

Hydration Structure of Acetone Studied with Concentration-Dependent Absorption Spectra in the Ultraviolet Region

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Hydration structure plays a fundamental role in our understanding of physical properties and chemical reactions of solutes. One of the typical aqueous solutions is acetone solution, but the physicochemical properties still need to be studied. Acetone is miscible with water in any ratio. The mixture has a negative excess enthalpy in the dilute region [1], indicating an attractive interaction between acetone and water. The interaction is a hydrogen-bond type, with an additional weak C–H···O bond in a very dilute region [2]. The purpose of this study is to explore the hydration structure of acetone using UV absorption spectroscopy.

The experiments were performed on the beamline for vacuum-ultraviolet circular dichroism spectroscopy, BL-12. The sample chamber [3] was filled with the nitrogen gas. The sample cell consisted of two CaF₂ windows and a Teflon spacer with a thickness of 200 μm . The measurement range was 170–320 nm, and the spectrum of liquid water was used as a reference. The sample acetone–water binary mixture was prepared with molar fraction of acetone ranging from 0.05 to 0.50. Acetone was obtained commercially from FUJIFILM Wako Pure Chemicals Corp., Japan.

The peak of $\pi^* \leftarrow n$ absorption band non-linearly shifts to the longer wavelength with the molar fraction of acetone, x_A . The absorption band and the peak shift are shown in Fig. 1. All the spectra have a tail toward the shorter wavelength. This implies that the spectra consist of some components. The components include hydrated acetone. The hydration structure depends on x_A . Judging from the shift of the peak position, there are three regions: Region 1; $x_A = 0.05\text{--}0.10$; Region 2, $x_A = 0.15\text{--}0.35$; and Region 3, $x_A = 0.40\text{--}0.50$.

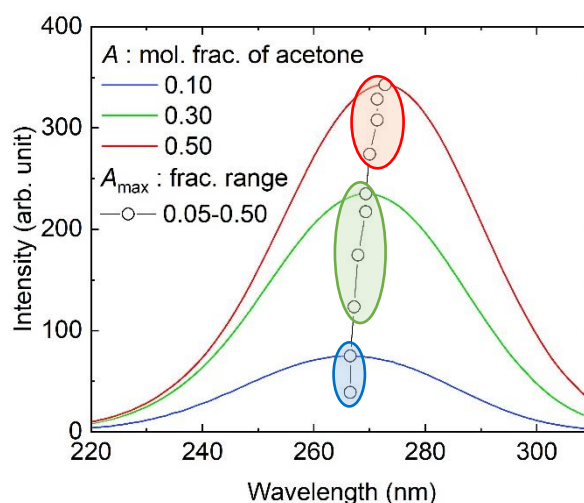


FIGURE 1. The $\pi^* \leftarrow n$ absorption band of acetone aqueous solution at different molar fractions.

Quantitative analysis of the change of the band has been carried out by the principle component analysis (PCA). The result of PCA is shown in Fig. 2. The measurement spectra are well explained by two components (total 99.99%). The primary component (PC1) has a peak at 270.70 nm and the secondary component (PC2) has a peak at 252.64 nm and a valley at 287.36 nm. The vector of PC1 corresponds to the average spectrum, and the score of PC1 is almost proportional to x_A . The score of PC2 increases in $x_A = 0.05$ – 0.20 , reduces in $x_A = 0.25$ – 0.35 , and is negative in $x_A = 0.40$ – 0.50 . The PC1 is similar to the spectrum for $x_A = 0.35$. This indicates that the dominant hydration structure is the 1:1 acetone–water complex. Additional hydration structures are analyzed as PC2.

The physical meaning of PC2 is made clearer if we plot the difference spectra from PC1. The difference spectra have a sinusoidal-like shape. The behavior of peak shift is reproduced by the difference spectra. Peaks come at shorter wavelengths in the spectra for Region 1, suggesting an additional attractive interaction with water. A possible interaction model is shown in Fig. 3(a): The acetone molecule interacts with two water molecules. This kind of hydration model is the same as that proposed in an IR and NMR spectroscopic study [2]. In Region 2, two acetone molecules are hydrated with one water molecule like in Fig. 3(b). In Region 3, there are not enough water molecules for hydration due to the large x_A : The solution contains non-hydrogen-bonded acetone molecules. The presence of the non-hydrogen-bonded molecules is supported by the coincidence of the peak of PC2 with the absorption peak position of gaseous acetone [4].

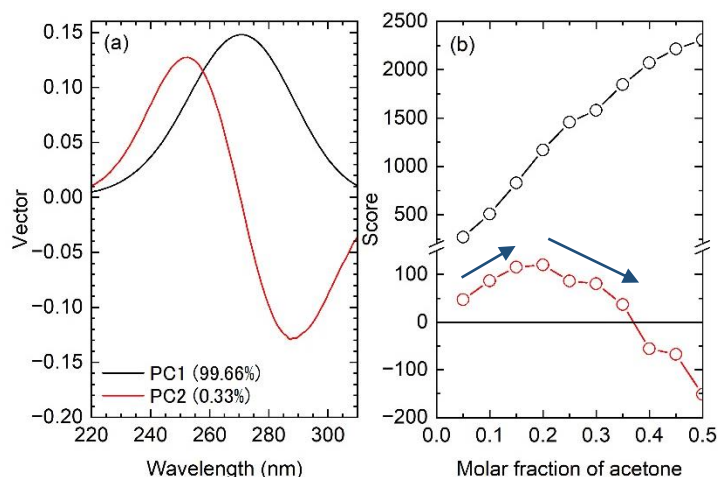


FIGURE 2. Spectral components (a) and scores (b) obtained by PCA for the UV absorption data presented in Fig. 1.

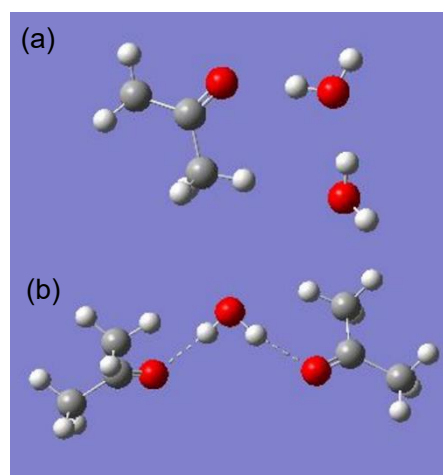


FIGURE 3. Plausible hydration structures of acetone; (a) 1:2 complex, (b) 2:1 complex.

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