Near-infrared spectroscopic study of molecular interaction in ethanol-water mixtures ranging from 0 to 10% (*v/v*)

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Introduction:

A deep understanding of the microscopic behavior of aqueous alcohol solution is indispensable for many chemical and biological processes [1-3]. Despite many researches on alcohol-water binary mixtures, it has remained an intriguing topic in numerous theoretical and practical investigations for many decades. Many studies have indicated that alcohol and water undergo incomplete or non-ideal mixing, as shown by the anomalous thermodynamics or physicochemical properties changing nonlinearly with alcohol-water mixing ratio[4]. This study was aimed to focus on the intermolecular interaction between ethanol and water ranging from 0 to 10% (*v/v*). The excess NIR spectroscopy was used to explain microscopic information of ethanol-water mixtures at the molecular level within the entire concentration for the first time. Gaussian fitting combined with genetic algorithm (GA) optimization was adopted to distinguish water species with the knowledge of aquaphotomics for understanding the changes caused by ethanol in the structure of water.

Methods: Reagents and sample preparation: Ethanol anhydrous was of analytical grade. Ethanol-water mixtures of 0-10% with the increment of 1% were prepared using deionized water. FT-NIR spectroscopy: All NIR spectra were measured from 10000 to 4000 cm^{-1} using Antaris II FT-NIR spectrometer (American Thermo Fisher scientific company) with 1 mm cuvette. A tungsten-halogen light source and InGaAs detector were used. The resolution was 4 cm^{-1}, and both an air reference and its spectra were measured, with a scan number of 64. The spectrum of each sample was collected triples and averaged as final spectrum. Data processing: (1) excess infrared spectrum: an excess infrared spectrum is defined as the difference between the spectrum of a real solution and that of the respective ideal solution under identical condition. (2) The generalized 2D correlation spectral analysis: programmed based on the algorithm developed by Noda[5]. In the present paper, solid and dashed lines represent positive and negative correlation intensities in 2D correlation contour map, respectively. (3) Gaussian fitting method: A Gaussian fitting method was used to separate the spectral components from the overlapping first overtone of O-H spectra and a GA method was adopted for optimization of the peak position and width of different water species for 0-10% ethanol solution.
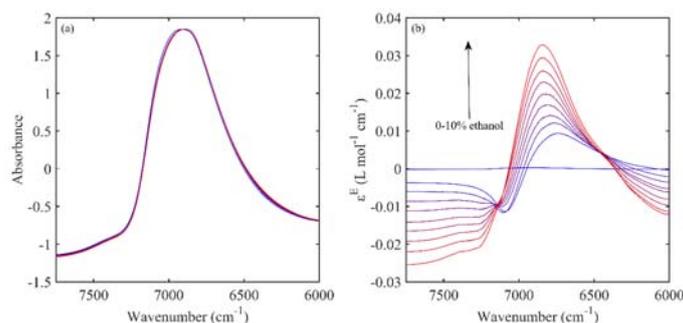
Results and Discussion:

Figure 1. NIR (a) and excess NIR (b) spectra of the ethanol-water mixtures in the range of the first overtone of O-H groups. (a): SNV preprocessed spectra;(b): From the bottom to top, the volume fraction of ethanol increases from 0 to 10% with an increment of 1%.
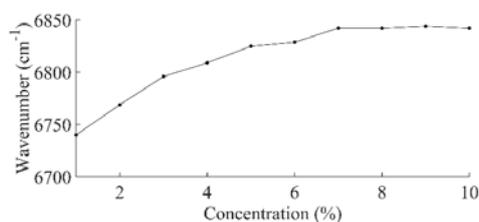

Figure 2. Peak position for the excess spectra in Figure 2(b) with ethanol concentration
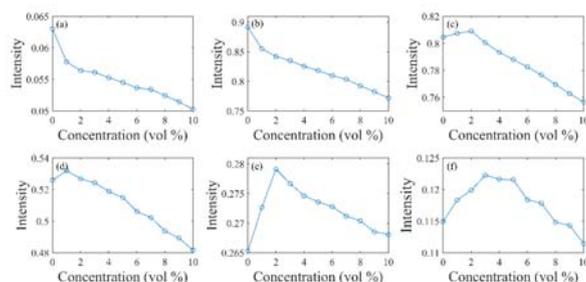
Figure 4. Variation of the intensities for the spectral components including S_r (a), S_0 (b), S_1 (c), S_2 (d), S_3 (e), and S_4 (f) in ethanol-water mixtures with different concentrations of ethanol.

NIR and excess NIR spectra of ethanol-water binary mixtures ranging from 0% to10% in the region of the first overtone of O-H are shown in Figure 1. As can be seen in Figure 1 (a), along with the increasing volume fraction of ethanol, the dominant peak at around 6890 cm^{-1} decreases and shifts slightly to higher wavenumber. The relative intensities of the peaks at 6740 cm^{-1} and 7750-7010cm^{-1} in Figure 1(b)suggest that the population of the former overpowers the latter with increasing concentration of ethanol. The position of positive excess peak is plotted against ethanol concentration in Figure 2. As shown, from 1% to 7%, there is an upward shift in excess peak indicating that hydration effect between ethanol and water plays a main role and in 1-3% the shift velocity is the fastest and from 3% to 7%, it slows down. In the range of 7-10%, the peak position remains almost constant, therefore hydrogen bonding interaction becomes the main factor affecting the spectra of mixtures. A Gaussian fitting combined with GA method was employed to separate the spectral components from the overlapping spectra in the range of first overtone of O-H. The height of each peak of the water component was recorded and plotted in Figure 3. It is clear that the intensities of S_r and S_0 decrease but those of S_1, S_2, S_3, and S_4 go through a rising phase firstly and then decrease as the ethanol concentration increased and the addition of ethanol promotes the conversion of free water to hydrogen bonded water. The decrease of Sr might also be explained by the strengthening of the hydrogen bonding. Rotation becomes harder for the O-H in hydrogen bonded water network than that without hydrogen bonding. S_1, S_2, S_3 and S_4 all experience increasing firstly and then decreasing with different turning point concentrations. For S_4 in Figure 3(f), the intensity is enhanced when ethanol concentration is less than 3% and weakened when ethanol concentration is greater than 3%. The 3% ethanol concentration happens to correspond to the turning point of the excess peak shift velocity in Figure 2. It is speculated when a small amount of ethanol ($\leq$ 3%) is added into water, hydrophobic hydration plays a major role, followed by hydrophilic hydration in 3-7% ethanol concentration. Compared with S_4, as relative weaker hydrogen bonds, S_1, S_2 and S_3 may be located outside the ethanol hydration shell and are therefore more susceptible to the ethanol newly added and easier to be destroyed at relatively lower concentration of ethanol.

Conclusions: The ethanol solution under 10% was investigated with excess spectroscopy and Gaussian fitting method, indicating that hydrophobic hydration plays a key role when the concentration of ethanol is lower than 3%, while the hydrophilic hydration dominates the hydrogen bonding network with the ethanol concentration ranging from 3% to around 7%. When the ethanol concentration is higher than 7%, the hydrogen bonding interaction is the main acting force and the energy of hydrogen bonding.

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