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Long-range periodic structure induced by coupling of the solvation effect and concentration fluctuation in water and 3-methylpyridine with salts

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塩の添加により、相分離が誘発されることが知られている水と3-メチルピリジン（3MP）の混合溶液系の臨界挙動について、小角中性子散乱（SANS）により測定を行なった。その結果、溶媒の臨界揺らぎと塩の溶媒和効果がカップルすることで、数百 Å を特徴的長さとする周期構造が形成されることが示された。

Solvation effect plays an important role in various fields of natural science. One of the most interesting issues regarding the solvation effect is its large influence on near critical binary mixtures. Experimentally, it is well-known that the addition of salt ions to a binary mixture causes a shift of the critical temperature. Many investigations have been performed to reveal the effect of ions near-critical solutions. Several authors suggested that small-sized clusters of each component are formed even in one-phase region experimentally [1].

Recently, Onuki and Kitamura theoretically showed that the solvation of salt ions induces a long-range periodic structure in conjunction with a critical concentration fluctuation [2]. However, to the best of our knowledge, no experimental evidence of such the structure exists.

The mixture of water and 3-methylpyridine (3MP) is known to have a large salt effect on the critical temperature. Thus we have performed small-angle neutron scattering (SANS) experiments on the mixtures of water, 3MP and salts, such as LiCl, NaCl, KCl and $MgSO_4$, to investigate the concentration fluctuations and structures below the critical temperature with and without salt.

SANS measurements were performed using SANS-U at JRR-3M of the Japan Atomic Energy (JAEA). The momentum transfer, Q ($=4\pi\sin\theta/\lambda$, where λ is the wavelength, and 2θ is the scattering angle), ranged from 4.2×10^{-3} to 5.2×10^{-2} Å^{-1}. The temperature was increased from room temperature to the critical point by a water circulation system.

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Figure 1(a) shows SANS profiles from the binary mixture of D_2O/3MP. The critical phenomena belong to the universality class of 3D-Ising: the SANS profiles are explained by the Ornstein-Zernike function, the forward scattering I_0 and the correlation length ξ diverge with approaching critical point, and their critical indexes are $\gamma = 1.24$ and $\nu = 0.63$, respectively.

On the other hand, the results of the ternary mixtures could not be explained with the standard 3D-Ising behavior. (See Fig. 1(b)) Thus, we tried to apply the scattering function proposed by Nallet et al. [3], which can be successfully applied the periodic structure of lamellar phase,

$$I(q) = \frac{I_0}{1 + \xi^2 q^2} + \frac{A}{1 + \xi'^2(q - 2\pi/d)^2}. \tag{1}$$

The first term indicates critical concentration fluctuation and the second term is derived from a periodic structure. All the profiles from the samples with salt are well explained by eq (1). The concentration fluctuation follows the 3D-Ising behavior, and the long periodic structure is enhanced as we approach the critical point (See Fig. 1(c)).

These results suggest that a structural modification is induced by the coupling of solvation and critical concentration fluctuation [4].
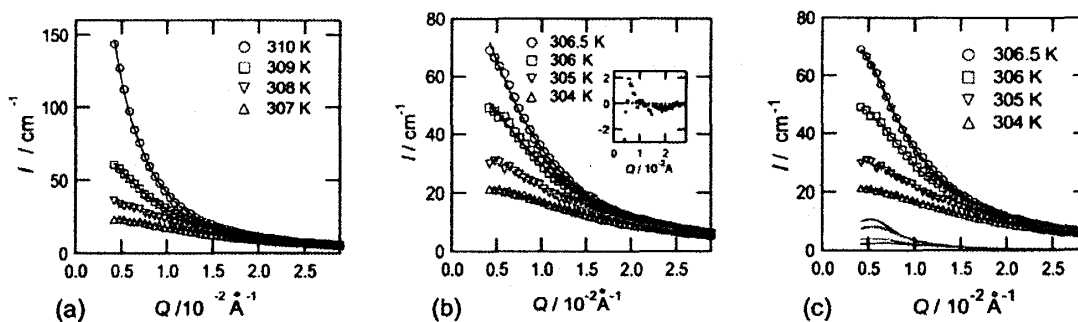

Figure 1: (a) SANS profile from binary D_2O/3MP system and the result of the Ornstein-Zernike fitting. (b) SANS profile from ternary D_2O/3MP/LiCl and the Ornstein-Zernike function. The inset shows the difference between the measured intensity and the Ornstein-Zernike function at 306.5K. (c) Temperature variation from D_2O/3MP/LiCl and the long-range periodic structure indicated by the second term of Eq. (1).

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