A long-range periodic structure in a mixture of D_2O/3-methylpyridine/$NaBPh_4$ induced by solvation effect

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The solvation effect plays an important role in various fields of natural science. One of the most interesting issues is its influence on water and organic solvent mixtures. Recently, Onuki and Kitamura theoretically showed that the solvation effect of salt ion induces a long-range periodic structure in conjunction with a concentration fluctuation of those mixtures. [1]

The binary mixture of water and 3-methylpyridine (3MP), which shows LCST type phase separation, is known to have a large salt effect on the phase separation. Thus, we have investigated the concentration fluctuation and structural formation of the mixture of D_2O, 3MP and salt at SANS-U. In this study, we focused on the effect of sodium tetraphenylborate ($NaBPh_4$) because the solvation effect of anions and cations should be very large.

The SANS profile of D_2O/3MP without salt could be explained by the Ornstein-Zernike function, which is generally applied to near-critical binary mixture,

$$I_{OZ}(Q) = \frac{I_0}{1+\xi^2 Q^2}\,, \qquad (1)$$

where ξ is the correlation length and I_0 the forward scattering proportional to the osmotic compressibility.

On the other hand, the SANS profiles from D_2O/3MP/$NaBPh_4$ can not be explained by Eq. (1) because a single peak is observed around $Q = 0.1$ Å^{-1} (See Fig. 1). Thus, we tried to apply the scattering function proposed by Onuki and Kitamura [1], which shows the existence of a long-range periodic structure induced by solvation effect of salt ion,

$$I_{OK}(Q) = \frac{I_0}{1+(1-\gamma^2/(1+\lambda^2 Q^2))\xi^2 Q^2}\,, \qquad (2)$$

where γ is a dimensionless parameter corresponding to the difference of the strengths of the cation and anion, and λ the Debye screening length. In this expression, the peak position Q_m is given by $Q_m = \sqrt{\gamma - 1}/\lambda$. All the SANS profiles of D_2O/3MP/$NaBPh_4$ can be well explained by Eq. (2), and the characteristic repeat distance d increase with increasing temperature (See Fig. 1).

This result could be interpreted that the long-range periodic structure is induced by a cooperation of the solvation effect and the concentration fluctuation [2].

[1] A. Onuki and H. Kitamura, J. Chem. Phys., **121**, 3143 (2004).
[2] K. Sadakane, H. Seto, H. Endo and M. Shibayama, J. Phys. Soc. Jpn., **76**, 113602 (2007).

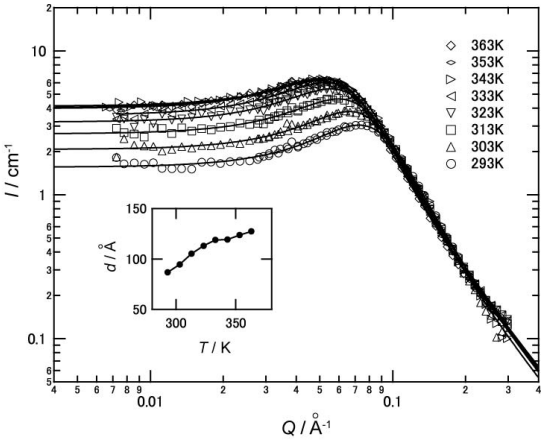

Fig. 1. SANS profile of D_2O/3MP (the weight fraction of 3MP is 0.32) with 100 mM of $NaBPh_4$. The solid line shows the fitting function given by Eq. (2). The inset shows the temperature dependence of repeat distance, d.