Concentration dependence of mixtures of water and 3-methylpyridine using MD simulations

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Hydrogen bonding is extremely important as a factor governing the physicochemical properties of aqueous solutions. It is expected that a better understanding of its nature will lead to its application in various research fields. In this study, we investigated the behavior of hydrogen bonding in mixtures of water and organic compounds using Fourier Transform Infrared Spectroscopy (FTIR) and theoretical calculations. As an organic compound, 3-methylpyridine (3MP) was chosen. In this compound, it is known that OH...N hydrogen bonds are formed between a lone pair of nitrogen atoms in the pyridine ring and water molecules in aqueous solution.

First, Attenuated Total Reflection (ATR) FT-IR measurements were performed using mixed solutions of various concentrations, and it was found that the peak of the in-plane angular vibration of the pyridine ring corresponding to the vibration at 1029 cm^{-1} (Figure 1) shifted to the higher wavenumber side as the ratio of water increased. This peak shift was also observed for other organic compounds with pyridine rings. The smaller the dipole moment, the weaker the hydrogen bond formed, so the experiment was conducted using chloroform as the solvent. Since the peak shift was smaller than that of water, we considered that this peak change was due to hydrogen bonding.

Next, several aqueous solution models were created with different concentrations of water molecules and 3MP molecules, totaling 50000 molecules, and Molecular Dynamics (MD) simulations were performed with ambient conditions under NPT ensemble. After equilibration, phase separation was observed in each model (Figure 2). This suggests that phase separation may occur even at room temperature in this mixed solution from a microscopic viewpoint.

X-ray absorption spectroscopy (XAS) calculations were performed. The calculations were performed using a cluster model consisting of 19 molecules around a single molecule of water. In the obtained spectra, no pre-edge peaks were observed, which were observed experiments.

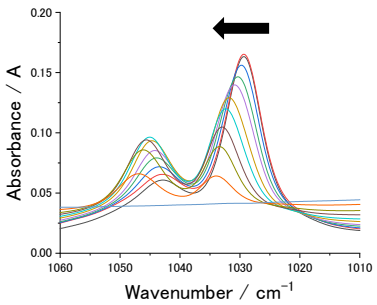

Figure1 ATR FT-IR spectra of water/3MP mixture

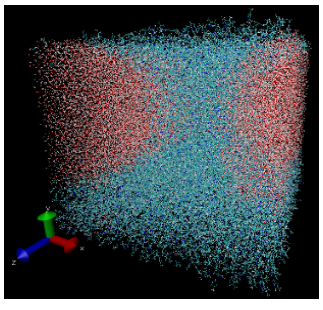

Figure2 Results of MD simulation of water/3MP mixture

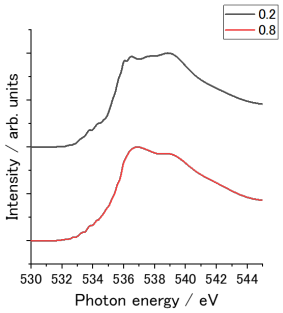

Figure3 Results of XAS calculations for water/3MP mixtures