BL-15A2/2014G688

Structural fluctuation of supercritical aqueous solution of *n*-pentane in entire concentration range

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1 Introduction

Hydrophobic material are rarely dissolved into water at ambient condition. Due to hydrophobic interaction, inhomogeneity of concentration increases, and the system approaches to phase separation. However, they perfectly mix at supercritical phase. Supercritical aqueous solutions of hydrophobic materials have applied to many applications. The ability strongly connects to the inhomogeneity (Boero *et al*, 2004).

To examine the inhomogeneity of supercritical aqueous solution of hydrophobic material (*n*-pentane), small-angle X-ray scattering (SAXS) measurements with synchrotron radiation were conducted.

2 Experimental

At BL-15A2, SAXS measurements for supercritical aqueous solution of *n*-pentane were performed along an critical isotherm of water at 647 K. The concentration of *n*-pentane are 0, 0.088, 0.2, 0.4, 0.7, and 1. The measured points are exhibited in Fig. 1. We selected gas- (●) and liquid-like states (□). An X-ray beam was monochromatized to = 1.50 Å and the observable region was 0.2 to 1.5 nm^{-1}, where the scattering parameter, s, is defined as $4\pi\sin\theta/\lambda$ (2θ : scattering angle, λ : wavelength).

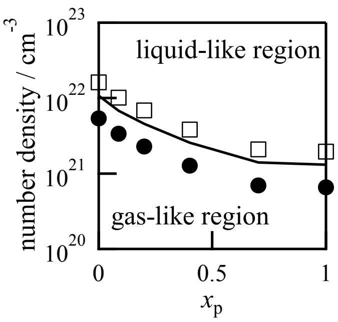

Fig. 1. Measured points. The solid line represents boundary between two regions.

For the SAXS measurement under high-pressure and high-temperature conditions, a sample holder was newly constructed. The body is entirely made of titanium alloy (Ti-6Al-4V), which has relatively low thermal extreme condition. Two diamond disks, 4.0 mm in diameter and 0.7 mm in thickness, were used as X-ray windows, and they were inserted into the cell body. Temperature and pressure of the sample were measured using a thermocouple and a stain gauge, respectively.

3 Results and Discussion

Fig. 2 shows SAXS profiles in only liquid-like region. We analyzed the fluctuation from the SAXS profiles using Bhatia-Thornton theory (Bhatia and Thornton, 1970). Fig. 3 shows the analyzed fluctuation behaviors. The density fluctuation were represented by F_w and F_p express the inhomogeneity of water and *n*-pentane in the system, respectively. The cross fluctuation, F_c, reflects attractive and repulsive interactions between water and *n*-pentane.

As shown in Fig. 3, the fluctuations in two states have almost same behavior at all the concentration except for x_p=0.088. The fluctuations of water have large value, which is generally observed in supercritical phase. This corresponds to coexistence of sparse and dens areas of water molecules. On the other hand, the fluctuation of *n*-pentane has the value close to zero. The result reflects uniformity distribution of *n*-pentane molecules in the space. *n*-Pentane molecules exist in dens area of water, as well as in sparse area, because the cross fluctuation has positive value (attractive interaction).

At x_p=0.088, the fluctuations of water and *n*-pentane became increasing as transferring from gas-like to liquid-like regions. Furthermore, the cross fluctuation changes to negative value (repulsive interaction). These results suggest that the system approach to phase separation at higher density condition.

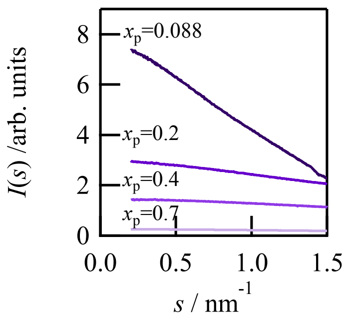

Fig. 2. Scattering profile of the present system in only liquid-like region. ($I(s)$: scattering intensity)

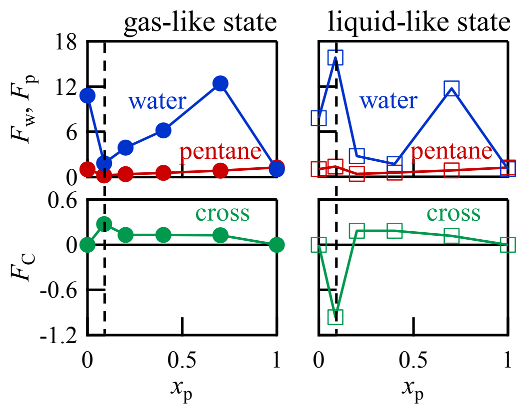

Fig. 3. Fluctuation behaviors in supercritical aqueous solution. x_p=0.088 (- - - -)

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