

Studies on Phase Separation of Water-Miscible Organic Solvents-Water Mixtures by Addition of Several Solutes

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We have investigated the mechanism for phase separation of aqueous mixtures of water-miscible organic solvents, such as alcohol and acetonitrile, at the molecular level. Under an ambient condition, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) is miscible with water at any ratio due to its hydrophilic hydroxyl group. In contrast, HFIP molecule may easily interact with the hydrophobic moieties of organic solutes like peptide and protein because of the dispersion force of the hydrophobic CF₃ groups [1,2]. We have found that HFIP-water mixtures are separated into HFIP-rich (lower) and water-rich (upper) phases by addition of electrolytes and organic solutes, such as amide. Acetonitrile is also mixed with water at any ratio under an ambient condition, although acetonitrile molecule cannot strongly form hydrogen bond with water molecule [3]. However, it has been well known that acetonitrile-water system has the UCST at 272 K and acetonitrile mole fraction of 0.38. We have discovered that the phase separation temperature of the mixtures is increased by addition of electrolyte, such as NaCl. In the present investigation, the evolution of D₂O clusters formed in the mixtures toward phase separation has been observed using SANS-U spectrometer. In addition, we have aimed at elucidating the dynamics of clusters in the mixtures using iNSE spectrometer.

The phase diagram of HFIP-H₂O mixtures with 0.15 mol/dm³ alkali chloride MCl (M = Li⁺, Na⁺, and K⁺) showed that MCl-HFIP-water ternary mixtures are separated with elevating temperature, although phase separation of HFIP-water binary mixtures does not occur until the boiling point of HFIP, 332 K. Phase separation of the ternary mixtures more easily oc-

curs at the low temperatures in the order of NaCl = LiCl > KCl. Fig. 1 indicates the Ornstein-Zernike correlation lengths ξ_i determined for the MCl-HFIP-D₂O mixtures as a function of temperature T normalized by the phase separation temperature T₀. This suggests that the mechanism of phase separation of the KCl system differs from those of the LiCl and NaCl systems. Probably, the properties of K⁺ as a structure breaker significantly contribute to the underlying mechanism of phase separation.

HFIP-water mixtures are also separated by addition of amide, such as N,N-dimethylformamide (DMF) [4]. In the present iNSE experiments, we have succeeded in observation of the intermediate scattering functions of clusters formed in DMF-HFIP-D₂O mixtures with 1 mol% of DMF. To elucidate the dynamics of clusters, iNSE experiments will be further made.

MCl (M = Li⁺, Na⁺, and K⁺)-induced phase separation of acetonitrile-water mixtures is more easily taken place in the order of NaCl > KCl > LiCl. This order does not agree with that of the hydration enthalpies of M⁺. To clarify the mechanism of phase separation, SANS measurements have been conducted on 0.10 and 0.15 mol/dm³ MCl-acetonitrile-D₂O mixtures (M = Li⁺, Na⁺, and K⁺) with lowering temperature from 308 to the phase separation one. The temperature dependence of the Ornstein-Zernike correlation lengths ξ_i showed that MCl-induced phase separation of acetonitrile-water mixtures occurs through the 3D-Ising mechanism. We will fully clarify the underlying mechanism of phase separation by the SANS results, together with IR and NMR ones, in the near future.

References

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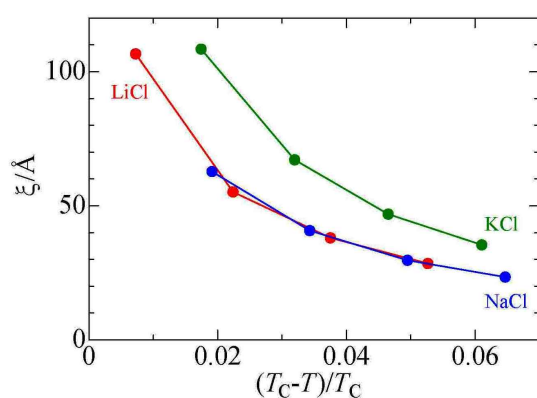


Fig. 1. Temperature dependence of Ornstein-Zernike correlation lengths ξ of MCl-HFIP-H₂O mixtures.