Resonance and non-Resonance Raman Spectroscopic Measurements of Solvatochromic Probe Molecules in Supercritical Water

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Elucidation of the solvation properties in supercritical water (SCW) is one of the important subjects of the physical chemistry of SCW. Until now, various kinds of spectroscopic methods such as NMR, X-ray absorption, UV-Vis absorption spectroscopy, fluorescence spectroscopy, and Raman spectroscopy have been applied to the solution of SCW. Among them, Raman spectroscopic method is a powerful tool to reveal the molecular nature of the solvation, especially the effect of the hydrogen-bonding characteristic to SCW. Since the hydrogen-bonding affects the local solvation structure around the solute molecule, it is generally difficult to extract the effect of the hydrogen-bonding from the spectroscopic method such as UV-Vis absorption or fluorescence which monitors the electronic state of the molecule. On the other hand, the shift and broadening of the vibrational bands of the solute molecule can be good indicators of the solute-solvent local interactions such as the hydrogen-bonding. In this paper, we will present the study on the resonance and non-resonance Raman spectroscopic measurements of solvatochromic dye molecules in SCW by using a high-pressure and high-temperature optical flow system.

The high-temperature and high-pressure optical flow system was designed for Raman measurement under the back scattering geometry using an electronically cooled CCD camera as a detector which was attached to a 64 cm monochromator with 1800 and 600 lines mm\(^{-1}\) gratings. The high-pressure cell was equipped with two sapphire windows (3.5 mm diameter, 2 mm thickness). The aperture angle of the window was 45° in order to collect the scattering from the sample effectively and the optical path length was approximately 5 mm. The sample solution, which was bubbled by dry nitrogen or argon continuously, was flowed into the high-pressure cell at a rate of 1.0-1.5 ml/min using an HPLC pump in a single-pass configuration. The temperature of the cell was regulated within an accuracy of ±1K by a sheathed heater wounded around the cell and a thermocouple directly inserted to the sample chamber.

Depending on the excitation condition of the sample solution (resonance or non-resonance), the probe wavelength was selected from various kind of choices (an Ar ion laser, a Kr ion laser, or a Nd:YAG laser). We have applied this system on the study of the solvation of p-nitroaniline and p-aminobenzonitrile in SCW. The solvent density dependence of the characteristic vibrational modes such as NO\(_2\), NH\(_2\), and CN stretching vibrations was clarified.

Session: ICPWS XV / 09. Apparatus, Materials, Monitoring Instrumentation for Applications at High Temp. and Pressures (Mon. 03)
Recommendation: accepted for oral