

DMF-induced Phase Separation of HFIP-Water Mixtures

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At an ambient condition, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) is miscible with water at any ratio. However, the mixing state of HFIP-water solutions at a nano-scale is not homogeneous [1]. We have been found in the previous study that phase separation of HFIP-water solutions occurs by adding amide molecules, such as N-methylformamide (NMF) [2]. The amide-induced phase separation of HFIP-water mixtures occurs in a circular area of triangle phase diagram, and the area becomes wider with increasing hydrophobicity of amide in the sequence of N-methylpropionamide (NMP) > N-methylacetamide (NMA) > NMF. This may be due to the enhancement of nano-heterogeneity of HFIP-water solutions arising from solvation for hydrophobic parts of amide molecules by hydrophobic HFIP clusters formed in the solutions. In the present study, phase separation of HFIP-water solutions by addition of N,N-dimethylformamide (DMF) has been clarified by using small-angle neutron scattering (SANS) technique. A DMF molecule cannot form N-H...O-H hydrogen bond due to the methylation of both amino hydrogen atoms, although the carbonyl oxygen can form C=O...H-O hydrogen bond as well as the other amide molecules.

The phase diagram of amide-induced phase separation of HFIP-water solutions at 298 K indicated that the circular area of DMF-induced phase separation of HFIP-water solutions is wider than that of the NMA system, but slightly narrower than that of the NMP one. According to the phase diagram, SANS experiments using the SANS-U spectrometer have been made on DMF-HFIP-D₂O ternary solutions at HFIP mole fraction of 0.14, which corresponds to the volume ratio of HFIP to water of 1:1, with varying DMF content.

The Ornstein-Zernike correlation lengths ξ_i were estimated from SANS spectra for the ternary solutions. Figure 1 (a) and (b) show the ξ_i values for all the ternary solutions below and above the circular area of phase separation, respectively. As seen in Figure 1 (a), the ξ_i values for all the amide systems increase with increasing amide content, suggesting that the nano-heterogeneity of the solutions is enhanced when the amide content increases. The increase in the ξ_i with increasing amide content agrees with the fact that the amide-induced phase separation toward the lower critical line takes place at lower amide content in the sequence of NMP = DMF < NMA < NMF. On the other hand, Figure 1(b) reveals that the nano-heterogeneity of the solutions diminishes with lower amide content in the sequence of NMF < NMA = DMF < NMP. This is consistent with that one-phase solution is recovered above the upper critical line with lower amide content in the sequence. The present results suggest that the hydrophobicity of DMF is between those of NMA and NMP.

References

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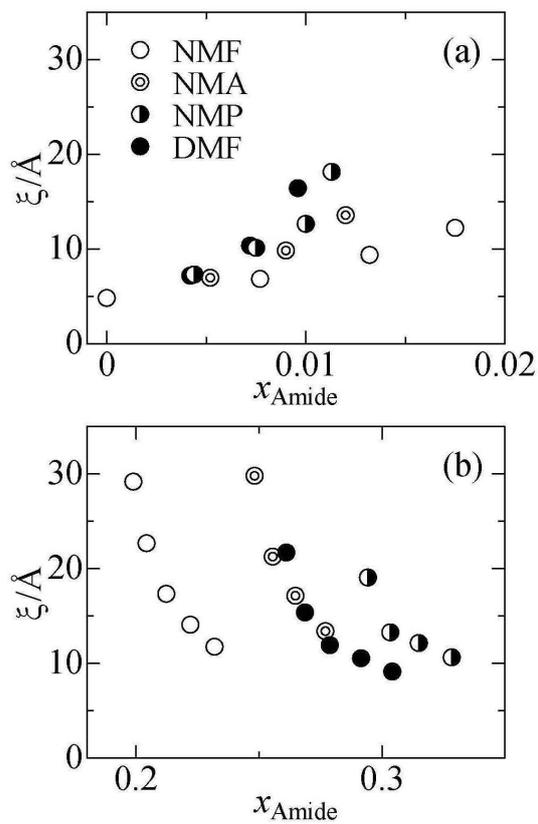


Fig. 1. Amide mole fraction dependence of ξ for amide-HFIP-D₂O ternary solutions (a) below and (b) above two-phase area of phase diagram.