Crossover from mean field to 3D-Ising critical behavior in water/organic solvent mixtures

K. Sadakane[A]

[A]*Faculty of Life and Medical Sciences, Doshisha University*

When light, X-rays, and neutrons are irradiated to a water/organic solvent mixture near the critical temperature, critical scattering due to concentration fluctuations is observed, and the scattering profile follows the Ornstein-Zernike equation. Furthermore, the temperature dependence of I_0 and ξ follows the power law regardless of the type of solution. In particular, it has been known that the critical phenomena in the binary mixture, composed of water and low-molecular organic solvent, follows 3D-Ising critical universality; i.e., γ = 1.24, ν = 0.63.

However, we recently discovered a phenomenon that defies this common sense. For example, in a water/acetonitrile mixtures that exhibits UCST-type critical behavior, it was found that the mean field behavior (γ = 1.00, ν = 0.50) instead of 3D-Ising behavior was observed when water and acetonitrile was mixed at non-critical composition. A similar phenomenon was also found in mixed solution systems containing ionic liquids (M. Kawano, K. Sadakane, et al., PCCP, 23, 24449 (2021)).

In this study, the generality of the above phenomenon was confirmed using D_2O/2,6-dimethylpyridine mixtures that exhibit LCST-type critical behavior. Figure 1(a) shows the temperature dependence of the SANS profiles for a D_2O/2,6-dimethylpyridine mixture at non-critical composition (the volume fraction of 2,6-dimethylpyridine is 0.4). Unlike the water/acetonitrile mixtures, this sample was observed to behave according to the 3D-Ising rather than the mean field (see the Fig. 1(b)). This result suggests that the mixtures which shows UCST-type critical behavior follows the mean field behavior at conditions outside the critical composition, whereas the samples which shows LCST-type critical behavior follows 3D-Ising at all sample compositions.

In the future, we will investigate the critical behavior more extensively using binary mixtures other than water/acetonitrile and water/2,6-dimethylpyridine, and clarify the details of the crossover phenomenon of criticality universality.

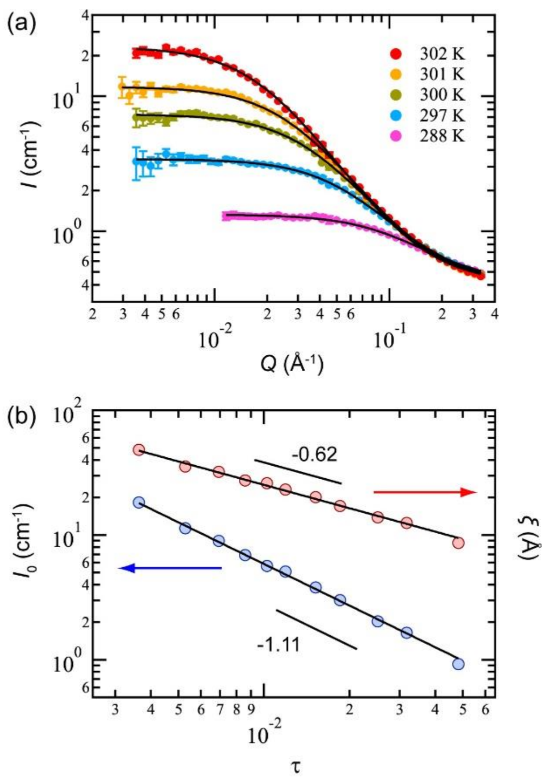

Figure 1: (a) Temperature dependence of the SANS profiles for the D_2O/2,6-dimethylpyridine mixture at ϕ = 0.4 (where ϕ is the volume fraction of 2,6-dimethylpyridine). The solid lines are the fitting results according to Ornstein-Zernike equation. (b) Temperature dependence of I_0 and ξ.