbers of obtained components. Concentration of ethanol is 50%.

of the solution, the decomposition of each Raman spectrum of water–ethanol solutions in the region from 2500 up to 3800 cm^{-1} was performed three times, to test the reproducibility of the results. The obtained estimation for the error of decomposition of the components parameters was less than 4 cm^{-1} for component position and less than 5 cm^{-1} for Gaussian half-width.

5. Behaviour of the spectral components of OH and CH stretching bands with changing ethanol concentration

To analyse the structure of stretching Raman bands as a function of ethanol and water content, the following main components caused by the vibrations of CH and OH groups were selected:

- No.2, symmetric stretching vibrations of CH_2 groups of ethanol;
- No.4, symmetric stretching vibrations of CH_3 groups of ethanol;
- No.5, asymmetric stretching vibrations of CH_3 groups of ethanol;

- No.6, vibrations of strongly hydrogen-bonded OH groups of ethanol and water;
- No.8, vibrations of weakly hydrogen-bonded OH groups of ethanol and water;
- No.9, vibrations of free OH groups without hydrogen bonding.

Figures 3–5 display the concentrational dependences of maxima positions, contour half-width and amplitudes ratios of the obtained Gauss-shaped components for alcohol solutions. The maxima wavenumbers $v_{2,4,5}^{max}$ of Gauss-shaped components of Raman stretching bands of CH groups decrease slightly for 6–9 cm^{-1} with increasing alcohol concentration from 0 to 90%. Maxima wavenumbers $v_{6,8,9}^{max}$ of the components of stretching band of OH groups with increasing ethanol concentration in the same range are monotonously shifted for 20–25 cm^{-1} towards smaller wavenumbers, except for the Gaussian component No.6. Dependence of the maximum wavenumber of the component No.6, responsible for stretching vibrations of strongly hydrogen-bonded OH groups, on ethanol concentration $v_6^{max}(C)$ is non-monotonous in the concentration range from 20 to 30%.
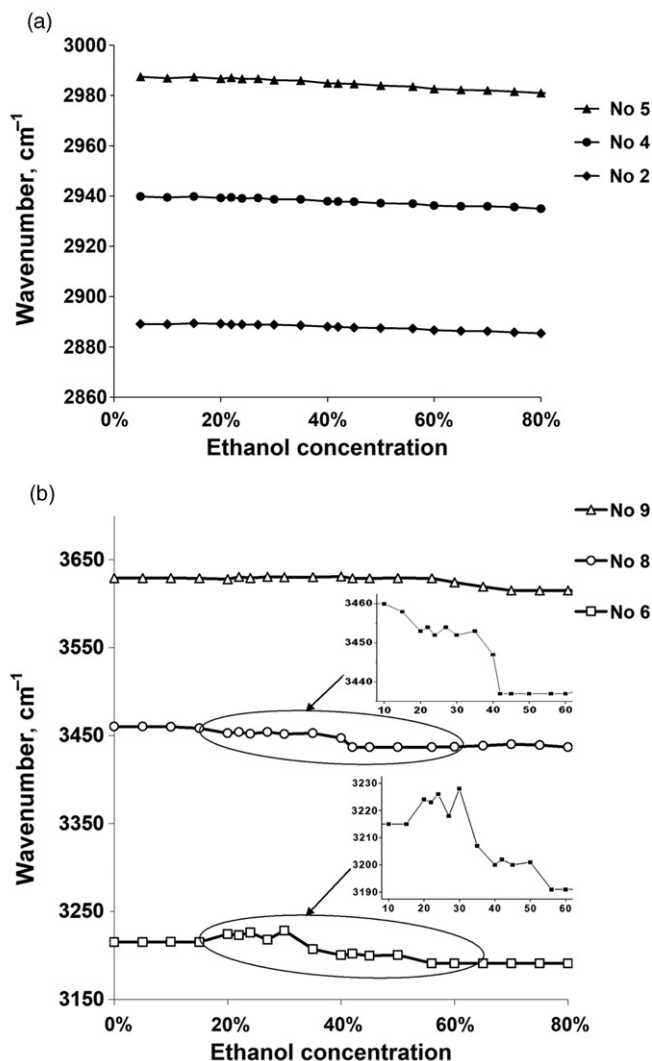
Figure 3. Dependences of position of components maximum on concentration of ethanol in water–ethanol solutions: (a) for Gauss-shaped curves no.2, 4, 5 (CH bands, closed symbols); (b) for Gauss-shaped curves no.6, 8, 9 (OH bands, open symbols).

At concentrations higher than 30% the wavenumber v_6^{max} decreases monotonously with increasing ethanol concentration The same behaviour of $v_6^{max}(C)$ was also observed when the decomposition of the spectra was repeated.

The shift of both spectral bands for CH and OH groups towards low frequencies at increasing ethanol amount in water means that the connexity of water and alcohol molecules in the solutions increases with rising ethanol concentration, and Hydrogen bonds between OH groups themselves, and also between OH and CH groups, are strengthened. Non-monotonous behaviour of the dependence v_6^{max} (C) in the concentration range from 20 to 30% is evidence of the fact that at these concentrations some structural rearrangement takes place in the solutions (see below).

A similar conclusion was made recently in the work [17] where the ratio of Raman intensities at 3200 and $3420 \, cm^{-1}$ of water stretching band was analysed as a function of ethanol concentration. The maximum of the intensities ratio was found within ethanol concentration of 20...25% by volume. Since the wavenumber region around $3200 \, cm^{-1}$ corresponds to strong hydrogen bonding of OH groups and the region of around $3420 \, cm^{-1}$ corresponds to weak hydrogen bonding, the maximal intensities ratio reveals the strengthening of hydrogen bonding in water–ethanol mixture around ethanol concentration 20...25%.
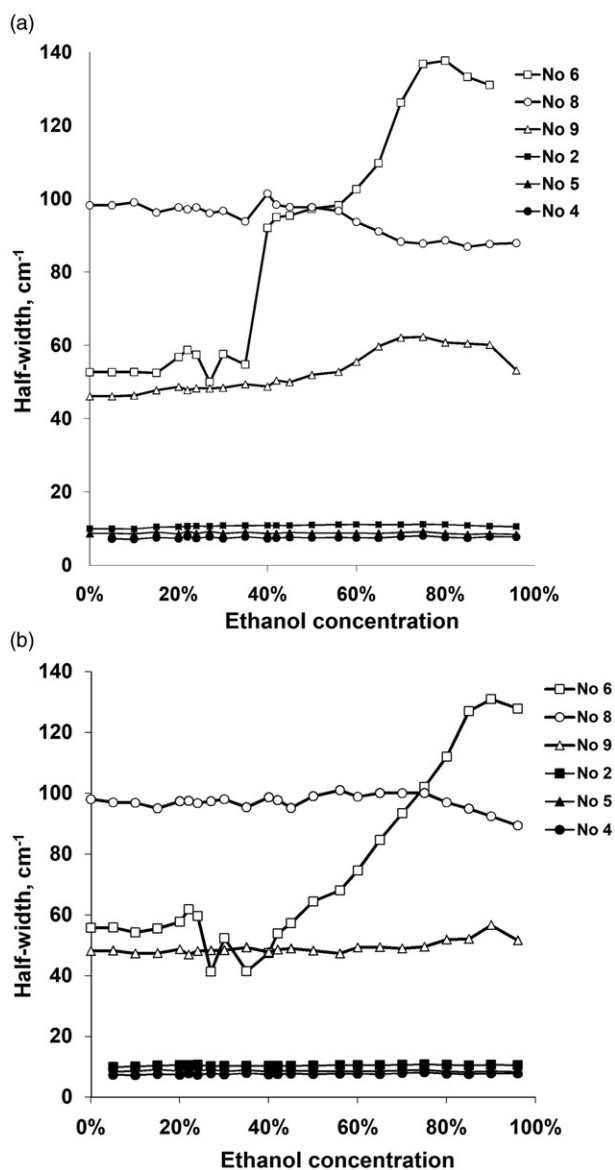
(a)

(b)

Figure 4. Dependences of components half-width on concentration of ethanol in water–ethanol solutions: (a) the first decomposition into Gauss-shaped curves no. 2, 4, 5, 6, 8, 9; (b) the second decomposition into Gauss-shaped curves no. 2, 4, 5, 6, 8, 9.

The conclusion of strengthening of hydrogen bonding between OH groups at certain ethanol concentration is in a good agreement with the conception of transient hydrates in aqueous ethanol solutions [18]. In that study multivariate curve resolution–alternating least squares analysis (MCR-ALS) was applied to the Raman and FT-IR data over the entire composition range of water–ethanol binary
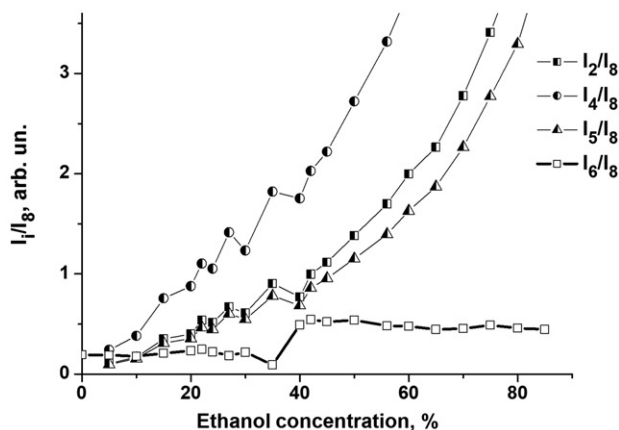

Figure 5. Dependences of amplitude ratios of Gauss-shaped curves on concentration of ethanol in water–ethanol solutions.

mixtures. The resolved MCR-components from a four-component analysis are pure water, two hydrates, and pure ethanol. In water-rich ethanol mixtures a hydrate of composition Ethanol $\cdot 4.7 H_2O$ was observed. This composition is close to that of a semi-clathrate, suggesting that a transient clathrate-like structure exists in liquid solution. The shape of OH stretching band in the MCR-resolved water-rich hydrate component with increased intensity around $3200\,cm^{-1}$ resembles that of the water Raman stretching band in the spectrum of a solid gas hydrate [19]. From the shape of MCR-resolved hydrate it is concluded that hydrogen bonding between water molecules is strengthened in the water-rich hydrate compared with that of pure water.

Changing in Hydrogen bonding between OH groups in water–ethanol solutions at increasing concentration of ethanol is also evidenced by the behaviour of the half-width of Gauss-shaped components of OH stretching band $\Delta\nu_{6,8}(C)$ with rising ethanol concentration. As can be seen from Figure 4, half-widths $\Delta\nu_{2,4,5}$ of components of ethanol stretching bands remain practically unchanged at increasing alcohol concentration in the solutions; while half-width of components No.6 and 8, caused by OH groups with strong and weak Hydrogen bonds, remains practically unchanged (within the stated error) only in dilute solution to approximately 15%. Half-width of component No.8 has non-monotonous behaviour in the range between 30 and 42% and starts monotonously decreasing at concentrations higher than 56%. The component No.6 caused by vibrations of OH groups

with strong Hydrogen bonds shows the largest variations of half-width. In ethanol concentration range from 20 to 30% one can observe non-monotonous behaviour of the $\Delta\nu_6$(C) curve; with concentration exceeding 42%, half-width of Gauss-shaped component No.6 ramps up. We mark that in all trials stretching bands decompositions into Gauss-shaped components, good reproducibility of the results is observed for plots of half-widths of components as a function of ethanol concentration $\Delta\nu_i$(C) (Figures 4 and 5).

The observed behaviour of the components of stretching band of the OH groups – a jump in half-width of component No.6 and decrease in half-width of component No.8 at ethanol concentrations higher than 40% – may be explained by rearrangement of molecules in binary ethanol–water mixtures [20]. In dilute solution with concentration up to 15%, the structure is similar to that of pure water. At alcohol concentrations from 20 to 30%, new structural formations – ethanol hydrates – are probably settled in the solution. The composition of such hydrates is similar to that of clathrate, which means 4.75 molecules of water per one ethanol molecule. This stoichiometric ratio corresponds to ethanol concentration 42% by volume. Restructuring of the solution takes place when maximal concentration of clathrate-like structure is achieved and all cavities in water framework are filled by ethanol molecules. At high alcohol concentrations we have incomplete mixing of ethanol with water which means coexistence of several structures: distorted clathrate-like and ethanol-rich clusters. Due to this effect one can expect appearance of two types of strong hydrogen bonding in solution: (1) between water molecules and (2) between water and ethanol molecules. The energy distribution of these two types of strong hydrogen bonds is similar, however not the same. This causes the broadening of the component No. 6. the component No.8 is also broadened in the range between 42 and 56%, but not to the extent of the component No.6.

As the result of all decompositions of Raman spectra of water–ethanol solutions into Gauss-shaped components, non-monotonous behaviour of the dependences of amplitude ratios I_2/I_8(C), I_4/I_8(C), I_5/I_8(C), and I_6/I_8(C) on ethanol concentration in the concentration range from 20 to 40% has been observed, compared to other concentration ranges (Figure 5). At an alcohol concentration of about 35%, increasing intensity of component No.6 compared to the intensity of component No.8 is observed, confirming once more

an essential rearrangement of hydrogen bonds in the solution.

Thus, analysis of the behaviour of dependences of parameters for Gauss-shaped components of stretching bands of CH and OH groups on ethanol concentration in the solutions shows that at alcohol concentrations from 22–24% to 30–35% one can observe non-monotonous behaviour of ν_i^{max} (C), $\Delta\nu_i$(C), and I_i/I_j(C) curves. This may be explained by structural rearrangements in the solutions at the specified concentrations of alcohol.

It is known [6,21–29] that in the concentration range of alcohol 20...25% by volume stabilization of structure of water solution by ethanol molecules and reinforcement of hydrogen bonds between hydroxyl groups take place. This fact is confirmed not only by the results of investigation of thermodynamic characteristics of water–ethanol solutions [22–24], but also by data obtained in studies of the solutions by different optical methods. In the experiments on Rayleigh scattering of light in water-alcohol solutions [25,26] it was found that at 25% v/v ethanol concentration in the solution, sharp maxima of light scattering were observed, whose intensity decreased with increasing temperature. In [27], based on studies of absorption spectra of rhodamine in water–alcohol solutions, calculations of binding energy in rhodamine dimer have been performed. It turned out that the binding energy had its maximum at the concentration of the solution about 25% by volume. Using differential thermal analysis at low temperatures Yu.M. Zelenin [6] found in frozen binary ethanol–water mixtures one stable (Ethanol $\cdot$ 2H$_2$O) and two metastable hydrates (Ethanol $\cdot$ 3H$_2$O and Ethanol $\cdot$ 4.75H$_2$O), the latter being a semi-clathrate, where the ethanol hydroxyl group is linked by hydrogen-bonding to the surrounding water framework.

As in this range of alcohol concentrations the majority of hydrogen bonds are formed among water molecules, it is possible to speak about reinforcement of hydrogen bonds between water molecules, and about increasing of the fraction of water molecules with strong hydrogen bonding. In [6,27–29], based on different experimental data and theoretical calculations it is supposed that in water–ethanol solutions water molecules form clathrate-like structure around hydrophobic part of an ethanol molecule. In other words, at ethanol concentrations 22–35% alcohol molecules fill cavities of water framework, forming 'guest–host' clathrate-like formations. When such clathrate is formed, the hydroxyl groups of ethanol penetrate the

water framework [6] displacing one water molecule and thus stabilizing water network structure. When the water framework is stabilized by ethanol molecules, hydrogen bonds between water molecules of the framework strengthen at certain ethanol concentration. Increase of ethanol content in binary solution compared with semi-clathrate composition ethanol $\cdot 4.75H_2O$ causes breakage of clathrate-like structure of the solution and rearrangement of its structure in favour of an ethanol hydrate type other than semi-clathrate. In contrast to water-rich semi-clathrate of composition ethanol $\cdot 4.75H_2O$, in the ethanol-rich hydrate the hydrogen bonding is weakened compared with pure water, as was revealed from MCR analysis of Raman and FT-IR spectra [20].

The results presented in this study favour the hypothesis of formation of clathrate-like structure in water–ethanol solutions. Non-monotonous behaviour of the dependences of the characteristics of Gauss-shaped components of valence bands of ethanol and water in the alcohol concentration range 20–30% is caused by reinforcement of hydrogen bonds between water molecules in clathrate-type formations. (Figures 3–5). Shift towards low frequencies and broadening of Gauss-shaped component No.6, caused by stretching vibrations of strongly bonded OH groups, at alcohol concentrations higher than 35% (Figures 3 and 4) is evidence of essential structural rearrangements in water–ethanol solutions.

6. Conclusions

In this study, a new approach to investigation of structure of a wide spectral band based on modern optimization mathematical methods for solving multi-parameter inverse problems – combination of Genetic Algorithm and Generalized Reduced Gradient method – has been demonstrated. Such a combination allows one to use the advantages of both methods: the GA has high probability of finding the region of the global minimum of the residual functional, while the GRG provides quick convergence to the point of minimum. Application of this approach to decomposition of Raman stretching bands of water–ethanol solutions allowed obtaining new interesting results practically without *a priori* information, what was previously impossible at such a high dimensionality of the optimization problem. High efficiency of the suggested approach is also evidenced by good reproducibility of the results when the decomposition is repeated.

The behaviour of Gauss-shaped spectral components of Raman stretching OH band in water–ethanol solutions with rising of ethanol concentration observed as the result of three separate decompositions of spectra is in a good agreement with the concept of clathrate-like structure of water–ethanol solutions suggested in scientific literature. The results presented in this paper confirm the existence of an essential structural rearrangement in water–ethanol solutions at concentrations 20–30% by volume.

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