Structural and Optical Characteristics of Aqueous Solutions of Acetic Acid

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ABSTRACT

A refractometric method, coupled with molecular dynamics study, attenuated total reflection Fourier transform infrared (ATR FT-IR), and Raman spectroscopy, were used to determine optical characteristics of concentration features of aqueous solutions of acetic acid. Measurements of refractive index of aqueous solutions of acetic acid in the wide range of acetic acid concentrations ($\sim 0 \div 1$ mole fraction) in solution at a room temperature were conducted. Maximum value of refractive index was detected at a concentration of ~0.3 mole fraction. The deviation from the parabolic form of the dependence of the refractive index on the concentration occurs at a concentration of ~0.8 mole fraction. As far as we know, this deviation has been observed for the first time. The maximum is attributed to the largest number of molecular interaction between water and acetic acid molecules, while the deviation is associated with the parallel orientation of acetic acid molecules. To identify the reconstructing of molecules in system FT-IR and Raman spectra of these solutions at a concentration of ~0.3 and ~0.8 mole fraction were recorded and compared with pure solutions. The data obtained by ATR FT-IR and Raman spectroscopy support the idea that the refractometric method is sensitive to determine the structural states of aqueous solutions of acetic acid.

Keywords: Attenuated total reflection Fourier transform infrared spectroscopy, ATR FT-IR, excess refractive index, excess dielectric permittivity, molecular dynamics method, Raman spectroscopy, aqueous solution of acetic acid, hydrogen bonding, structural change, heteromolecular structure

INTRODUCTION

Aqueous solutions of alcohols and acids associated with hydrogen bonds take special place among binary liquids. A particular interest to the study of optical properties of acetic acid and its aqueous solutions in a wide range of concentrations is related to their wide application in modern chemical engineering, for example, in the production of drugs (aspirin, phenacetin),[1] acetates and maleic anhydride,[2] and others. Acetic acid and its aqueous solutions are involved in the tricarboxylic acid (TCA) cycle,[3] the metabolism of ethanol by two dehydrogenases.[4]

The presence of a highly branched hydrogen bond in acetic acid leads to the formation of dimers of different configurations,[5] which remain to exist in the gas phase. The liquid acetic acid contains a mixture of acetic acid dimers linked with H-bond and more complex associates of acetic acid. However, it was observed[6] that acetic acid molecules form not only cyclic dimers, but chain structures. Thus, detailed investigations of the concentration dependence of structure-sensitive properties of solutions are required to determine conditions and specific mechanisms of formation of molecular associates, including heteromolecular associates, in aqueous solutions of acetic acid.

There is a wide range of techniques for analysis of aqueous systems, allowing to establish the nature of interaction between the components.[7–10] Refractometry is one of the methods for obtaining information about intermolecular interactions, the structure and properties of solutions.[11–13] The advantages of this method are high accuracy, simple and quick determinations of parameters of a substance. Refractometry is usually used both for structural analysis of a system and for quantitative analysis of binary, ternary and complex systems of various solutions. Therefore, we measured the refractive index of pure water and acetic acid at first, and that of aqueous solutions of acetic acid in the concentration range of 0÷1.0 mole fraction.

According to Maxwell's electromagnetic theory for the transparent dielectric fluids with magnetic permeability close to unity ($\mu \approx 1$), the squared refractive index of the medium n^2 is approximately equal to the value of the relative permittivity of the medium at infinite angular frequency as follows $\varepsilon_r(\infty)$:

$$n^2 = \varepsilon_r(\infty) \quad (1)$$

However, in binary liquids, deviations from the linear behavior of some functions can be observed, which is caused by the formation of hydrogen bonds between solvent and solute molecules, van der Waals and dipole–dipole interactions. Usually, these deviations are expressed by excess parameters.

The excess parameters were calculated using the following equations:[14,15]

$$n^E = n_m - [n_W(1 - x) + n_A \cdot x] \quad (2)$$

$$\varepsilon^E = (\varepsilon_m - \varepsilon_{m\infty}) - [(\varepsilon_W - \varepsilon_{W\infty})(1 - x) + (\varepsilon_A - \varepsilon_{A\infty}) \cdot x] \quad (3)$$

where suffix m, W, and A are mixture, water, and acetic acid, and x is the acetic acid concentration.

The curves of the concentration dependence of the excess dielectric permittivity of solutions calculated from the data of molecular dynamics ε^E with the experimental values n^E of the excess refractive indices of solutions were compared and presented in Figure 1.

Comparison of the curves shows that in the concentration range of 0÷0.7 mole fraction, the shape of the curves has the form of a parabola with a maximum at a concentration of ~0.3 mole fraction of acetic acid (Fig. 1). The quadratic dependence of the excess refractive index on the concentration has the form of a parabola and is typical for many aqueous solutions.[16] However, a noticeable deviation from the shape of the parabola in the curves of concentration dependences is observed at a concentration of ~0.8 mole fraction of acetic acid. To determine and compare the degree of structural changes, the infrared (IR) and Raman spectra of pure water, acetic acid and aqueous solutions of acetic acid were measured at a concentration of ~0.3 and ~0.8 mole fraction

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EXPERIMENT

Materials

Acetic acid (99.9%, Sigma-Aldrich, USA) and double-distilled water.

Preparation of Solutions

Aqueous solutions of acetic acid were prepared by gravimetric method described in a paper[17] and others.[18,19]

Study of Refractive Indices of Solutions

Measurement of the refractive index *n* of pure components (water and acetic acid) and solutions of various concentrations *x* was carried out at the wavelength D_1 of atomic sodium line (λ = 589.3 nm) using a highly sensitive the RX-7000 alpha digital refractometer with the temperature recording function (Atago, Japan). The measurement error *n* is less than 0.0001. The measurement of both *n* and temperature of solutions took not more than 20 seconds.

For the refractive index measurements, solutions of acetic acid–water were prepared in a concentration range of 0÷1.0 mole fraction.

For each solution, several values (at least three) were measured at a fixed temperature of 298±0.05 K. The end result is obtained by averaging over the entire series of measurements. The volume of the sample solution for a single measurement of *n* did not exceed 0.5 ml. Between individual measurement steps, samples of solutions were stored in a dark room in a hermetically sealed container.

Investigation of FT-IR and Raman Spectra of Solutions

The Fourier transform infrared spectra (FT-IR) were recorded using Agilent technologies Cary 640 series FT-IR spectrometer. The spectra were measured using a MIRacle single reflection ATR accessory, which is available for all brands of FT-IR spectrometers (PIKE Technologies). The diamond/Ge crystal plate with specular reflection analysis at 45° angle of incidence was used, that makes it ideal for analyzing acidic samples.[20] All spectral data were obtained with a resolution of 2 cm^{-1} and by transmitting the infrared beam along the ATR Ge substrate. For recording FT-IR and Raman spectra, the same solutions as for measuring the refractive index of solutions with concentrations of ~0.3 and ~0.8 mole fraction and for pure water and acetic acid were used. The water spectra obtained by us, more or less coincide with those obtained by other investigators. The obtained spectral dependences are shown in Figs. 4–6. The intensity and positions of the bands vary with the concentration of the components.

Raman spectra were collected by Renishaw InVia Raman spectrometer using an excitation neodymium-doped yttrium aluminum garnet (Nd:YAG) laser source of 532 nm awaking 1200 l/mm grating. A micro-Raman in Via Renishaw spectrograph equipped with a charge-coupled device camera (1024×256 pixels). Raman spectra were obtained in wavenumber range from 400–4000 cm^{-1} with resolution <1 cm^{-1}.

MOLECULAR DYNAMICS

The calculations were made using the software package GROMACS 5.1.3.21 OPLS-acetic acid force field[22] was used to calculate interaction parameters followed by optimization of diameters of oxygen and carbon atoms to reproduce dielectric constants of acetic acid. Intermolecular interactions were calculated by pair potential $V_{ij}(r_{ij})$, written as the sum of the Coulomb and Lennard–Jones potentials. The in, was primarily used for the parameters of interaction in order.

$$V_{ij}(r_{ij}) = V_{ij}^{el}(r_{ij}) + V_{ij}^{LJ}(r_{ij}) = \frac{1}{4\pi\varepsilon_0}\frac{q_i q_j}{r_{ij}} + 4\varepsilon_{ij}[(\frac{\sigma_{ij}}{r_{ij}})^{12} - (\frac{\sigma_{ij}}{r_{ij}})^{6}] \quad (4)$$

where q_i and q_j are charges of the *i*- and *j*-atoms, r_{ij} is the distance between the centers of interaction of atoms in the molecule, σ_{ij} is the van der Waals diameter of the *i*- and *j*-atoms, and ε_{ij} is the depth of the potential well of the *i*- and *j*-atoms. For pair interactions between atoms, the parameters σ_{ij} and ε_{ij} were determined using the Lorentz–Berthelot rule:

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}, \varepsilon_{ij} = \sqrt{\varepsilon_i \cdot \varepsilon_j} \quad (5)$$

The calculations were made at fixed pressure and temperature using Berendsen’s pressure coupling and thermostatic control algorithms in a cubic box filled with acetic acid and water molecules at different concentrations of acetic acid. The equation of motion was solved using Verlet algorithm with a time step of 1.0 fs. The long-range Coulomb forces between molecules were calculated using Ewald method with an accuracy of 1×10^{-6} kJ/mol. The equilibrium of the acetic acid–water binary system was achieved within 5 ns. The calculation procedure was repeated in a wide range of solution concentrations (0÷1 mole fraction) at a room temperature (T=298 K). The isothermal compressibility of water was taken as 4.5×10^6 Pa.

We used the methodology of calculation of excess dielectric constant, which is given in detail in our work for dimethylformamide and tetrahydrofuran solutions,[15] and which authors used for other systems.[23]

RESULTS AND DISCUSSION

Changes in numerical values of parameters ε^E and n^E of acetic acid–water solution with the increase of concentration of acetic acid give an indication of structural changes occurring in the solution. A negative value of parameter ε^E of the solution indicates changes in the structure of a local environment of H-bonds in the solution[24–26] leading to the formation of associated structures.

Figure 1 shows plots of experimental values of the excess refractive index (curve 1) and calculated values of the excess dielectric constant (curve 2) of freshly prepared aqueous solutions of acetic acid over a wide range of component concentrations.

Extreme values of parameters ε^E and n^E of the solution are observed at concentrations of acetic acid of $x \sim 0.3$ mole fraction, which correspond to the maximum number of heteromolecular structures with H-bond in the binary mixture acetic acid–water, formed by incorporation of acetic acid molecules between water molecules (see Figure 2). There is a full destruction of the structure of water and reduction of the number of effective dipole moments of water molecules that contribute to the dielectric polarization of the mixture.

As can be seen from the Figure 1 and Table I, the excess refractive index is positive in the entire concentration range. With an increase in concentration of the solution, n^E changes non-monotonically, passing through a maximum at $x \sim 0.3$ mole fraction. At high concentrations (0.7–0.8 mole fraction), some features are observed in isotherm: the behavior of $n^E(x)$ in this concentration range is different from the expected "smooth" reduction.

The behavior of $n^E(x)$ indicates that changes in the concentration of acetic acid in solution over the entire investigated interval x are accompanied by changes in the structure of the solution. Acetic acid molecule consists of a non-polar hydrophobic radical (CH_3) and a polar hydrophilic group (C–O–H), and refers to diphiphilic (heterofunctional) molecules capable of participating in both hydrophobic and a hydrophilic interactions with water molecules.

Furthermore, acetic acid molecule can act not only as a donor, but also as a proton acceptor (by oxygen in C=O), i.e., simultaneously form two hydrogen bonds, which apparently leads to strong self-association of molecules in a pure acetic acid.

For this reason, changes in the structure are caused by processes of competition for the formation of hydrogen bonds between water molecules and acetic acid, depending on the ratio of components in the solution. In other words, increase in the concentration of acetic acid in solution, consecutive change of priorities of hydrogen bonds such as water–water, water–acetic acid, and acetic acid–acetic acid occurs, including breaking the old and the formation of new bonds. To verify the assumptions made above, dielectric permittivity of acetic acid–water solutions in the entire concentration range were studied using the method of molecular dynamics. In the region of low concentrations ($x \leq 0.1$), change of a mechanism of priority hydrophobic interaction between acetic acid molecules with water molecules to a mechanism of hydrophilic dissolution of acetic acid in water may play a significant role: incorporation of acetic acid molecules in cavities of structure of water or not the entire molecule, but its methyl tail. At the same time, free water molecules are forced out of the cavity and either move into existing vacant space, or are “sewed” into the water framework. This effect shall be accompanied by reinforcement of hydrogen bonds network until all existing cavities are completely filled.
Fig. 3a shows that at a concentration of $x = 0.1$, dissolution of acid molecules occurs in such a way as to not destroy the structure of hydrogen bond network. Such behavior of the system is associated with the entropy effect, where hydrophobic parts of acid molecules are oriented antiparallel to each other, and hydrophilic parts are exposed to water molecules
Further, with the increase of concentration of acetic acid (in the range of mean concentrations $x \approx$ 0.3 – 0.4 mole fraction), the formation of hydrogen bond between water and acetic acid molecules, leading to the formation of heteromolecular structures, was observed. When molecules of acetic acid are dissolved in water, they break the hydrogen-bond network into separate fragments by embedding acetic acid molecules in disordered structure of water with the formation of heteroassociates water–acetic acid. The greatest number of heteroassociates is achieved at a concentration of $x = 0.3$ mole fraction At this concentration, n^E parameter reaches its maximum value (Fig. 3b).

At high concentrations of solutions ($x > 0.5$ mole fraction), changes in the excessive refractive index are caused by the formation of acetic acid–acetic acid associates. At a concentration of $x = 0.8$ mole fraction, formation of elementary "building blocks" of acetic acid structure with dispersion interaction between C-atoms of separate molecules that are oriented parallel to each other, were observed in the solution (Fig. 3c). This means that there is an alignment of dipole moments of individual molecules in a certain direction. Molecules located at the end of rows of "building blocks" are linked with water molecules.[27–28]

We do not present ab initio calculations here, since as has already been shown by other authors,[29] however we have measured IR and Raman spectra of water, acetic acid and its mixtures.

Fourier infrared spectroscopy is one of the methods allowing to obtain information about relative positions of molecules over very short periods of time, as well as to assess the nature of the relationship between them and therefore, is widely used for studying intra- and intermolecular interactions, for example, the formation of hydrogen bonds. Water shows strong absorbance due to the presence of hydroxyl group, –OH. The presence of water caused difficulties in the interpretation of the spectra, and one of the solution methods was to remove the solvent and to study the spectra of acetic acid in gaseous and liquid phases in other acids.[30–33] Fig. 4 and Fig. 5 show the IR spectra of pure water and acetic acid, and aqueous solutions of acetic acid at concentrations of ~0.3 and ~0.8 mole fraction Peaks with maxima of 3050 cm^{-1} and 2934 cm^{-1} correspond to the vibrations of CH_3 and OH– for pure acetic acid and its aqueous solutions.

In the literature, there is many experimental data on the study of infrared spectra of acetic acid.[29,34–37] To identify the spectra, depending on the method of measurement, the absorption bands are divided into ranges,[29,34] in each of which local normalization of peak intensities is carried out. For example, ultrafast pump–probe studies show a sharp decrease in absorption in the range of 2600 to 3100 cm^{-1} and 2050 to 2250 cm^{-1} for O–H and O–D excitations, associated with the presence of cyclic dimers of different molecular structures.[29]

The Fourier spectrometer differs from other spectrometers in the ability of simultaneous recording of the entire spectrum under study. It is shown that the infrared spectrum at a concentration of ~0.3 mole fractions of acid reproduces frequencies for both pure water and acetic acid.

Based on our experimental (on the excess refractive index and on the IR Fourier spectra) and literature data,[29, 34] it can be concluded that at a concentration of ~0.3 mole fraction, the formation of cyclic dimers of acetic acid in the presence of water molecules occurs.

The location of peak intensities at ~0.8 mole fraction, which are located below those for ~0.3 mole fraction, is associated with a sharp decrease in the number of open and cyclic dimers of acetic acid formed. Moreover, at a concentration of ~0.8 mole fraction, the nature of interactions between molecules of water and acetic acid varies drastically, and the predominant interaction is the dipole–dipole interaction between molecules of acetic acid, characterized by the appearance of a maximum at 1379 cm^{-1} (Fig. 5), which is assigned to the CH_3 s-deformation with a maximum at 1408 cm^{-1},[35] at 1382 cm^{-1},[38] and at 1380 cm^{-1},[39] in the area of "fingerprints".

The cyclic dimer is characterized by an absorption band of 1714.4 cm^{-1},[37] which is observed for pure acetic acid as well, and slightly shifted to the frequency range of 1717 cm^{-1} for its aqueous solutions at a concentration of ~0.3 and ~0.8 mole fraction The absorption band of 1762.2 cm^{-1} characterizes the monomeric state[37] and is present in pure acetic acid and at a concentration of ~0.8 mole fraction (Fig. 5). Its absence for a concentration of ~0.3 mole fraction is explained by the fact that all acetic acid monomers and the formation of a cyclic dimer occur with the participation of water molecules.

The peak around ∼3450 cm^{-1} at a concentration of ~0.3 mole fraction of acetic acid of Raman spectrum (Fig. 6) assign to the asymmetric oscillating water molecules[40] and weak bounded OH-group.[41]

At small concentration of the acetic acid, many possibilities of inclusion of water into the dimer appear. The water molecules can be included into the cyclic dimers formed by hydroxylic COOH groups. Dipolar interactions appear between the acetic acid of carboxylic groups and water molecules OH parts. So, the peak which generally appears around ∼3450 cm^{-1} is attributed to acid molecules bonded to water molecules via the hydrogen directly influencing the OH bond, and can be identify as asymmetric OH band in symmetrical oscillation of open cyclic dimer. The Raman intensity appears in the 3450 cm^{-1} region at the concentration of ~0.3 mole fraction is concomitant with an OH stretching in cyclic open dimer. Additionally, the peak which appears around ∼1710 cm^{-1} is attributed to cyclic dimer.[42]

Wu[42] analyzed the enhancement of the 1675 cm^{-1} under the assumption that several structural fragments with different frequencies of their hydroxyl groups and different hydrogen bonding can exist in acetic acid. The component at 1764 cm^{-1} was assigned to the linear monomer. It has been suggested that the bands of 2945 cm^{-1} and 895 cm^{-1} are associated with CH_3 and C–C modes. It should be noted that the intensity these different modes are stronger at ~0.8 mole fraction than for ~0.3 mole fraction and pure acetic acid. This behavior indicates that the dipole–dipole interaction reveals in system at a concentration of ~0.8 mole fraction as stated above.**<AQ>Please see note RE: Ref. 39 being a duplicate of Ref. 31 and the need to renumber remaining refs. and in text citations in the References and correct the citation to Wu here if necessary.</AQ>**

CONCLUSION

The comparison of concentration dependence curves of excess dielectric permittivity calculated based on molecular dynamics data and experimental values of refractive indices of solutions was carried out.

It was shown that with change of the concentration of acetic acid in aqueous solution changes occur in the structure of the solution. The structure of the solution is significantly different from that of pure components.

To determine the concentration features of optical characteristics of aqueous solutions of acetic acid, Fourier transform infrared and Raman spectra of pure water, acetic acid and aqueous solutions of acetic acid at concentrations of ~0.3 and ~0.8 mole fraction were obtained.

The formations of open and cyclic dimmers were observed at a concentration of ~0.3 mole fraction At a concentration of ~0.8 mole fraction, the formation of elementary ‘bricks’ of the structure takes place: acetic acid molecules oriented almost in parallel to each other and linked together by water molecules. Thus, it was shown that the refractometric method is sensitive to determine the structural states of aqueous solutions of acetic acid.

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CONFLICT OF INTEREST

The authors report there are no conflicts of interest.

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Tables

Table I. Experimental mole fraction x, refractive index *n*, excess refractive index n^E, and squared excess refractive index.

$(n^E)^2$ of aqueous solution of acetic acid

x	n	n^E	$(n^E)^2$
0.00000	1.33250	0.00000	0.000000
0.03376	1.34190	0.00814	0.000066
0.07289	1.35050	0.01527	0.000233
0.11878	1.35810	0.02116	0.000448
0.17333	1.36350	0.02452	0.000601
0.23925	1.36720	0.02575	0.000663
0.32054	1.36980	0.02531	0.000641
0.42324	1.37010	0.02177	0.000474
0.55713	1.37020	0.01686	0.000284
0.73894	1.37050	0.01036	0.000107
0.85664	1.37160	0.00706	0.000050
0.93906	1.37180	0.00418	0.000017
1.00000	1.36990	0.00000	0.000000

Table II. Dielectric permittivity ε and excess dielectric permittivity ε^E at different mole contents of acetic acid in water with the corresponding of number of molecules, N_A is Number of acetic acid molecules, N_w is number of water molecules.

x	N_A	N_w	ε	ε^E
0	0	524	71	0
0.1	52	472	58.33	–6.185
0.2	105	419	49.49	–8.54
0.3	157	367	42.77	–8.775
0.4	210	314	37.03	–8.03
0.5	262	262	31.49	–7.085
0.6	314	210	25.76	–6.33
0.7	367	157	19.85	–5.755
0.8	419	105	14.1	–5.02
0.9	472	52	9.28	–3.355

1	524	0	6.15	0

Figure Captions

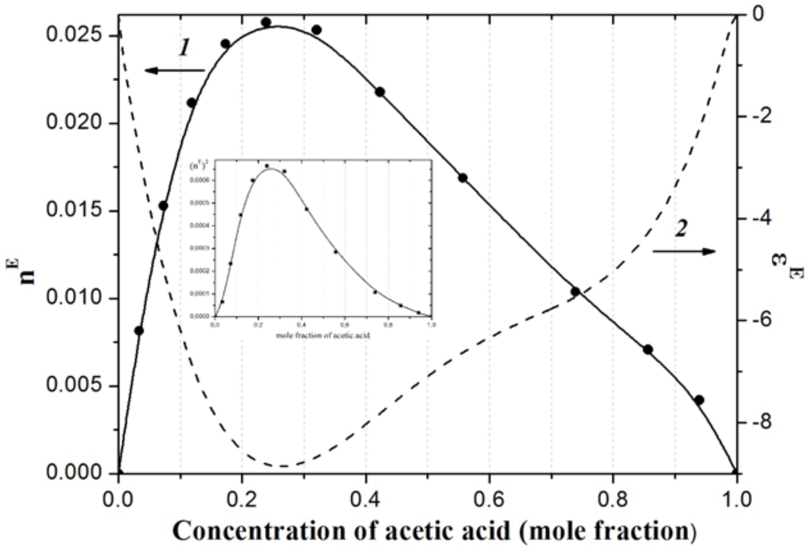

Fig. 1. Changes of excess refractive index n^E of freshly prepared aqueous solutions of acetic acid at different initial concentrations of components (curve 1), calculated values of excess dielectric constant $\boldsymbol{\varepsilon}^{E}$ (curve 2) and squared excess refractive index $(n^E)^2$.

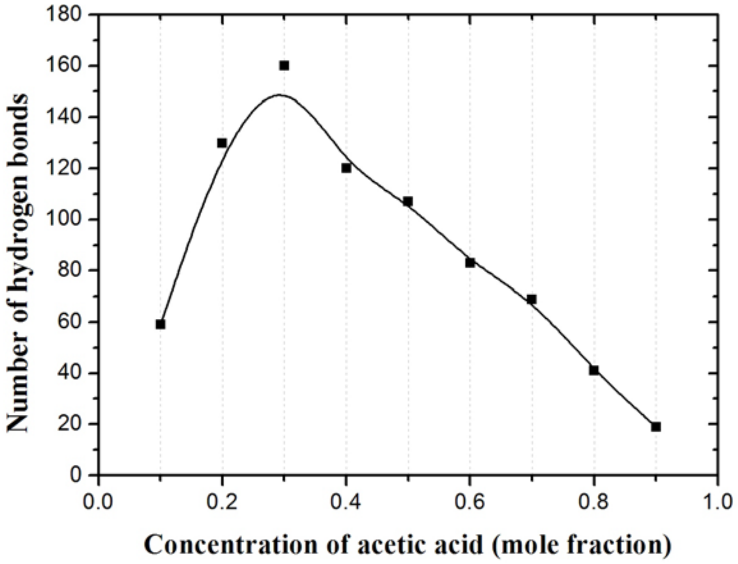

Fig. 2. The number of hydrogen bonds forms between water and acetic acid molecules at different concentrations of component.

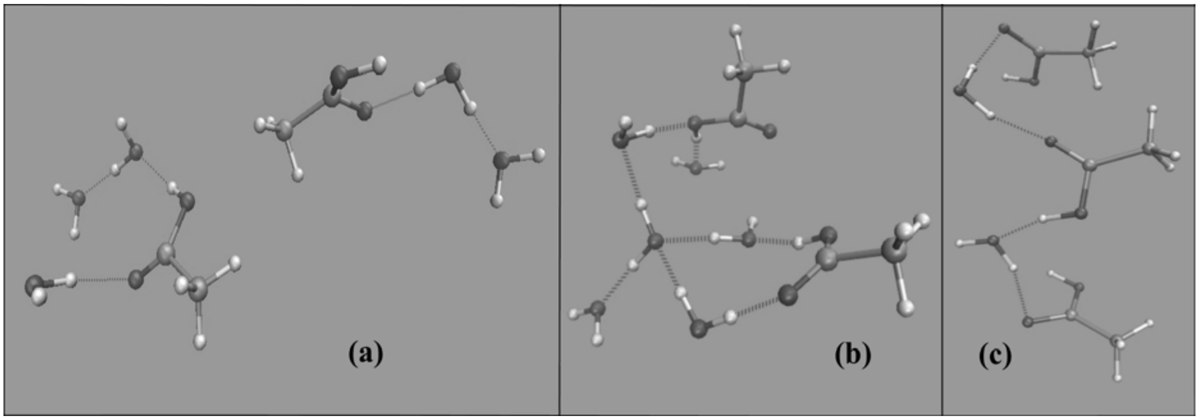

Fig. 3. A snapshot of a few molecules taken from a computer simulation: Due to the influence of water, hydrophobic CH_3 groups are oriented antiparallel to each other at the concentration of acetic acid of 0.1 mole fraction (a). Formation of heteromolecular structures with H–bond between water and acetic acid molecules at the concentration of 0.3 mole fraction in solution (b). Molecules of acetic acid are arranged in parallel due to dipole interaction at a concentration of 0.8 mole fraction (c).

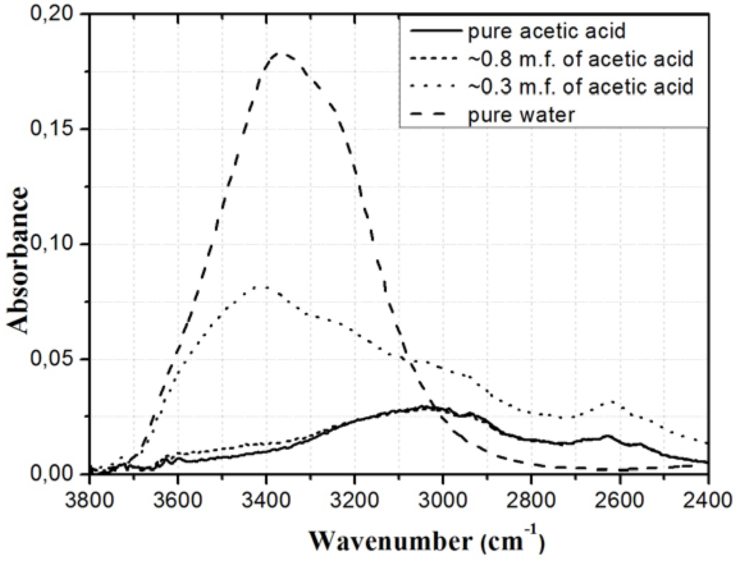

Fig. 4. FT-IR spectra (2400–3800 cm^{-1}) for water and acetic acid, as pure substances and aqueous solutions of acetic acid for concentrations of ~0.3 and ~0.8 mole fraction in wavelength range.

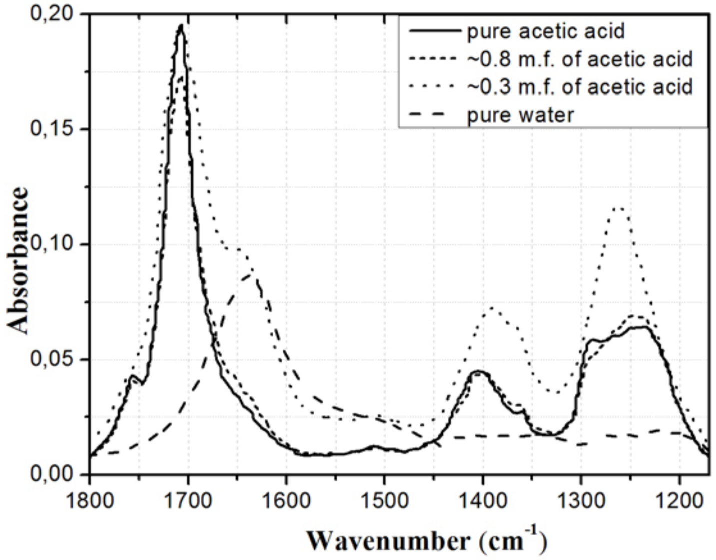

Fig. 5. FT-IR fingerprint spectra (1180–1800 cm^{-1}) for water and acetic acid, as pure substances and aqueous solutions of acetic acid for concentrations of ~0.3 and ~0.8 mole fraction in wavelength range.

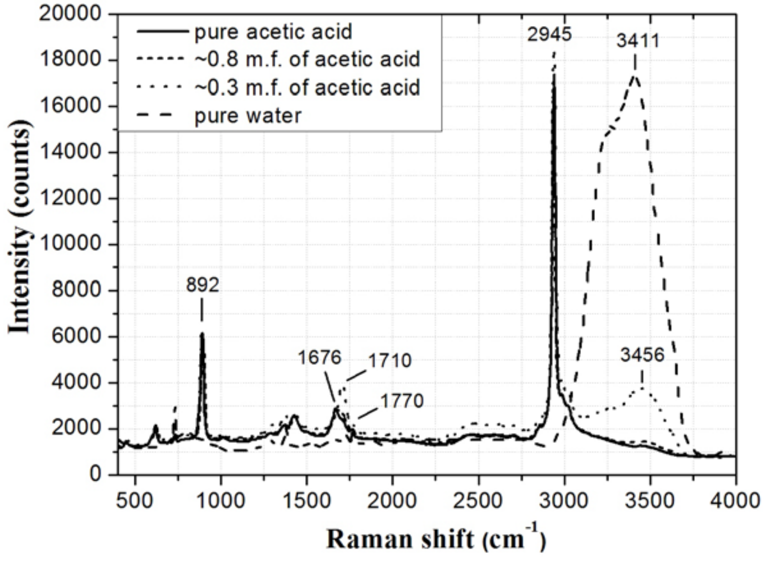

Fig. 6. Raman spectra (400–4000 cm^{-1}) for water and acetic acid, as pure substances and aqueous solutions of acetic acid for concentrations of ~0.3 and ~0.8 mole fraction in wavelength range.