Large scale structure and crossover of critical phenomena induced by solvation effect

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The binary mixture of water and 3-methylpyridine, which shows LCST type phase separation, is known to have a large salt effect. In this study, we selected sodium tetraphenylborate ($NaBPh_4$), whose affinities of anion and cation with water are largely different, as a salt because the solvation effect should be intensive and the formation of large clusters is expected theoretically. In cases of the lower amount of $NaBPh_4$ and water-rich concentration, the mixture becomes colored in blue, and changes to orange with approaching critical temperature. This result suggests that a periodic structure is formed, and its repeat distance increases with increasing temperature. For the mixtures with 100 mM $NaBPh_4$, the SANS profiles have a peak around Q =0.1 A^{-1}, and the peak position shifts to lower-Q with increasing temperature. (K. Sadakane et al., J. Phys. Soc. Jpn. 76, 113602 (2007).)

In order to investigate the solvation effect by adding $NaBPh_4$, further experiments are performed at SANS-U. The scattering profiles are successfuly interpreted with the function proposed by Onuki and Kitamura. The temperature dependence of the critical concentration fluctuation shows 3D-Ising behavior when the salt concentration is low enough. On the other hand, the critical behavior is changed to 2D-Ising with increasing the salt concentration. This result can be interpreted that the concentration fluctuation is limited in 2 dimensional region due to the emergence of the layered structure. This crossover is reproduced in the cases of adding ionic surfactant such as AOT and SDS. Thus we conclude that a membrane-like structure is formed near the critical point by the coupling of the salvation effect and the critical concentration fluctuation as suggested by Onuki and Kitamura theoretically.

Neutron Spin Echo experiments are performed at iNSE in the mixture of water, 3MP and $NaBPh_4$. The intermediated correlation function can be interpreted with the model proposed by Zilman and Granek. This evidence verifies the formation of the membrane-like structure by adding $NaBPh_4$.