

6 Soft Matter Project

– Hierarchical Structure and Dynamics of Soft Matter –

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6-1 Introduction

Soft matter is a subfield of condensed matter comprising a variety of physical states that are easily deformed by thermal stresses or thermal fluctuations. They include liquids, colloids, polymers, liquid crystals, amphiphilic molecules, and a number of biological materials. These materials often self-organize into mesoscopic physical structures that are much larger than the microscopic scale (the arrangement of atoms and molecules), and yet are much smaller than the macroscopic scale of the material. The properties and interactions of these mesoscopic structures may determine the macroscopic behavior of the material. In spite of the various forms of these materials, many of their properties have common physicochemical origins, such as a large number of internal degrees of freedom, weak interactions between structural elements, and a delicate balance between entropic and enthalpic contributions to the free energy. These properties lead to large thermal fluctuations, a wide variety of forms, sensitivity of equilibrium structures to external conditions, macroscopic softness, and metastable states.

From these viewpoints, we are investigating the structural properties of soft matter such as liquids and amphiphilic molecules.

6-2 Lamellar / disorder phase transition in a mixture of water / 2,6-dimethylpyridine / antagonistic salt

Recently, we investigated the effect of an antagonistic salt which is composed of hydrophilic cations and hydrophobic anions, on a mixture of deuterium oxide (D_2O) and 3-methylpyridine (3MP). When sodium tetraphenylborate ($NaBPh_4$)

is dissolved in the D_2O and 3MP mixture, the two-phase region shrinks as the amount of salt increases, and it disappears above 15 mmol/L; thus, the mutual solubility of D_2O and 3MP increases in the presence of $NaBPh_4$ on the macroscopic scale. This result implies that the antagonistic salt can act as a surface-active agent in the D_2O and 3MP mixture. Moreover, a periodic structure with a characteristic length scale of hundreds to thousands of angstroms was observed by means of small-angle neutron scattering (SANS), even far from the phase separation point. In the D_2O -rich mixture in particular, an ordered lamellar phase (L_α phase) was found at a $NaBPh_4$ concentration of ca. 85 mmol/L.

These experimental observations are explained in the framework of the theory proposed by Onuki and Kitamura. In their model, a charge-density-wave structure is induced by coupling the solvation effect and critical concentration fluctuations. In addition, they showed that hydrophilic and hydrophobic ions tend to adsorb near the interface between the water and the organic solvent. These ions act as an electric double layer at the interface, and reduce the interfacial tension between the water and the organic solvent.

Although pairs of hydrophilic and hydrophobic ions act as a surface-active agent under certain conditions, the detailed mechanism of formation of a salt-induced ordered structure has not yet been clarified.

In the present study, we investigated the effect of $NaBPh_4$ on a mixture of D_2O /2,6-dimethylpyridine, which shows macro-phase separation above room temperature, as in the case of the mixture of D_2O and 3-methylpyridine.

Figure 1 shows the phase diagram of the D_2O /2,6-dimethylpyridine mixture with and without

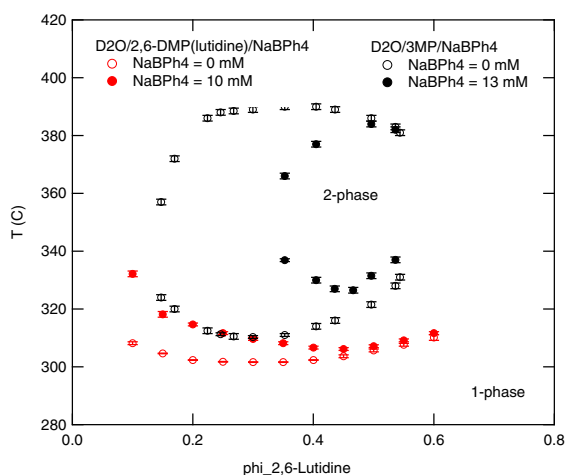


Fig. 1: (a) Phase diagrams of the mixtures of $D_2O/2,6$ -dimethylpyridine with and without $NaBPh_4$. (b) Phase diagrams of the mixtures of $D_2O/3$ -methylpyridine with and without $NaBPh_4$.

$NaBPh_4$. For comparison, the phase diagram of $D_2O/3$ -methylpyridine with and without $NaBPh_4$ is also shown. Phase separation is observed above 301 K in a mixture of $D_2O/2,6$ -dimethylpyridine, and this temperature increases upon addition of $NaBPh_4$; that is, the mutual solubility of D_2O and 2,6-dimethylpyridine increases. This tendency is similar to that of the mixture of $D_2O/3$ -methylpyridine with $NaBPh_4$.

Figure 2 shows the temperature dependence of the SANS profiles for the mixtures of $D_2O/2,6$ -dimethylpyridine/ $NaBPh_4$ at $\phi_L = 0.09$ and $C_{salt} = 85 \text{ mmol L}^{-1}$. The SANS profile at 343 K shows a broad single peak profile arising from the disordered structure, while the profiles below 333 K show a sharp peak profile together with higher-order peaks arising from the lamellar structure. The profile at 343 K is analyzed in terms of the charge-density-wave structure, and the profiles below 333 K are analyzed by the model for the lamellar structure.

From these results, we confirmed that $NaBPh_4$ acts as a surface-active agent in the 2,6-dimethylpyridine solution, as is the case with 3-methylpyridine solution. In particular, the temperature dependence of the parameters for the lamellar phase of the present system shows a similar trend to that in the lamellar phase of the 3-methylpyridine solution. On the other hand, we found a considerable difference in the morphology of the lamellar structure between the 2,6-dimethylpyridine and 3-methylpyridine solutions. For example, the diameter of the multilamellar vesicles in the 2,6-dimethylpyridine

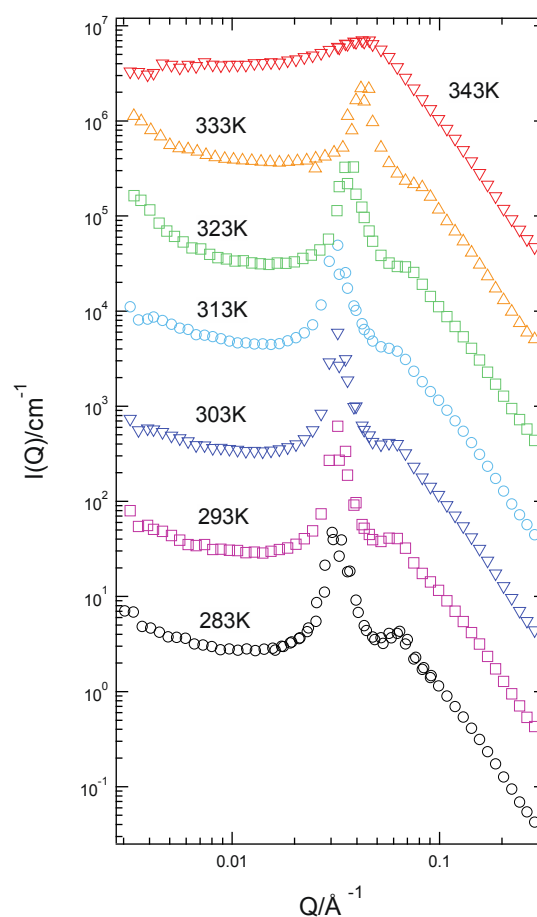


Fig. 2: Temperature dependence of the SANS profiles for $D_2O/2,6$ -dimethylpyridine/ $NaBPh_4$ ($\phi_L = 0.09$ and $C_{salt} = 85 \text{ mmol L}^{-1}$). The data at higher temperatures are shifted by a multiplication factor of 10 for visibility.

solution at $T = 338 \text{ K}$ is significantly larger than that in the 3-methylpyridine solution at $T = 318 \text{ K}$: the former is ca. $35 \mu\text{m}$, while the latter is ca. $20 \mu\text{m}$. Such difference is likely due to the difference in interactions among the solvents and the ions.

References

K. Sadakane, et al., *J. Solution Chem.* **43** (2014) 1722.