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Density and Concentration Fluctuations of Supercritical CO_2-CH_3OH Mixture

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Introduction

A supercritical fluid is defined as the fluid which exceeds the critical temperature and critical pressure. It is well known that the fluid has large inhomogeneity in the molecular distribution. Our group has studied the inhomogeneous structure of many supercritical fluids of one component as “density fluctuation” and revealed the close relation between the fluctuation and physico-chemical properties.

This time, we focused on the entrainer effect, especially solubility or selectivity change by means of addition of small amount of solute to a supercritical solvent. Namely, we studied the density and concentration fluctuations of CO_2-CH_3OH mixture to relate them to the efficiency entrainer effect.

The density fluctuation is the measure of the inhomogeneous molecular distribution. Therefore, large density fluctuation indicates intense aggregations occur. The concentration fluctuation is the measure of inhomogeneous mixing of different molecules. Hence, large concentration fluctuation denotes that identical molecules get together. These fluctuations can be derived from the data of isothermal compressibility, partial molar volume and small-angle X-ray scattering intensity [1].

Experimental

The examined sample is supercritical CO_2-CH_3OH mixture with x = 0.07 (x: mole fraction of CH_3OH). Temperature was set to 321.8 K corresponding to the 4% higher than critical temperature of the mixture, that is T_r = 1.04. And pressure range is from 9 to 15 MPa.

To obtain the isothermal compressibility and partial molar volumes were yielded by the accurate density measurements in our laboratory. From the result of small-angle X-ray scattering measurements, the intensities at s = 0, where s = $4\pi/\lambda \sin\theta$, were obtained. Using these values, we obtained the overall density and concentration fluctuations. Moreover, they were separated into the density fluctuations of each component by applying the Kirkwood-Buff theory [1].

Results and Discussion

Fig. 1 shows the density dependence of obtained overall density fluctuation, S_{NN}, and concentration fluctuation, S_{CC}, of the mixtures. For comparison, fluctuations of other supercritical mixtures are tabulated in Tab. 1. From Fig. 1 and Tab. 1, it is recognized clearly for supercritical CO_2-CH_3OH mixture to denote larger density fluctuation and larger concentration fluctuation.

The density fluctuations of each component against density of mixture are shown in Fig. 2. It exhibits CH_3OH molecules gathering drastically. Comparing Fig. 1 and Fig. 2, it can be seen that the density fluctuation of mixture has a maximum near the maximum of the density fluctuation of CO_2. The concentration fluctuation has the largest value around the maximum point of the density fluctuation of CH_3OH. These results can be interpreted as follows. With the gathering of dominant CO_2 molecules, the density fluctuation of the mixture increase. On the other hand, the CH_3OH is too dilute to influence the overall density fluctuation of the mixture. From the viewpoint of concentration fluctuation, CH_3OH molecules predominate rather than CO_2 molecules even if its ratio is small.

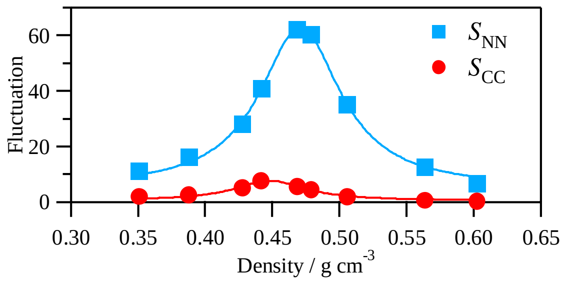

Fig. 1. Fluctuations of mixture vs. density

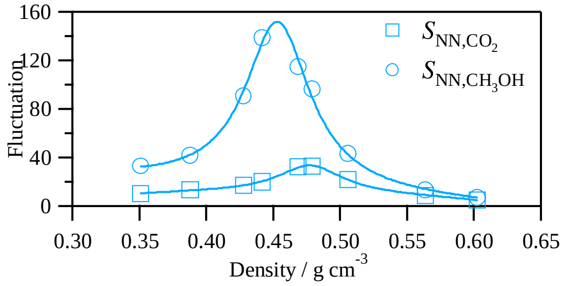

Fig. 2. Fluctuations of components vs. density

Tab. 1 (Mole ratio in the brackets)

Maximum at T_r = 1.04	S_{NN}	S_{CC}
CO_2	12	-
CO_2-CHF_3 mixture (0.75:0.25)	12	1.5
Xe-Kr mixture (0.50:0.50)	54	1.3
CO_2-CH_3OH mixture (0.93:0.07)	62	7.2

It was denoted that both the density fluctuation and concentration fluctuation of supercritical CO_2-CH_3OH are large. By the separation of the fluctuations of the each component, it was found the density fluctuation of CH_3OH is amazingly large. Because large concentration fluctuation means great aggregation, CH_3OH molecules are gathering even if at high temperature and high pressure.

References

[1] K. Nishikawa, *Chem. Phys. Lett*. **132**, 50 (1986).

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