

Amide-Induced Phase Separation of HFIP-Water Mixtures

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Aqueous mixtures of several water-miscible organic solvents, such as propanol and acetonitrile, separate into organic solvent-rich and water-rich phases, when salt is added into mixtures. The key of the salt-induced phase separation is preferential solvation of both cation and anion by water molecules [1-4]. Thus, water clusters are evolved around both ions with increasing salt concentration, and organic molecules, which are excluded from water clusters, simultaneously aggregate to form clusters. Finally, phase separation takes place, when the size of both water clusters and organic solvent clusters reaches a macroscopic scale. Recently, we have found that addition of amphiphilic molecules, such as amide, also induces phase separation of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP)-water mixtures. The phase diagrams obtained for the HFIP-water-amide ternary systems at 298 K have shown a closed-circle region of phase separation, and the more hydrophobic the amides, the larger the region of phase separation.

To clarify the mechanism of amide-induced phase separation of HFIP-water mixtures, in the present study, SANS experiments have been made on HFIP-water-amide mixtures with three different amides, N-methylformamide (NMF), N-methylacetamide (NMA), and N-methylpropionamide (NMP). The hydrophobicity of the amides is larger in the order of $\text{NMF} < \text{NMA} < \text{NMP}$.

HFIP-D₂O-amide ternary solutions below the lower critical composition and above the upper critical one were prepared in accordance with the phase diagrams. SANS measurements at 298 K were made on the sample solutions by using the SANS-U spectrometer with the camera lengths of 1 and 4 m. The scattering intensities were accumulated on the detector at the camera

lengths of 1 and 4 m for 10 min and 1 h per sample, respectively.

Fig. 1(a) shows the Ornstein-Zernike correlation lengths ξ estimated from the SANS intensities for the HFIP-D₂O-amide mixtures below the lower critical composition as a function of amide mole fraction. For each amide system, the ξ value increases with increasing amide mole fraction. It is suggested that the heterogeneity of the mixtures increases with the increase in the amide concentration toward the critical one. The NMP system requires the smallest amount of amide to enhance the heterogeneity among the systems. Fig. 1(b) shows that the amide mole fraction dependence of the ξ values for the HFIP-D₂O-amide mixtures above the upper critical composition. The ξ value for each system gradually decreases when the amide concentration increases apart from the critical one. The NMP system requires the largest amount of amide to recover the homogeneous mixing.

Below the lower critical composition, a small amount of amide added may be easily solvated by hydrophobic HFIP molecules rather than water ones, resulting in the enhancement of HFIP clusters around amide molecules. Hence, phase separation occurs when clusters are evolved to a macroscopic size. Above the lower critical composition, on the contrary, amide molecules further added may play a role as an interface between HFIP and water clusters because of the amphiphilicity of amide molecule, i.e., HFIP, water, and amide molecules are homogeneously mixed again. Thus, the HFIP-water-amide systems reveal a closed-circle region of phase separation, and the region for the HFIP-water-NMP system is the largest among the three systems due to the most hydrophobic NMP.

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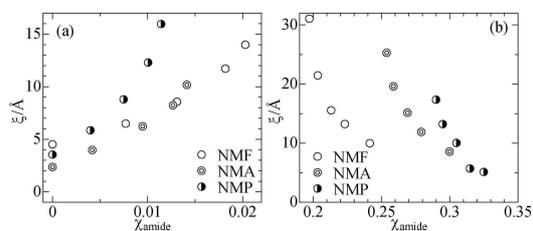


Fig. 1. ξ values for HFIP-water-amide mixtures (a) below the lower critical composition and (b) above the upper critical one as a function of amide mole fraction.