

The nanostructure of ions in the mixture of water / organic solvent

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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) / 2,6-Lutidine (or deuterated 2,6-Lutidine) / NaBPh₄ to investigate distributions of ions in the mixture employing contrast variation SANS. Figure 1(a) shows a series of the contrast variation SANS profiles in water / 2,6-Lutidine (the volume fraction of 2,6-Lutidine against the whole mixture is 0.13) with 150 mM of NaBPh₄ at 298 K. In this system, the matching point is attained when the mixing ratio of D₂O and H₂O, [D₂O]/[H₂O], is 88.1 / 11.9. A sharp peak together with second and third peaks indicating the existence of lamellar struc-

ture is observed for all the samples. With changing the composition of H₂O in water, SANS intensities change since the scattering length density difference between water and 2,6-Lutidine, $\Delta\rho$, changes. The evidence of the existence of the peak profile at the matching point confirms the charge-density-wave structure; Na⁺ and BPh₄⁻ ions distribute periodically in the mixture at a length scale of about 100 Å.

Next, we performed the SANS measurement using the mixture of D₂O / NaBPh₄ without mixing organic solvent. As shown in Fig.1(b), single broad peaks are shown at $Q \approx 0.2 \text{ \AA}^{-1}$. At present, we consider that these profiles reflect the micell-like structure composed of Na⁺ and BPh₄⁻ ions with a scale of 30 Å. In order to investigate the dynamical properties, we also performed the NSE measurement. Unfortunately, signals were too small compared to backgrounds, and we could not analyze the data.

References

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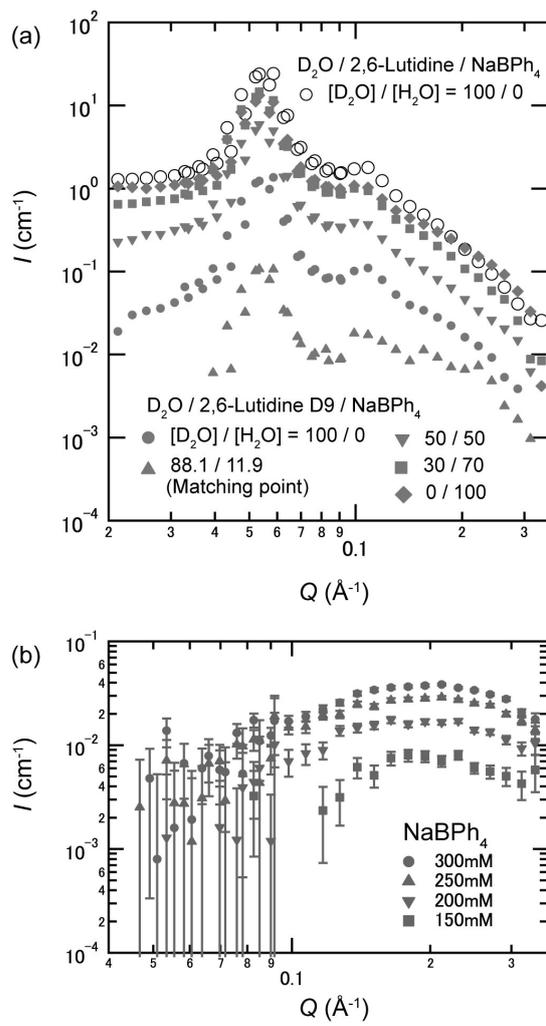


Fig. 1. (a) SANS profiles for the contrast variation series of water / 2,6-Lutidine / NaBPh₄. (b) SANS profiles for the mixture of D₂O / NaBPh₄.