Hydrogen Bonding Behavior in Response to Concentration Changes in Mixed Solutions of Water and Organic Compounds

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Aqueous mixtures are complexly intermingled within a solution owing to the effects of intermolecular interactions and polarization effects. Among these, hydrogen bonding is extremely important in governing the physicochemical properties of aqueous solutions. A deeper understanding of its nature is expected to lead to applications in various research fields. In this study, we investigated the behavior of hydrogen bonds in mixtures of water and organic compounds using Fourier-transform infrared spectroscopy (FTIR) and theoretical calculations. Pyridine and 3-methylpyridine (3MP) were selected as the organic compounds. For these compounds, it is known that OH...N hydrogen bonds are forming between the nitrogen atom bearing the nonbonding electron pair on the pyridine ring and the water molecules in the aqueous solution.

First, attenuated total reflection (ATR) FT-IR measurements were performed using water/3MP mixed solutions at various concentrations. As the water ratio increased, the in-plane angular vibration peak of the pyridine ring corresponding to the 1029 cm^{-1} vibration (Figure 1) shifted to the high-frequency side. This peak shift was also observed in other organic compounds containing a pyridine ring. Because hydrogen bonds formed with smaller dipole moments are weaker, experiments using chloroform as the solvent were conducted. The peak shift was smaller than that observed with water, leading us to conclude that this peak change is attributable to hydrogen bonding.

Next, multiple aqueous solution models (50,000 molecules in total) were created by varying the concentrations of water and pyridine molecules. Molecular dynamics (MD) simulations were then performed under NPT ensembles at room temperature. After equilibration, calculating the solution concentrations revealed discrepancies between the simulated values and experimental data. Therefore, we introduced the Charge-On-Particle (COP) model and reran the MD simulations. The results showed less molecular bias compared to before introducing the COP model, and the solution density values were closer to the experimental values, achieving more accurate solution modeling (Figure2).

Additionally, we constructed an apparatus for measuring X-ray absorption spectroscopy (XAS) of liquid samples at HiSOR's BL-6 (Figure3). Moving forward, we aim to advance research on the concentration dependence of water and organic compounds in XAS from both computational and experimental perspectives.

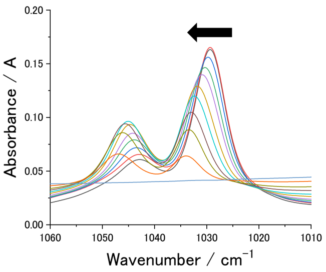

Figure1 ATR FT-IR spectra of water/3MP mixture

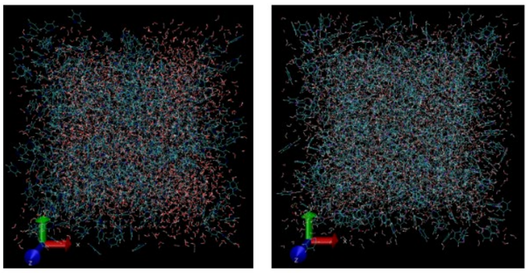

Figure2 Water solution model before cop model implementation (left) and after implementation (right)

Figure3 BL-6 Experimental Facility