Structural investigation on super crtical CO_2 and co-solvent system

Masaaki Sugiyama, Takashi Sato, Keiji Ito, Kazuhiro Mori and Toshiaru Fukunaga
Research Reactor Institute, Kyoto University

Supercritical carbon dioxide (sc-CO_2) is widely recognized as an environmentally accepted solvent for reaction chemistry. Unfortunately, this green solvent has lesser solubility than the other major organic solvents. To overcome this point, small amount of the second chemical, entrainer (co-solvent), is added to enhance the solubility. Therefore, it is very important to understand this entrainer effect from the both of fundamental and application chemistry.

The solvent property of sc-CO_2 is deeply related with its structure of density fluctuation in nano-scale. It means that the clarification of the nanostructure is very important to understand the solvent property of sc-CO_2 and that with co-solvent. Small-angle neutron scattering (SANS) is one of the most suitable technique to clarify the nanostructure. Because neutron has very high trasmission for many substances comaped with X-ray: artificial sapphire with the thickness of 10 mm can be used for the window of a pressure cell. In this study, we observe the SANS of sc-CO_2 with protonaed ethanol and deuterated-ethanol, and pure sc-CO_2 as a reference.

SANS experiments were performed with SANS-U spectrometer. Samples were sc-CO_2, sc-CO_2 with 1 mol% protonated ethanol, sc-CO_2 with 1 mol% deuterated ethanol. Along the isothermal line at 39˚C, we observed the nanostructure at 10 different density points from 0.275 g/cm^3 to 0.609 g/cm^3 (presuure: 7.89 MPa to 10.00 MPa, critical point of pur CO_2: 31.1˚C, 0.468 g/cm^3, 7.38 MPa).

The observed SANS data were analyzed with Ornstein-Zernike formula. The results were shown in Fig. 1. As you can see, the peak positions of correlation length and density fluctuation are shifted to lower density. In the peak position, several characteristic values, for example dissolving power, show drastical change: in the higher density, the dissolving power becomes enhanced. Therefore, from the view point of nanostructure, the entrainer effect has been confirmed in this study.

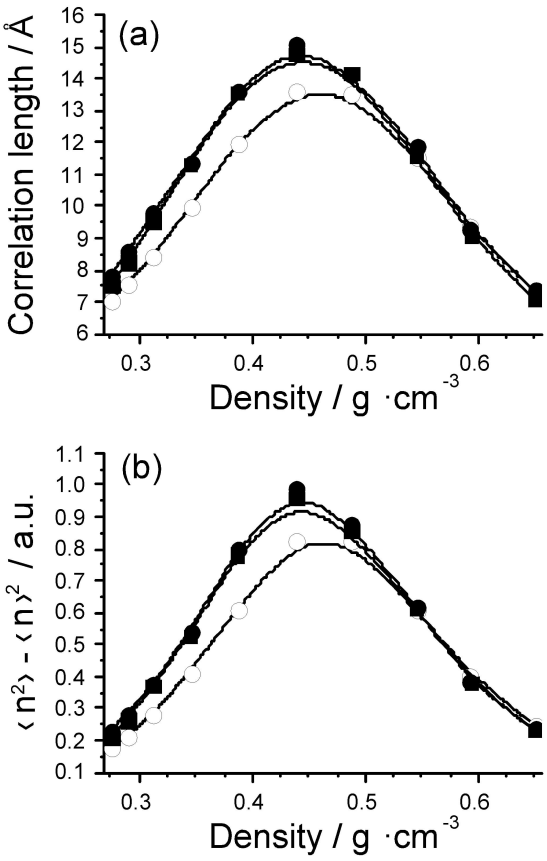

Fig. 1. Density dependece of observed correlation-length (a) and density fluctuation (b). Open circles, closed squares and closed circle shows those of sc-CO_2 and sc-CO_2 with 1 mol% protonated ethanol, respectively,