Novel critical behavior in a mixture of water/organic solvent under high-pressure condition

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We previously investigated pressure-induced phase separation in aqueous 3-methylpyridine solutions using high-pressure small-angle neutron scattering (HP-SANS). A notable finding was that the pressure-induced critical behavior followed the mean-field universality class, whereas the temperature-induced phase separation in the same system exhibited the 3D-Ising universality class. To clarify the origin of this unusual behavior, we extended our study to other binary liquid mixtures exhibiting lower critical solution temperature (LCST) behavior. Simultaneously, we continued to improve the HP-SANS experimental setup to obtain more reliable measurements.

In our previous experiments, SANS profiles were successfully measured during an increase in pressure. However, measurements during pressure decrease were difficult because the pressure had to be controlled manually by releasing a valve, which made the fine adjustment unstable. To overcome this problem, we modified the pressure system by installing two Heise pressure gauges. One gauge monitors the pressure on the pump side, whereas the other directly monitors the pressure inside the high-pressure cell. This configuration allows the pump pressure to be reduced first, followed by a controlled release of the pressure inside the cell, resulting in a much finer pressure control.

Using this improved setup, we successfully measured the SANS profiles during a pressure decrease for the first time at SANS-U. Figure 1 shows the scattering profiles of the D_2O/2-butoxyethanol mixture at 58°C as the pressure was decreased from 161 MPa to 50 MPa. A pressure of 161 MPa corresponds to a state near the one-phase region, whereas 50 MPa is close to the critical pressure. As the pressure decreased, the scattering intensity increased markedly, indicating the growth of critical concentration fluctuations as the system approached the critical point. Although the overall critical behavior was clearly observed, the scattering profiles exhibited an artificial dip around $Q \approx 0.01$ Å^{-1}, suggesting the presence of instrumental artifacts or imperfect background subtraction. Therefore, further investigation of the noise source and optimization of the background correction are necessary.

The present results demonstrate that the upgraded HP-SANS system enables stable pressure control during both pressure increase and decrease processes. This capability will facilitate more detailed investigations of pressure-induced critical phenomena in LCST-type binary mixtures. Further HP-SANS experiments are currently in progress to improve the measurement accuracy and clarify the universality class of pressure-induced phase transitions.

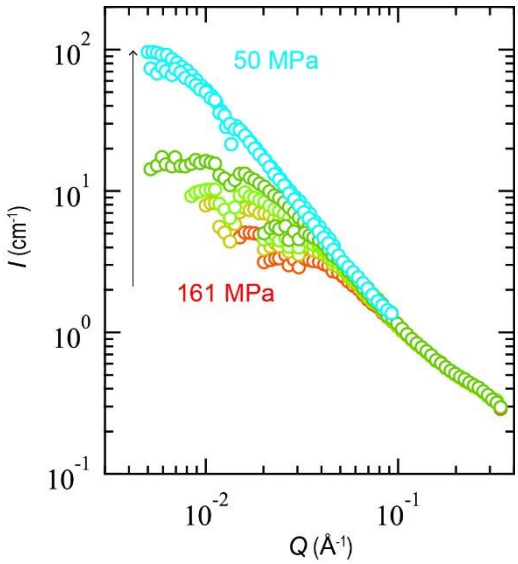

Fig. 1. SANS profiles of the D_2O/2-butoxyethanol mixture measured during the pressure decrease from 161 MPa to 50 MPa at 58°C. The increase in the scattering intensity reflects the development of critical concentration fluctuations near the critical point.