6 Soft Matter Project

– Hierarchical Structure and Dynamics of Soft Matter –

Project Leader: Hideki Seto

6-1 Introduction

Softmatter 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 the above viewpoint, we are investigating the structural properties of softmatter such as liquids and amphiphilic molecules.

6-2 Membrane formation by preferential solvation of ions in mixtures of water, organic solvent, and antagonistic salt

Binary mixtures of water and organic solvents have been investigated for the study of phase separation and associated critical phenomena.

From experiments, it is known that the two-phase region of a binary mixture expands when a hydrophilic salt such as NaCl or NaBr is added.

It is well known that the interfacial energy between water and an organic solvent increases with the addition of a hydrophilic salt, and this could be a factor in salt-induced phase separation. Thus, the effect of a hydrophilic salt on a mixture of water and an organic solvent is opposite to that of surfactant molecules, which serve to increase the mutual solubility of water and the organic solvent by decreasing the interfacial energy.

Recently, we investigated the effect of the salt, sodium tetraphenylborate ($NaBPh_4$), which is composed of the hydrophilic cation Na^+ and hydrophobic anion BPh_4^-, on a mixture of deuterium oxide (D_2O) and 3-methylpyridine (3MP). Figure 1 shows the phase diagrams of D_2O / 3MP / $NaBPh_4$ drawn from our previous and present experiments. The binary mixture of D_2O and 3MP shows closed-loop-type phase separation. When an antagonistic salt, $NaBPh_4$, 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
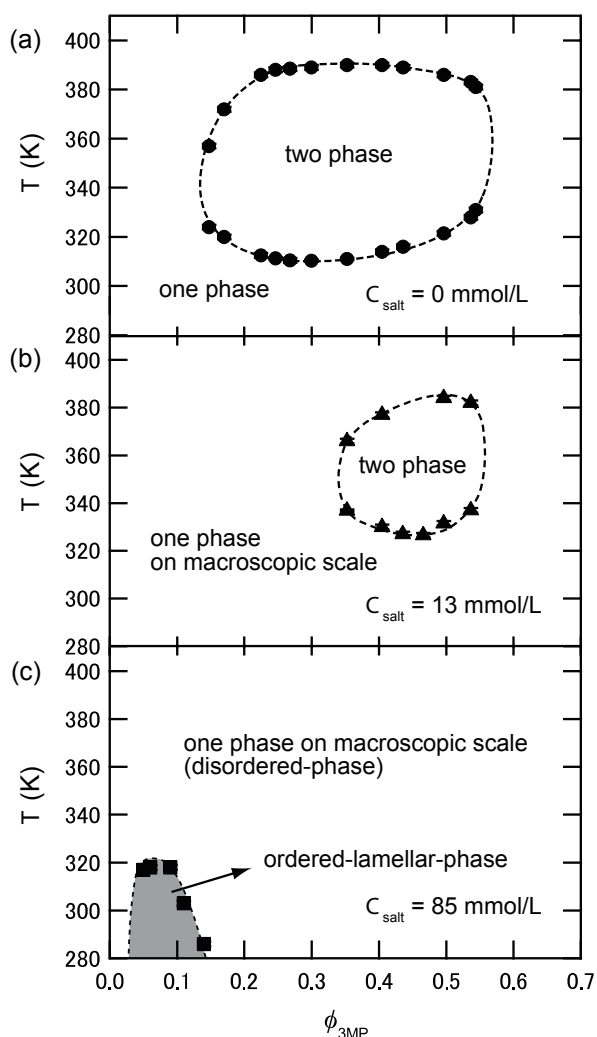
Fig. 1: Phase diagrams of D₂O / 3MP / NaBPh₄ with salt concentrations of 0 mmol/L (a), 13 mmol/L (b), and 85 mmol/L (c). The horizontal axis indicates the volume fraction of 3MP, and the vertical axis is the temperature. The symbols in (a) and (b) show the cloud point obtained in previous research, while the symbol in (c) shows the phase transition point of the disordered-phase and the ordered-lamellar-phase investigated through the present SANS measurements. The dotted lines are visual guides.

structures are formed under a delicate balance among various interactions.

In the present study, we focused on the static and dynamic structures of the ordered-lamellar-structure in the mixture of D₂O / 3MP / NaBPh₄ to understand how the ordered structure is stabilized. Neutron scattering techniques were employed to study the system because of the good scattering contrast between D₂O and 3MP. The SANS results indicate that various kinds of nanoscale structures are formed depending on conditions, and neutron spin echo (NSE) experiments confirm the membrane picture by measuring the collective dynamics of the system on the nanosecond timescale.

Figure 2(a) shows the SANS profiles of D₂O / 3MP / NaBPh₄ with changing salt concentration C_{salt} at ϕ_{3MP} = 0.09 and T = 280.5 K. When the concentration of NaBPh₄ is below 1 mmol/L, the SANS profile shows a monotonic decrease with increasing Q. These profiles are explained by the
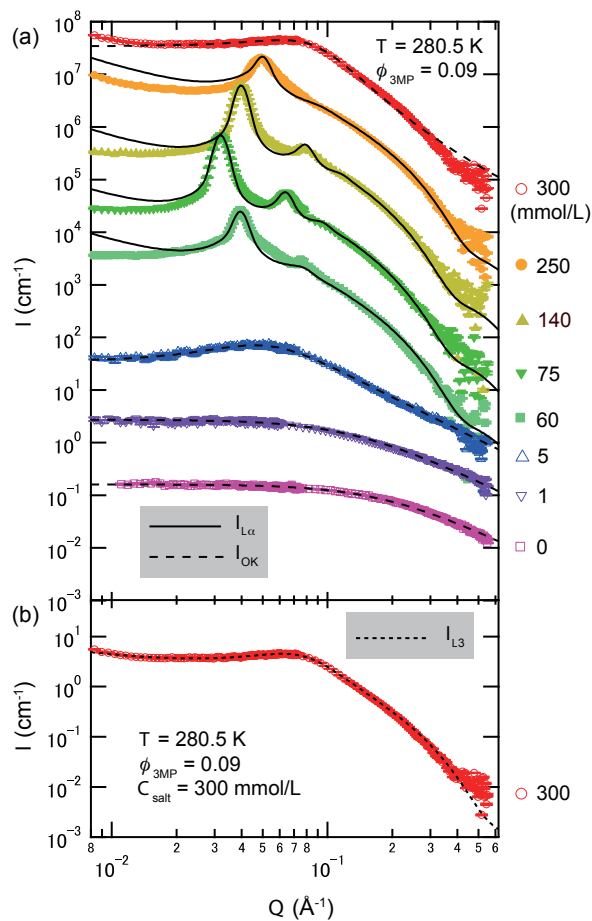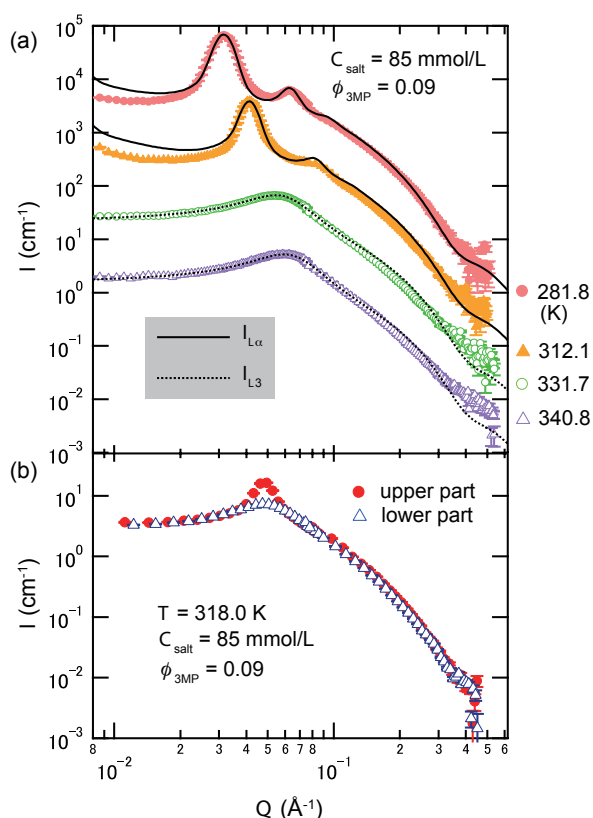
effect and critical concentration fluctuations. In addition, they showed that hydrophilic and hydrophobic ions tend to adsorb near the interface between the water and the organic solvent. These ions act as an electric double layer at the interface, and reduce the interfacial tension between the water and the organic solvent.

Although pairs of hydrophilic and hydrophobic ions act as a surface-active agent under certain conditions, the details of the formation mechanisms of a salt-induced ordered structure have not yet been clarified. As shown in Fig. 1(c), the composition and temperature ranges for the ordered-lamellar-structure are very narrow, suggesting that these

Fig. 2: (a) SANS profiles for D₂O / 3MP / NaBPh₄ with changing C_{salt} at ϕ_{3MP} = 0.09 and T = 280.5 K. The data at higher C_{salt} are shifted by a multiplication factor of 10 for better visualization. (b) The same plot at C_{salt} = 300 mmol/L in absolute units and the fitting result with the function of the sponge structure.

Ornstein-Zernike function which describes the concentration fluctuations of binary mixtures. Above 5 mmol/L, the SANS profile deviates from this formula due to the growth of a peak from the formation of nanoscale structures. In cases of the salt concentration between 60 mmol/L and 250 mmol/L, the SANS profiles show a sharp peak profile together with higher-order peaks of an ordered-lamellar-phase. The SANS profile at C_{salt} = 300 mmol/L shows a broad shoulder again. This profile was successfully analyzed by the model function of the sponge phase of surfactant solutions.

Figure 3 shows the SANS profiles of the D_2O / 3MP / $NaBPh_4$ system (ϕ_{3MP} = 0.09 and C_{salt} = 85 mmol/L) with changing temperature. The open and closed symbols indicate the data for the disordered-phase and ordered-lamellar-phase, respectively. The dotted and solid lines in Fig. 3(a) are the fitting results according to the sponge phase and the lamellar phase, respectively.

The SANS profiles from the disordered-phase

fit well with the function of the sponge phase, whereas the multi-peak profiles are well described by the function of the ordered lamellar phase.

At T = 340.8 K, the disordered-phase is confirmed from the broad peak profile, and the peak position Q_m shifts to lower Q values with decreasing temperature.

As shown in Fig. 3(b), the two phases coexist in the sample at about T = 318 K; a single broad peak from the disordered-phase is observed in the lower

Fig. 3: (a) Temperature dependence of the SANS profiles for ϕ_{3MP} = 0.09 and C_{salt} = 85 mmol/L. The data at lower temperatures are shifted by a multiplication factor of 10 for better visualization. (b) SANS profiles at ϕ_{3MP} = 0.09, C_{salt} = 85 mmol/L, and T = 318.0 K. Under these conditions, the mixture separates into two phases; the lower part of the sample is in the disordered-phase, while the upper part is in the ordered-lamellar-phase.
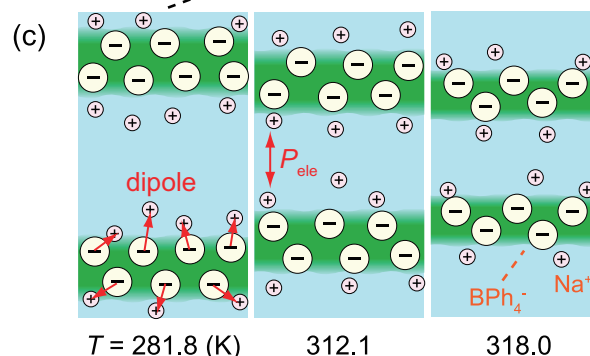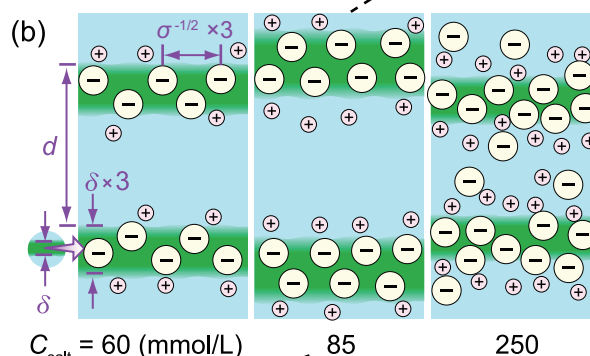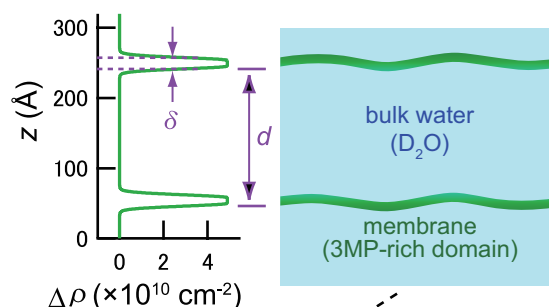
Fig. 4: (a) Scattering length density distribution obtained to describe the SANS profile for ϕ_{3MP} = 0.09, C_{salt} = 85 mmol/L, and T = 281.8 K (left), and the schematic illustration of the system, indicating the membrane structure mainly composed of 3MP according to the results of SANS and NSE measurements (right). The vertical axis indicates the distance normal to the layers. (b) Schematic illustration indicating the C_{salt} dependence of the lamellar repeat distance d, the membrane thickness δ, and the distribution of ions. (c) Schematic illustration indicating the temperature dependence of d, δ, and the distribution of ions.

part of the sample, and a sharp peak profile, from the ordered-lamellar-phase, is observed in the upper part. This evidence clearly shows that a 1st-order phase transition occurs at T = 318 K.

A further decrease in temperature makes the system uniform macroscopically, and the SANS profile shows multiple peaks resulting from the formation of the lamellar structure.

Figure 4(a) describes the scattering length density distribution obtained to describe the SANS profile for ϕ_{3MP} = 0.09, C_{salt} = 85 mmol/L and T = 281.8 K (left), and the schematic illustration of the system, indicating the membrane structure mainly composed of 3MP according to the results of SANS and NSE measurements (right).

Figure 4(b) models the ordered-lamellar-structure with changing C_{salt}. The membrane is composed of 3MP-rich domains and BPh_4^- ions. Na^+ ions are distributed around the surface of the membrane. The lamellar repeat distance increases with increasing C_{salt} up to 85 mmol/L, but decreases above 85 mmol/L.

Figure 4(c) models the ordered-lamellar-structure at ϕ_{3MP} = 0.09 and C_{salt} = 85 mmol/L with changing temperature.

From these results, we concluded that the 3MP-rich domains are stretched as a membrane owing to the solvation effects of Na^+ and $BPh4^-$. The periodicity of the ordered-lamellar-structure is stabilized mainly by the effects of the electrostatic interactions between neighboring membranes.

References
K. Sadakane, et al., J. Chem. Phys., **139** (2013) 234905.