

The effect of antagonistic salts on the mixture of water / organic solvent

Hideki Seto and Koichiro Sadakane
High Energy Research Organization

Binary mixtures of water and organic solvent have been used extensively to study universal aspects of critical behavior and phase separation dynamics. However, not enough attention has been paid to unique ion effects in such mixtures, where preferential hydration around each ion affects the critical fluctuations. Recently, we have investigated the effect of NaBPh₄, composed of hydrophilic cation Na⁺ and hydrophobic anion BPh₄⁻, for the mixture of water and 3-methylpyridine (3MP). As a result, a periodic structure having a mean repeat distance of about 100 Å was discovered by means of SANS [1]. This result is theoretically supported by Onuki and Kitamura [2]. They showed that a kind of salt composed of hydrophilic and hydrophobic ion pair tends to adsorb onto the interface between water and organic solvent. This structure, so-called electric double layer structure, reduces the interfacial tension between water and organic solvent, and induces microphase separated structures [2]. Furthermore, it has been shown that the electric double layer has a periodic charge-density-wave structure in a mixture coupling with concentration fluctuations and solvation effect [3].

In this experiment, we selected a mixture of water (D₂O+H₂O) / deuterated acetonitrile (AN-d₃) / NaBPh₄ to investigate distributions of ions in the mixture employing contrast variation SANS, since the phase separation temperature is not affected by the deuteration. Figure 1 shows a series of the contrast variation SANS profiles in water / AN-d₃ (the volume fraction of AN-d₃ against the whole mixture is 0.639) with 400 mM of NaBPh₄ at 283 K. A single peak profile due to a periodic structure is observed for all the samples. With increasing the composition of H₂O in water, SANS intensities decrease since the scattering length

density difference between water and AN-d₃, $\Delta\rho$, decreases. The evidence of the existence of the peak profile at the matching point ($\Delta\rho = 0$) confirms the charge-density-wave structure; Na⁺ and BPh₄⁻ ions distribute periodically in the mixture at a length scale of about 50 Å.

References

- [1] K. Sadakane, A. Onuki, K. Nishida, S. Koizumi and H. Seto, *Phys. Rev. Lett*, **103**, 167803 (2009).
- [2] A. Onuki, *J. Chem. Phys.*, **128**, 224 (2008).
- [3] A. Onuki, *J. Chem. Phys.*, **121**, 3143 (2004).

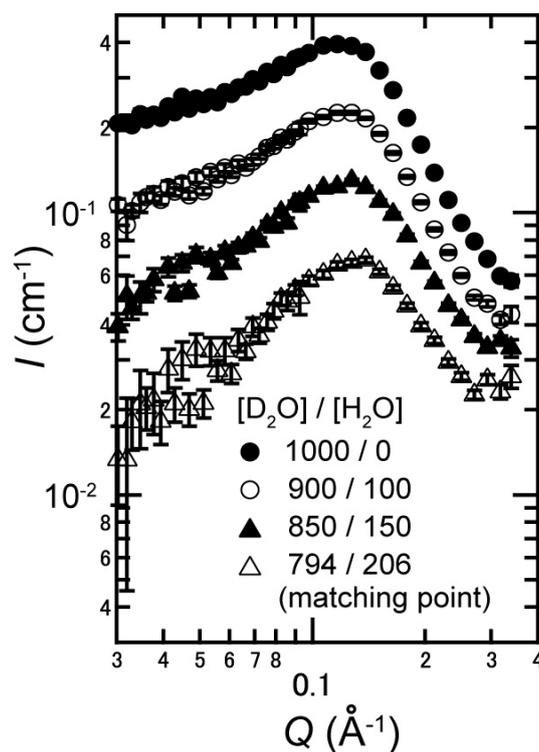


Fig. 1. SANS profiles for the contrast variation series of water/AN-d₃/NaBPh₄.