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SAXS MEASUREMENT OF SUPERCRITICAL CYCLOHEXANE

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Introduction

Supercritical (SC) fluids show various unique behaviors and their properties are closely related to inhomogeneity of molecular distribution. The structural fluctuation for some substances, for example CO_2, CHF_3, C_2H_4, C_6H_6, and H_2O, has been already obtained by small-angle X-ray scattering (SAXS) measurements. To clarify universality of structural fluctuation is very important subject for understanding of the properties of SC fluids. Accumulation of data for other substances is also important.

Cyclohexane is one of cyclic hydrocarbons, whose molecule is approximately spherical, and its main intermolecular interaction is not so particular. Though molecular size of cyclohexane is similar to C_6H_6 and larger than the others, it is one of representative sample for the study of the structural fluctuation and for the discussion on the universality. SAXS measurements for SC cyclohexane were carried out and correlation length was obtained. We focused on molecular size effect for the correlation length ξ.

Experimental

The SAXS measurements were carried out, using the apparatus settled at the BL-15A station. A sample holder made of SUS304 for high temperature and pressure was used, which has two diamond windows sealed with gold rings. The value of pressure and temperature of sample were monitored with a strain gauge and a thermocouple, respectively.

Critical constants of cyclohexane are reported to be T_c = 553.60 K, ρ_c = 0.273 gcm^{-3} and P_c = 4.075 MPa. SAXS measurements were performed along three isothermal conditions at reduced temperature of $T_r = T / T_c$ = 1.02, 1.04 and 1.06 (564.7 K, 576.8 K and 588.0 K) and the pressure was varied in the ranges from 4.30 to 5.75 MPa, from 4.45 to 7.19 MPa, and from 4.30 to 7.57 MPa, respectively. The of e accumulation time ach run was 300 s.

Results and Discussion

The values correlation length ξ were evaluated by using the Ornstein-Zernike plots for obtained intensities. The correlation length of cyclohexane against pressure is shown in Fig. 1. The father from the critical temperature the isotherms are, the smaller ξ becomes and the higher-pressure side the peak positions shift to. The comparison of ξ between cyclohexane and those for CO_2, andC_6H_6 is shown in Fig.2. The values of ξ for cyclohexane are almost the same as that of C_6H_6 and larger than CO_2. Because cyclohexane does not have peculiar intermolecular force such as hydrogen bonding or dipole moment, it is considered that the molecular size is the largest contribution to the values of ξ for cyclohexane as well as C_6H_6.

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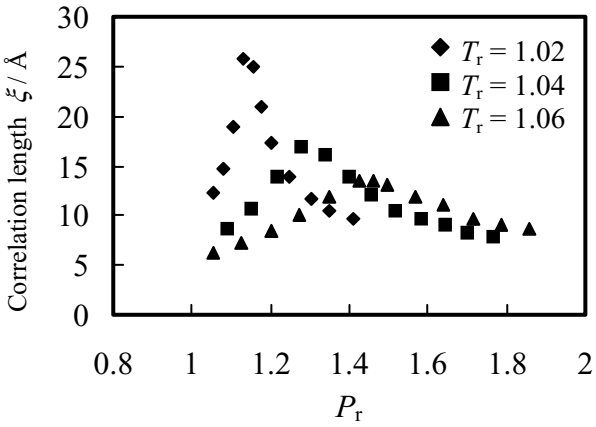

Fig. 1 Pressure dependence of the correlation length for Cyclohecane.

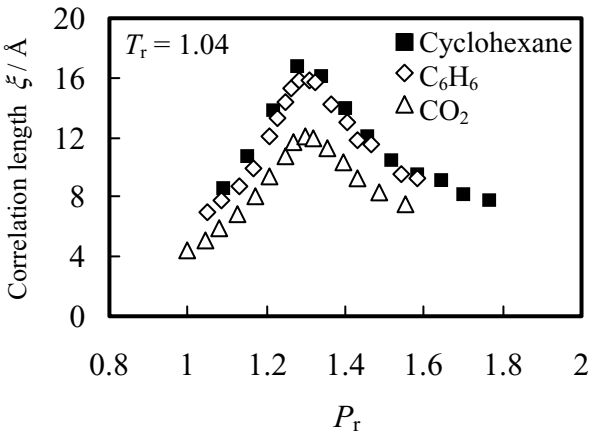

Fig. 2 Comparison of the correlation length.