Contents lists available at ScienceDirect



Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy



Study of hydrogen bonding in ethanol-water binary solutions by Raman spectroscopy



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A R T I C L E I N F O

Article history: Received 5 July 2017 Received in revised form 29 August 2017 Accepted 31 August 2017 Available online 01 September 2017

Keywords: Raman spectra Ethanol-water binary solutions Hydrogen bond Ethanol-water structure

1. Introduction

Water is one of the most basic and important materials in living systems. Despite its apparent molecular simplicity, it has long been considered as complex nature [1]. Ethanol has been widely used in medicine and food. Especially, the interaction between ethanol and water molecules by hydrogen bonding is a central issue [2–4]. Understanding the structure of hydrogen-bonding networks in ethanol-water binary solutions is crucial to elucidate role of water molecules in many biological and chemical processes occurring in aqueous solutions, and anomalous properties of the water itself [5,6]. Yui H et al. think that an ethyl group is a hydrophobic group and small enough to exist in the cage of hydrogen-bonding network structure in dilute ethanol solutions by stimulated Raman scattering [7]. Some researchers find that ethanol molecules stack on top of each other by hydrophobic interaction of ethanol ethyl groups in the region from 0 to 0.08 by using mass spectroscopy, X-ray diffraction and infrared spectroscopy [8,9]. However, the interaction of hydrogen bonds in ethanol-water binary solutions still lack of detailed description. Vibrational spectroscopis studies on the water molecular structure and dynamics have been shown to be beneficial both in the bulk and confined state, and the spectra are sensitive to local environment of molecule [10–12]. Raman spectroscopy is one of the most commonly used techniques to study liquid and solid water, as it provides direct information on inter- and intra-molecular vibrational modes [13,14]. At the same time, it can obtain the information of molecular vibration and rotation to understand the structure of water

ABSTRACT

Raman spectra of ethanol-water binary solutions have been observed at room temperature and atmospheric pressure. We find that with increasing ethanol concentration, the symmetric and asymmetric O—H stretching vibrational mode (3286 and 3434 cm⁻¹) of water are shifted to lower frequency and the weak shoulder peak at 3615 cm⁻¹ (free OH) disappears. These results indicate that ethanol strengthens hydrogen bonds in water. Simultaneously, our experiment shows that Raman shifts of ethanol reverses when the volume ratio of ethanol and the overall solution is 0.2, which demonstrates that ethanol-water structure undergoes a phase transition. © 2017 Elsevier B.V. All rights reserved.

molecules and the interaction between water molecules and other materials [15,16]. Raman shifts depend upon structural change or phase transition at the specific conditions (high or low temperatures and high pressure) [17].

In this article, we describe Raman measurements on ethanol-water binary solutions with varying mixing volume ratios. The results show that ethanol strengthens hydrogen bonds of water. In addition, Raman shift of ethanol in ethanol-water binary solutions have blue or red shift due to hydrogen bonding between water and ethanol molecules. More importantly, ethanol's shifts reverses when the volume ratio is 0.2, which demonstrates that ethanol-water association structure generates a phase transition. These results are significant to understand other the impurity species, such as methanol, acetone, etc., impacting on the structure of water and alcoholic molecules by hydrogen bonds.

2. Experimental

The liquid water of ethanol-water binary solutions has been deionized from triple distilled water. The pure ethanol has been used high performance liquid chromatography grade (>99.5 v/v%; Wako Pure Chemical Industries). The spectra of ethanol-water binary solutions with varying mixing volume ratios (0, 0.05, 0.1, 0.2, 0.4, 0.8, 1) have been measured by Raman micro spectrometer. The sample has been kept in the 10 mm of radius quartz disk. The binary solutions have been excited by an Argon laser at 5145 Å and an output power of 20 mW. The Raman spectra have been obtained using a Renishaw InVia Raman spectrometer. The Raman spectra in backscattering configuration have been obtained by using a $50 \times \log$ working distance objective lens located in the different mixing volume ratios ethanolwater solutions and detecting with a CCD detector. The spectra have

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been obtained at a scanning speed of $10 \text{ cm}^{-1}/\text{min}$. A 1200 lines/mm grating has been used, which resulted in a spectral resolution of 4 cm^{-1} .

3. Results and Discussion

3.1. Hydrogen Bond in Water

Fig. 1 shows Raman spectra of bulk water in ethanol-water binary solutions with different mixing volume ratios in the range from 3000 to 3800 cm⁻¹. The three peaks at 3286, 3434 and 3615 cm⁻¹ appear in the spectra. The peak at 3286 is attributed to symmetric O-H stretching vibrational mode. The assignment of the peak at 3434 cm⁻¹ is still controversial. J. Scherer et al. consider it to be the symmetric O—H stretching vibrational mode of asymmetrically bonded water molecules [18], where the two H of water molecules are bonded to the neighboring water molecules by strong and weak hydrogen bonds, respectively. Other researchers consider it to be the bifurcated hydrogen bond [19]. This peak strength is an indicator of bond disordering in water molecular arrangement in any case [20]. The shoulder peak at 3615 cm^{-1} results from free OH vibrational mode. Fig. 2 is Raman shift vs volume fraction of ethanol, which shows that the symmetric and asymmetric O—H stretching vibrational mode of water moved to lower frequency as the concentration ethanol increasing, and the weak shoulder peak at 3615 cm^{-1} (free OH) disappears at 0.2 mixing volume ratios. Especially, Raman shifts drop drastically at low mixing volume ratios (≤ 0.2), which is the same as the effect of cooling. We consider that ethanol can strengthen hydrogen bonds in water, which leads to the above phenomenon.

Previous studies have demonstrated that hydrogen bonding locate between ethanol and water in their binary solutions [21–24]. Hydrogen bonds result in peak shifts to low Raman shift. The energy shift of vibration depends on the volume ratios in the ethanol-water binary solutions by the effect of hydrogen bond. Hiroharu Yui et al. have found that the hydrogen-bonding network structure of water is reinforced by increase of a small amount of ethanol molecules [7].

It is well known that an ethanol molecule (C_2H_5OH) consists of an apolar ethyl group (C_2H_5 —) and a hydroxyl group (—OH). A hydroxyl group can rearrange the original network structure of water molecules through hydrogen bonding. In addition, an ethyl group is a hydrophobic group and is small enough to exist in the cage of hydrogen-bonding network structure. Some researchers think that no remarkable change resulted from the hydrophobic hydration take place in low mixing volume ratios. Thus, most of the ethyl groups are located in the cage of water hydrogen-bonding network in dilute ethanol solution [2]. From a viewpoint of structural change, a previous report has showed



Fig. 1. Raman spectra of water with varying mixing volume ratios.



Fig. 2. Raman shift vs volume fraction of ethanol.

that an O—O pair exhibited the decrease of "linear" hydrogen bonds (LHB) at 2.85 Å and the new peaks appearance at 3.3 Å by using X-ray radial distribution function. These changes are quite similar to those observed in low temperature pure water where interstitial water molecules are increased. It indicates that reinforcement of the original hydrogen-bonding network takes place in dilute ethanol solutions without recourse to the icelike LHB-based configuration [8]. From view of a vibrational spectroscopy, a bifurcated hydrogen bond (BHB) [19] and a cyclic trimer ring including another type of bifurcated hydrogen bond [25] are also believed to give a OH stretching band around 3400 cm⁻¹. Although LHB is somewhat distorted in these BHB and cyclic trimer ring hydrogen bonds, they can also produce stable hydrogen-bonded network structures [26]. As mentioned above, ethanol strengthens hydrogen bonds in water.

3.2. Influence of Hydrogen Bond in Ethanol

Raman spectra of ethanol in ethanol-water binary solutions with varying mixing volume ratios are shown in Fig. 3. The peaks at 2929 and 2974 cm⁻¹ are attributed to symmetric and asymmetric CH₃ stretching mode in Fig. 3a, respectively, while the CH₂ stretching mode is located in 2880 cm⁻¹. Fig. 3b shows the spectra of ethanol in ethanol-water binary solutions with varying mixing volume ratios in the range from 700 to 1600 cm^{-1} . The spectra includes all the peaks related to CH₂ character, the wagging mode at 1450 cm^{-1} and the deformation wagging mode at 1279 cm^{-1} . In addition, a weak mode at about 1470 cm^{-1} belongs to the symmetric deformation mode. The peak at 1095 cm^{-1} correspond to the skeletal CCO stretching and deformation modes, respectively [27,28]. Vibrational mode of ethanol is shown in Table 1.

Fig. 3a shows that the three peaks exhibit blue shift (Raman shift increase) for the ratios 0 and 0.2 and red shift (Raman shift decrease) for the ratios 0.2 and 1 with an increase concentration of the ethanol. Fig. 3b shows that red shift of all peaks take place in the region from 0 to 0.2 and blue shift happen in the region from 0.2 to 1. These phenomenon reveals that the Raman shifts of ethanol reverses when the volume ratio is 0.2, which demonstrates that ethanol-water association structure undergoes a phase transition. The blue and red shifts are caused by hydrogen bonds between water associates and ethanol associates [23,24]. Yui H et al. point out that an ethyl group is a hydrophobic group and small enough to exist in the cage of hydrogen-bonding network structure in dilute ethanol solutions [7]. Interestingly, some have found that ethanol molecules stack on top of each other by hydrophobic interaction of ethanol ethyl groups in the region from 0 to 0.08 by using mass

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