Structural Change of Supercritical Carbon Dioxide with Entrainer Molecule

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Recently, supercritical carbon dioxide (sc-CO_2) has attracted much attention as an environmentally accepted solvent. The solvent power of sc-CO_2 extremely increases with adding a small amount of entrainer molecule such as alcohol, carbon hydride, and water. Since the solubility of sc-CO_2 is strongly connected with its fluctuation structure, it is quite important to investigate the effects of entrainer for mesoscale structure of sc-CO_2. In the present study, the structural change of sc-CO_2 induced by adding the entrainer has been observed with small-angle neutron scattering (SANS).

A SANS experiment was performed using SANS-U of the Institute for Solid State Physics, the University of Tokyo installed at JRR-3M in Tokai, Japan. Scattering intensity with a Q range between 0.02 and 0.2 Å^{-1} can be measured by using 7 Å neutron in 2 m camera length. Methanol (CD_3OD) or ethanol (C_2D_5OD) was added into sc-CO_2 with 1 mol% concentration as entrainer. Measurement temperature was fixed at 38 °C and pressure was varied from 7.66 to 10.36 MPa.

The ovserved SANS intensity was simply analyzed with Ornstein-Zernike (OZ) equation to obtain OZ correlation length, ξ, and $I(0)$. Although the system consisted of both density and concentration fluctuations, all the SANS data can be well analyzed with a single OZ equation. Since the concentration of entrainer was dilute, the scattering intensity mainly came from the density fluctuation of the mixed solution. The pressure dependences of ξ and $I(0)$ along the isotherm are shown in Fig. 1(a) and 1(b), respectively. Results of both pure and alcohol entrained sc-CO_2 are displayed in this figure. Each data has a maximum along the isotherm corresponding to the ridge structure in supercritical region. The maximum values of ξ and $I(0)$ of sc-CO_2 with alcohol become considerably larger than those of pure sc-CO_2. Moreover, the pressure at which the fluctuation becomes maximum sifts to the lower. It was suggested that these changes could be induced by attractive interaction between the alcohol and CO_2 molecules. Magnitude of the interaction with the ethanol is stronger than that with the methanol. It is considered that these structural changes with alcohol molecules associate with the increase of solvent power of sc-CO_2.

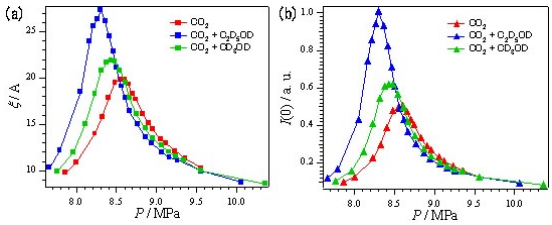

Fig. 1. Change of structural parameters ξ and $I(0)$ along the isotherm of 38 °C induced by adding 1 mol% methanol and ethanol.