Mesoscopic structure in near-critical mixtures of D_2O and 3-methylpyridine with salts

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Solvation effects on phase separations associated with critical phenomena have very much interested many researchers not only in the field of chemistry but also of physics. A large number of papers have been devoted on this problem from theoretical and experimental approaches. One of the most well-known system is an alcohol and water mixture. Addition of small amout of salt induces interesting behavior such as the reentrant phase separation phenomenon. By the solvation effects of ions, the clustering of polar molecules occurs and could be the origin of these behaviors.

The 3-methylpyridine (3MP) and water are known to mix uniformly at room temperature and separate into two phases with increasing temperature, and critical phenomena due to the density fluctuation could be observed near the critical point. The addition of salts, such as NaBr, results in the decrease of the critical temperature and the reentrant phase separation behavior. Jacob et al. have already investigated this behavior mainly by DLS [1] and SAXS[2], and showed that clustering of water molecules around ions is induced and the critical crossover behavior from meanfiled to 3D-Ising is observed because the interaction responsible to the phase separation is more long-ranged due to the clustering.

Theoretically, Onuki and Kitamura considered the solvation effects in near-critical binary mixtures. [3] They applied a Ginzburg-Landau theory to the density fluctuation of ciritcal mixtures with salts, and showed that the concentration has a longranged Ornstein-Zernike tail representing strong critical electrostriction with approaching the critical point. As a result, a drastic shift of the critical temperature and the formation of large scale clusters will arise due to strong coupling of the critical density fluctuation and the ions. This theory can give a unified understanding of the effects of salts to the phase separation behavior associated with critical phenomena from the viewpoint of the statistical physics.

In this viwpoint, we have measured the density fluctuation near the critical temperature of the binary and the ternary mixtures of 3MP, deuterated water with and without salts by SANS. The result of the mixture without salt indicates that the critical phenomena belong to the standard universality class for a low-molecular weight binary solution; the SANS profiles are explained by the Ornstein-Zernike function and the critical increases of the osmotic compressibility and the correlation length could be explained with the critical index of $\gamma = 1.26$ and $\nu = 0.63$ (3D-Ising behavior). On the other hand, the SANS profiles from the ternary mixtures could not be explained with the Ornstein- Zernike function. In order to analyze the data, we assumed spherical shape clusters exist even in one phase region. Thus, we tried to apply the scattering function as follows,

$$I(Q) = \frac{I_0}{1+\xi^2 Q^2} + C\int^{\infty} 0 f(R)|F(Q,R)|^2 dR, \tag{1}$$

where

$$f(R) = \left(\frac{Z+1}{R_m}\right)^{Z+1} R^Z \exp\left[-\left(\frac{Z+1}{R_m}\right)R\right] /\Gamma(Z \tag{2}$$

where the first term of the first equation corresponds to the density fluctuation which is identical with the Ornstein-Zernike function and the second term

comes from the form factor from spherical clusters with Schultz size distribution. R is a radius of cluster, Z is a width parameter, R_m is a mean radius of cluster, Γ is gamma function, and C is a constant.

Figure 1 shows the SANS profile of 3MP/D_2O with small amount of KCl. These profiles are well explained with the above function, which means that the mesoscopic size cluster exists in the present system. Temperature dependences of the osmotic compressibility, I_0, and the correlation length, ξ, follow the 3D-Ising critical behavior.

The estimated cluster size, R_m, becomes larger with approaching the critical point. This evidence indicates that the mesoscopic size cluster is formed near the critical point and their size increases with approaching the critical point. These behaviors were also observed in other ternary mixtures with NaCl and MgSO4 [4]. These are the first evidence that the coupling of the solvation effect and the critical density fluctuation induces mesoscopic scale clusters.

References

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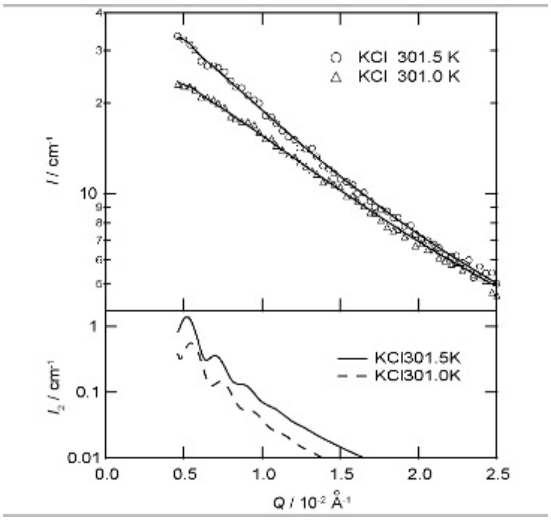

Fig. 1. The upper figure indicates the SANS profiles near the critical point. These profiles are fitted with a sum of the Ornstein-Zernike funtion and the scattering from spherical clusters indicated in the lower figure.