15A/00G069

SAXS Measurement of Supercritical CO_2 Solution Saturated by Naphthalene

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Introduction

Supercritical (SC) fluids have attracted much attention from both viewpoints of basic sciences and industrial applications, especially as novel media of extraction processes and chemical reactions. It has been revealed that the characteristic properties of SCFs are closely related to the inhomogeneous structure. The inhomo-geneity is described by density fluctuation or correlation length.

For industrial purposes, SC CO_2 is widely used as a solvent for organic solutes and Naphthalene (Nph) is one of the representative model solutes. Some physicochemical properties of CO_2-Nph are studied; for example, solubility, partial molar volume and so on. In the present study, the fluctuation and correlation length of the SC CO_2 solutions saturated by Nph are investigated by small-angle X-ray scattering (SAXS).

Experiment

The SAXS measurements were performed using the apparatus settled at BL-15A station. A sample holder made of SUS316 was used, which has two diamond windows. The temperature and pressure were monitored with a Pt sensor and a strain gauge, respectively. Enough Nph crystals were brought in the sample holder so that they always existed in the bottom. Nph was solved and saturated in SC CO_2 by stirring the stainless small balls in the holder by means of a magnet. The measurements were carried out along two isothermal conditions at $T_r = T/T_c = 1.031$ and 1.051 (T=316.85 and 322.95 K), and the pressure was varied in the range of from 7.5 to 13.1MPa. The accumulation time of each run was 300s.

Results and Discussion

The fluctuation term and correlation length ξ were obtained by the Ornstein-Zernike plot. In Figure, The values of ξ are plotted by symbols Δ (T_r=1.031) and © (T_r=1.051) against $P_r = P/P_C$. For comparison, the values of ξ of neat CO_2 at same T_rs are also shown with a solid and a dotted curves. The solubility changes drastically as the peaks being the boundary. It is interesting that the ξ values of the neat SC and the solution for higher-pressure region are almost the same where the solubility of Nph in SC CO_2 is large, while there exists the difference for lower-pressure region where the solubility is very small. This implies that the structure change is drastic in the case of the dilute solution. The fluctuation term of SAXS intensity from a solution involves the density fluctuation, concentration fluctua-tion and their cross terms. The division of the contributions is left for future studies, because some thermo-dynamic data are necessary for the analysis.