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SPECTRAL FEATURES AND HYDROGEN BOND STRUCTURE OF AQUEOUS SOLUTIONS OF ETHANOL

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Cover Page Footnote

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SPECTRAL FEATURES AND HYDROGEN BOND STRUCTURE OF AQUEOUS SOLUTIONS OF ETHANOL

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The aim of this work is develop an approach that makes it possible to study the spectral properties and structure of intermolecular hydrogen bonds in aqueous solutions of ethanol formed in systems whose existence in a gaseous medium or an isolated state is practically impossible. This approach bases on the combined use of infrared spectroscopy and molecular dynamics (MD) methods. An analysis give the structural reorganization of water molecules depending on the concentration of ethanol alcohol. It has been shown that the method of molecular dynamics with classical force fields makes it possible to explicitly take into account the molecules of the solvent and solute, and, thus, to investigate hydrogen bonds in the system and to interpret with the experimental data obtained by vibrational spectroscopy.

Keywords: molecular dynamics, infrared spectroscopy, velocity autocorrelation function

СПЕКТРАЛЬНЫЕ ОСОБЕННОСТИ И СТРУКТУРА ВОДОРОДНОЙ СВЯЗИ ВОДНЫХ РАСТВОРОВ ЭТАНОЛА

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Целью данной работы было развитие подхода, позволяющего изучать спектральные свойства и строение межмолекулярных водородных связей в водных растворах этанола, образующихся в системах, существование которых в газовой среде или изолированном состоянии практически невозможно. Данный подход основан на совместном использовании методов инфракрасной спектроскопии и молекулярной динамики (МД). Приводится анализ структурной реорганизации молекул воды в зависимости от концентрации этанольного спирта. Было показано, что метод молекулярной динамики с классическими силовыми полями позволяет явно учитывать молекулы растворителя и растворенного вещества и, таким образом, исследовать водородные связи в системе и интерпретировать экспериментальные данные, полученные методом колебательной спектроскопии.

Ключевые слова: молекулярная динамика, инфракрасная спектроскопия, автокорреляционная функция скорости

ETANOLNING SUVLI ERITMALARINING SPEKTRAL XUSUSIYATI VA VODOROD BOG'LANISHLARI TUZILISHI

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Ushbu ishning maqsadi gaz muhitida yoki izolyatsiya holatda mavjudligi deyarli imkonsiz bo'lgan tizimlarda hosil bo'lgan etanolning suvli eritmalaridagi molekullararo vodorod bog'lanishlarining spektral xususiyatlarini va tuzilishini o'rganishga imkon beradigan yondashuvni ishlab chiqish edi. Ushbu yondashuv infragizil spektroskopiya va molekulyar dinamika (MD) metodlaridan birgalikda foydalanishga asoslangan. Etanolning kontsentratsiyasi o'zgarishiga qarab suv molekullarining tarkibiy qayta tashkil etilishi tahlili berilgan. Klassik kuch maydonlari bilan molekulyar dinamika metodi erituvchi va erigan modda molekullarini aniq hisoblashga va shu bilan tizimdagi vodorod bog'lanishlarini o'rganishga va tebranish spektroskopiya metodi bilan olingan eksperimental natijalarni sharhlashga imkon beradi.

Kalit so'zlar: molekulyar dinamika, infragizil spektroskopiya, tezlik avtokorrelatsiya funktsiyasi

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Introduction

Aqueous solutions of ethanol chosen as the objects of the research. This system is a convenient model for studying intermolecular hydrogen bonds [1-22]. The major structural rearrangements in the concentration range of $0.15 < x \text{ EtOH} < 0.65$ were shown, where $x \text{ EtOH}$ denotes the ethanol mole fraction. The major change of structural/vibrational dynamics in this region detected by Brillouin scattering. Using simulation, it was observed that micro-segregated distributions of water and ethanol do-

mains lead to formation chain-like hydrogen-bonded water at large ethanol fraction [5]. The extended hydrogen bond network of different isomer clusters was study by molecular dynamics calculation. It was concluded that the primary structure orientation in system depended on location of hydroxyl group to each other locate, which is determine the hydrogen bond network and directly correlated to the size of this network [6, 7]. The X-ray Compton scattering study of hydrogen bond of ethanol-water systems studied in concentration region

of 0.2÷0.9 mole fraction of ethanol. The strong hydrogen bond network occurs at low concentration region and intermolecular distances between molecules became shorter at the higher concentration region [23].

The structure and spectral properties of strong intermolecular hydrogen bonds in an aqueous medium studied using the approach developed in this work. This approach consists in the combined use of infrared spectroscopy (IR spectroscopy) and molecular dynamics (MD) methods with classical force fields. In this work, we compare the experimental data on IR spectroscopy in the wavenumber range of 600-1400 cm^{-1} and the calculated data on MD. Fourier infrared spectroscopy used to obtain the IR spectrum of an aqueous solution of ethanol. The advantages of molecular dynamics are that it is possible to separately highlight the contribution of each molecule, study the structure of the first hydration shell, and calculate the IR spectrum of aqueous solutions of ethanol in the fingerprint region with explicit consideration of the dynamics of structural changes.

In this paper, we present a technique for modeling and calculating Infrared spectra by the molecular dynamics using classical force fields, and a comparison with the experiment in the field of fingerprints.

Research methods

Materials; Ethanol (99.9%, Sigma-Aldrich, USA) and double-distilled water.

Preparation of Solutions

Aqueous solutions of ethanol prepared by method described in papers. [24].

Study of Refractive Indices of Solutions

Measurements of refractive index of aqueous solutions of ethanol in the wide range of ethanol concentrations ($\sim 0\div 1$ mole fraction) in solution at a room temperature conducted and reported in [24].

Investigation of FT-IR of solutions

The Fourier transform infrared spectra (FT-IR) recorded using Shimadzu IRTracer-100 Fourier Transform Infrared Spectrophotometer (FTIR). The spectra measured using an Attenuated Total Reflectance (ATR). All spectral data recorded with the robust S/N ratio of 60,000:1 and a resolution of 0.25 cm^{-1} using a Mercury-Cadmium-Telluride (MCT) detector. For recording FT-IR spectra, the same solutions as for measuring the refractive index of solutions with concentrations of ~ 0.3 mole fraction and for pure water and ethanol used.

Molecular dynamics study

In this work, the calculation of IR spectra of aqueous solution of ethanol with explicit solution consideration were carried out by the molecular dynamics (MD) method using classical force fields OPLS-AA and SPC. This methodology of calculation presented in detail in our previous works [25, 26]. The cubic cell consisted of 524 molecules. The

ratio of molecules chosen according to the concentration in mole fractions. All MD calculations performed in the NVT and NPT ensemble. The cutoff radius of the Coulomb and short-range van der Waals interactions was taken to be 1.2 nm. The long-range Coulomb interactions were taken into account by Ewald method-PME. The simulation carried out at a constant temperature of 300 K. The step length was 1 fs. The system was considered "thermostated", that is, "reached equilibrium" if its total, kinetic, and potential energies fluctuated around certain values, which did not change during further MD calculations. The lengths of the trajectories used at the stage of reaching equilibrium were 30 ns.

Results and Discussion

A refractometric method (Fig. 1), coupled with molecular dynamics study, and attenuated total reflection Fourier transform infrared (ATR FT-IR), were used to determine optical characteristics of concentration features of aqueous solutions of ethanol solution.

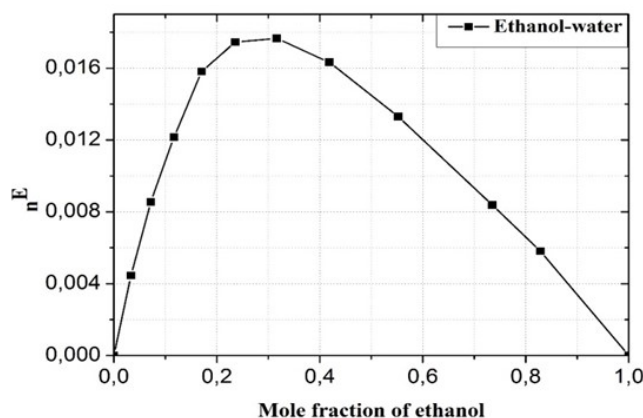


Figure 1. Changes of excess refractive index n^E of ethanol-water solution at different concentrations of components at room temperature. Figure taken from [8].

Maximum value of refractive index detected at a concentration of ~ 0.3 mole fraction. The maximum attributed to the largest number of molecular interaction between water and ethanol molecules. To identify this fact, the FT-IR spectra recorded and compared with those obtained of molecular dynamics simulations. Figure 2 shows that the IR-intense bands of 885 cm^{-1} skeletal CCO stretching, of 1055 cm^{-1} skeletal CCO and deformation of 1095 cm^{-1} CO stretching 885 cm^{-1} in the experimental recorded region [27, 28], which are corresponded to 880 and 940 cm^{-1} , 1080 cm^{-1} and 1120 cm^{-1} in calculated region. The combined use of calculation methods with explicit consideration of the solvent made it possible to reveal the spectral feature of aqueous solutions of ethanol, namely, the IR-active band in the region of 900 cm^{-1} , due to the strong bond in the formation of heterostructures between water and ethanol molecules.

According to our calculations (Fig. 3), the

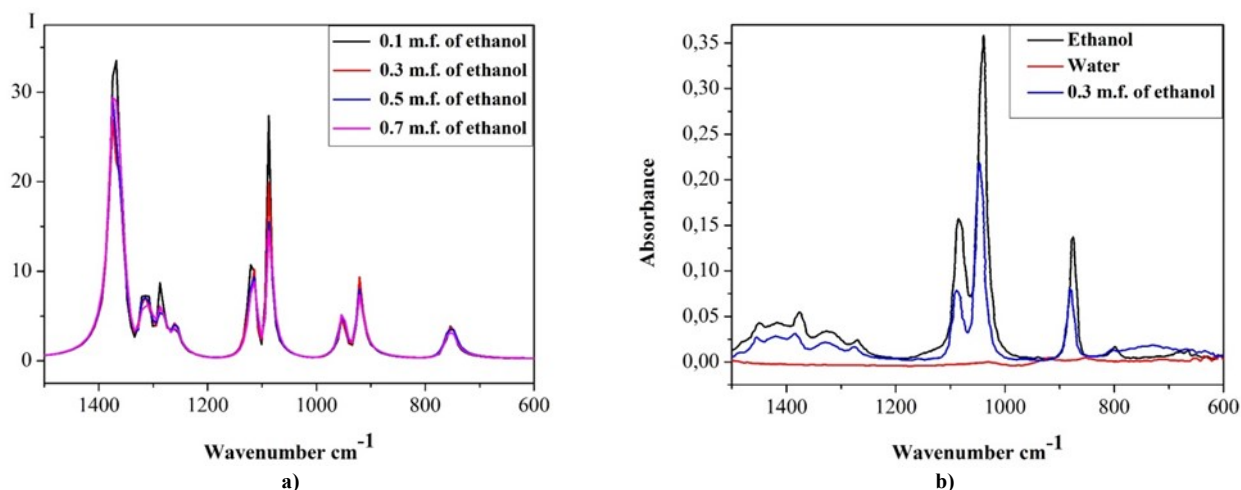


Figure 2. FT-IR spectra ($1500\text{--}600\text{ cm}^{-1}$) for water and ethanol, as pure substances and aqueous solutions of ethanol for concentrations of ~ 0.3 mole fraction in finger printed wavelength range: a) calculated values obtained from molecular study, which are extracted for ethanol contribution only and b) experimental data.

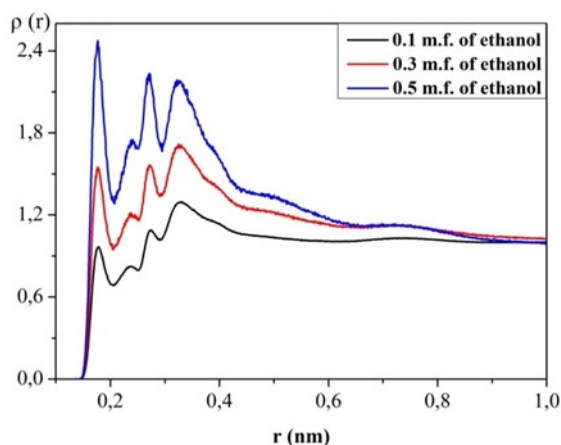


Figure 3. Radial distribution function of water molecules at the different concentration of ethanol: 0.1 m.f. (black); b) 0.3 m.f. (red); 0.5 m.f. (green).

majority of water molecules are located at a significant distance from each other at low concentration of ethanol. At high concentrations, the amount of water decreases, a close position of the water molecule observed, apparently associated with the formation of small clusters of water molecules. The intensity of the peaks for short and long bonds is the same at a concentration of 0.3 mole fractions.

The obtained result explained as follows: embedded ethanol molecules “broke” the hydrogen framework of water and there is a uniform distribution of short and long bonds of hydrogen bonds. These results suggest that the ethanol – cluster is the most stable structure, which is realized in an aqueous solution of ethanol at the 0.3 mole fraction of ethanol (Fig. 4).

Conclusion

Thus, the combined use of the molecular dynamics method, when compared with the experimental data obtained in this work by the spectroscopy method makes it possible to obtain a number of

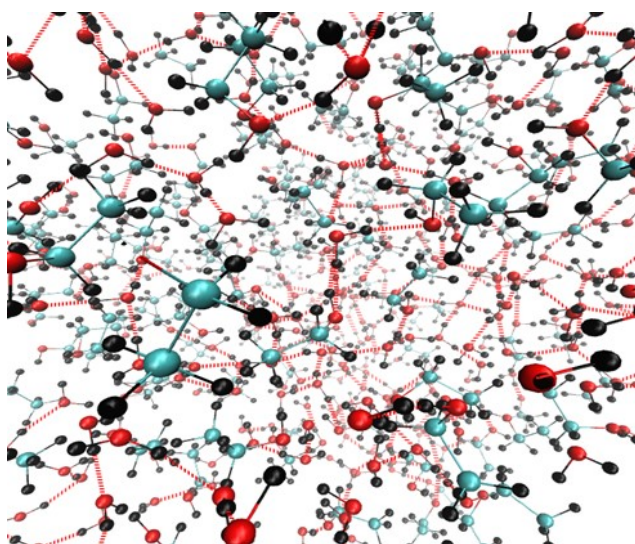


Figure 4. Snapshot of an aqueous solution of ethanol at a 0.3 mole fraction of ethanol taken from molecular dynamics simulation.

information about the structure and dynamic mechanisms in systems. These methods complement each other. A reasonable compromise is the molecular dynamics method with classical force fields. On the one hand, it allows explicitly consider solvent molecules, that is, to take into account short-lived systems with strong (short) H-bonds. Hence, the combined use of molecular dynamics with classical force fields seems to be the most promising approach for studying strong H-bonds in aqueous systems and allows one to interpret the experimental data obtained by IR spectroscopy.

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