

6 Soft-matter Project

Project Leader: Hideki Seto

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.

With this background, we are investigating the structural properties of soft-matters such as liquids and amphiphilic molecules. Especially, the contributions of electrostatic interactions due to the existence of ions, which are much stronger than the other interactions, are distinct and not well understood. Additionally, structures formed under far-from-equilibrium conditions are interesting. These investigations will yield basic knowledge that will help to solve the mystery of life.

6-2 2D-Ising-like critical behavior in mixtures of water and organic solvent including antagonistic salt or ionic surfactant

The effect of an antagonistic salt, composed of hydrophilic cations and hydrophobic anions, on the phase behavior and nanoscale structure of a mixture of D_2O and 3-methylpyridine (3MP) was investigated. The addition of the antagonistic salt, namely sodium tetraphenylborate ($NaBPh_4$), induces shrinkage of the two-phase region in contrast to the case in which a normal (hydrophilic) salt is added. This indicates that adding an antagonistic salt decreases the interfacial tension between D_2O and 3MP.

In order to investigate the nano-scale structure of the fluids, small-angle neutron scattering (SANS) experiments were performed at SANS-U, JRR-3. The SANS profile of the mixture with D_2O and 3MP without salt can be well explained by the Ornstein-Zernike

function below the phase separation point. The critical behavior belongs to the 3D-Ising critical universality as established in binary fluids. The SANS profiles from the mixtures with the antagonistic salt deviate from the Ornstein-Zernike function. With increasing salt concentration, a shoulder owing to the existence of a long-range periodic structure appears at finite-Q, which is induced by the coupling of solvation effect and critical concentration fluctuation. This long-range periodic structure was predicted theoretically by Onuki and Kitamura as a charge density wave structure.

At higher concentration of the salt, the critical exponents increase significantly, approaching the values of 2D-Ising behavior. These results suggest that the concentration fluctuation of the mixture of solvents is limited to a quasi two-dimensional space by the periodic structure induced by the addition of the salt. The same behaviors were also observed in mixtures composed of water, 3MP, and ionic surfactant such as SDS and AOT.

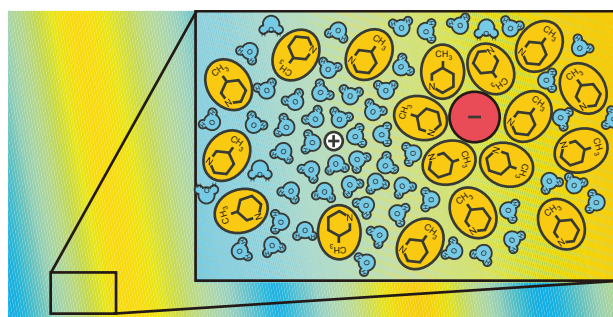


Fig. 1 Schematic picture of the periodic structure induced by the coupling of solvation effect and critical concentration fluctuation.

Reference

K. Sadakane, et al., *Soft Matter*, **7** (2011) 133.

6-3 Curvature of surfactant self-assembly determines the diameter of gold nanorods

The effect of the structure of surfactant self-assembly on the diameter of gold nanorods was investigated. It is known that gold nanorods with a diameter of ~ 20 nm grow spontaneously in surfactant solution. We have synthesized gold nanorods in gelled surfactant self-assembly and observed the time series of the growth process of gold nanorods by completely stopping the growth reaction. This growth process was compared to that in solution without gelation. The comparison indicated that the self-assembly of surfactant molecules affected the resulting shape of gold nanorods; those with a diameter of ~ 80 nm grow in gelled surfactant self-assembly. Small-angle X-ray scattering (SAXS) experiments at BL-15A, Photon

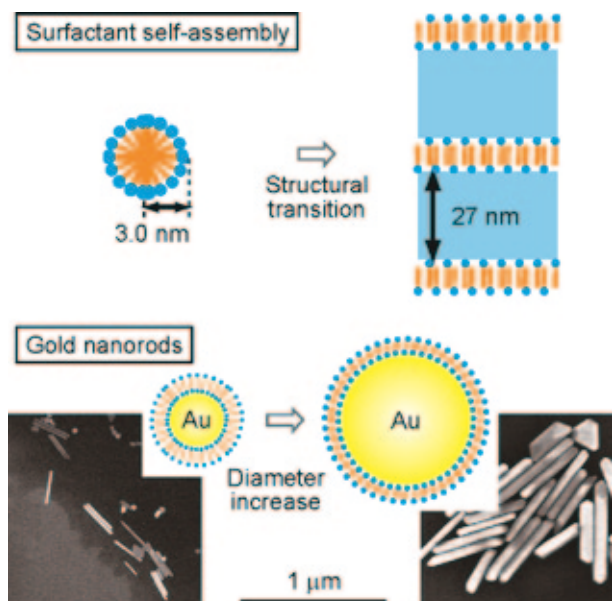


Fig. 2 Schematic picture of the structural transition of surfactant self-assembly and the corresponding increase in the diameter of a gold nanorod.

Factory and SANS experiments at SANS-U, JRR-3 revealed that the gelled surfactant self-assembly forms a lamellar structure with interdigitation whereas a non-gelled surfactant solution forms a spherical micelle. It is well known that the gold nanorods are covered with a surfactant bilayer during the growth process. From these results, the authors propose the following model: the diameter of gold nanorods is affected by a decrease in the spontaneous curvature of the outer surfactant layer and/or an increase in the bending modulus of the surfactant membrane neighboring the gold surface.

References

- Y. Takenaka, et al., *J. Colloid Interf. Sci.*, **356** (2011) 111.
 Y. Takenaka, et al., *J. Nanosci. Nanotechnol.*, in press.

6-4 Phase separation on a giant vesicle induced by small cations

Phase separation of giant vesicles composed of neutral saturated lipid (dipalmitoyl-sn-glycero-3-phosphocholine: DPPC), negatively charged unsaturated lipid (1,2-dioleoyl-sn-glycero-3-phosphocholine: DOPS), and cholesterol, is observed at different calcium concentrations. Confocal microscopy provides information on where the phase separation becomes distinct as the calcium concentration is increased. The charged domains tend to bud toward the interior of the vesicle. This budding is assumed to be due to an increase in the osmotic pressure, in cooperation with

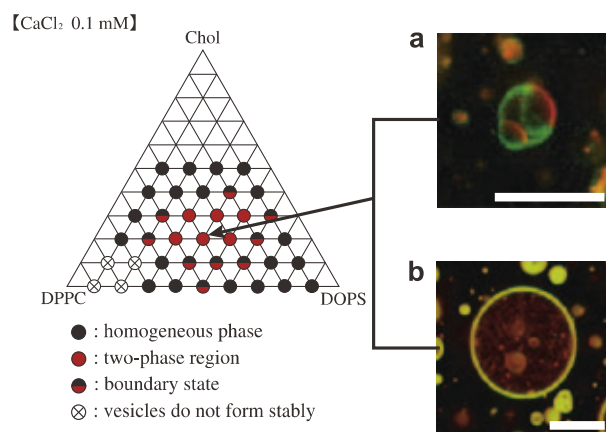


Fig. 3 Ternary phase diagram of DPPC / DOPS / Chol / CaCl₂ at room temperature and corresponding giant vesicles observed by confocal microscopy.

the spontaneous change in curvature in the outer leaflet of the bilayer caused by the adsorption of calcium ions and charge screening effect. The effect of small cations on the phase separation is interpreted based on the theoretical model with the Poisson–Boltzmann equation.

Reference

- N. Shimokawa, et al., *Chem. Phys. Lett.*, **496** (2010) 59.

6-5 Lamellar-lamellar phase separation of phospholipid bilayers by the addition of salt

The multilamellar structure of phospholipid bilayers is stabilized by the interactions between bilayers. Although the lamellar repeat distance is uniquely determined at the balance point of interactions between bilayers, a lamellar-lamellar phase separation, where the two phases with different lamellar repeat distance coexist, has been reported in the case of adding a salt to an aqueous solution of lipids. In order to understand the physical mechanism of the lamellar-lamellar phase separation, the effects of adding monovalent salt on the lamellar structure are being studied by visual observation and by SAXS performed at BL-15A of the Photon Factory. Further, a theoretical model based on the mean field theory has been introduced. It is concluded that the salting-in and -out effects of lipid bilayers trigger the lamellar-lamellar phase separation.

Reference

- M. Hishida and H. Seto, *J. Phys.: Conf. Ser.*, **272** (2011) 012008.

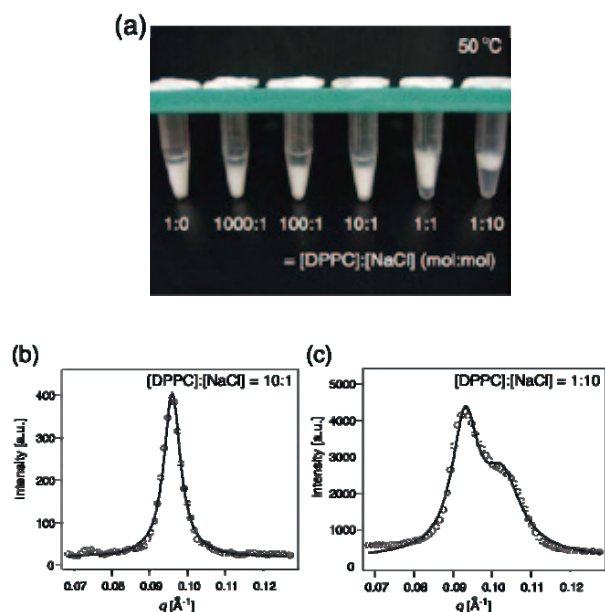


Fig. 4 (a) Picture of 8 wt% DPPC solutions with different NaCl concentrations at $T=50^{\circ}\text{C}$. The white suspension is phospholipid multilamellar vesicles. (b)(c) SAXS profiles of $[\text{DPPC}]:[\text{NaCl}]=10:1$ and $[\text{DPPC}]:[\text{NaCl}]=1:10$ solutions, respectively.

6-6 Spontaneous blebbing of oil droplet induced by surfactant aggregates

One of the important mechanisms for biological motility is the generation/collapse of elastic aggregate of biopolymers. In order to mimic the essential feature of the mechanism, we constructed a system where spontaneous deformation of an oil droplet is induced by surfactant aggregate generation. Upon placing a droplet of tetradecane with palmitic acid on an aqueous phase with cationic surfactant (trimethylstearyl ammonium chloride: STAC), the oil droplet spontaneously deformed intensively for more than 1 hour. During the appearance of deformation, the aggregate was generated at the oil-water interface. The structure of the aggregate was confirmed with SAXS experiments performed at BL-15A of the Photon Factory, indicating that the aggregate was highly-ordered lamellar with an interlayer distance of 405 Å.

References

- Y. Sumino, et al., *Phys. Rev. E*, **76** (2007) 055202(R).
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 Y. Sumino, et al., *Soft Matter*, **7** (2011) 3204.

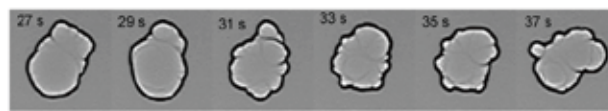


Fig. 5 Shadowgraph image of an oil droplet during its blebbing stage. Scale bar corresponds to 10 μm .

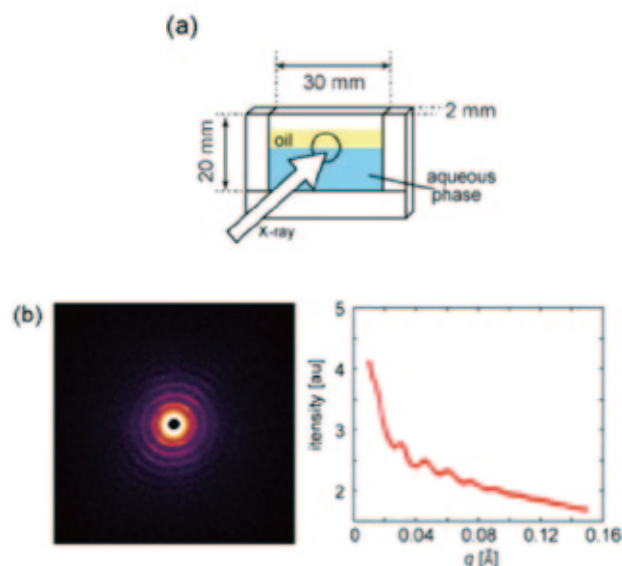


Fig. 6 Inspection of aggregate generation: (a) Schematic diagram of experimental setup. (b) SAXS image and its radial intensity distribution.

6-7 Swollen structure of polyelectrolyte brushes in saline water

A polymer brush is a polymer layer with an end tethered on a solid substrate and exhibits unique behaviors due to the special morphology. For example, a poly(2-(methacryloyloxy)ethyl phosphorylcholine) (poly(MPC)) brush, phosphorylcholine-containing polyampholytes, presents good blood compatibility, low friction, and anti-protein adsorption. In general, conformation of polyelectrolyte brushes depends on ionic strength because of the charge shielding effect. An aqueous solution of NaCl, however, hardly affects the conformation of a poly(MPC) brush up to 5000 mM.

In this study, the chain conformation of polyelectrolyte brushes in NaCl aqueous solution was investigated using the neutron reflectometer ARISA-II in J-PARC/MLF. Figure 7 shows the neutron reflectivity profiles of poly(MPC) in contact with NaCl aqueous solutions depending on the concentration. As in the case of previous reports, no significant difference was observed up to 5000 mM. On the other hand, the neutron reflectivity profiles of a poly(2-(methacryloyloxy) ethyltrimethylammonium chloride) (poly(MTAC)) brush, another kind of polycation brush, strongly depend on NaCl concentration as shown in Fig. 8. Although the detailed mechanism is not clarified, the

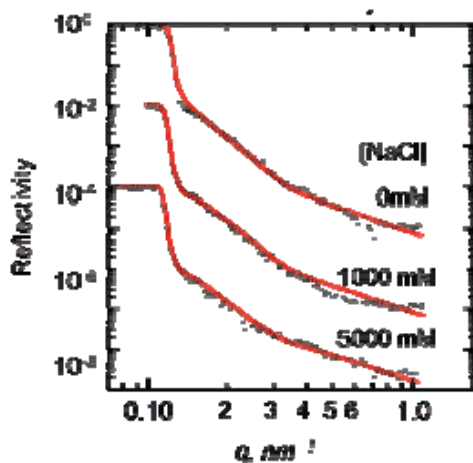


Fig. 7 Neutron reflectivity profiles of poly(MPC) in contact with NaCl aqueous solutions.

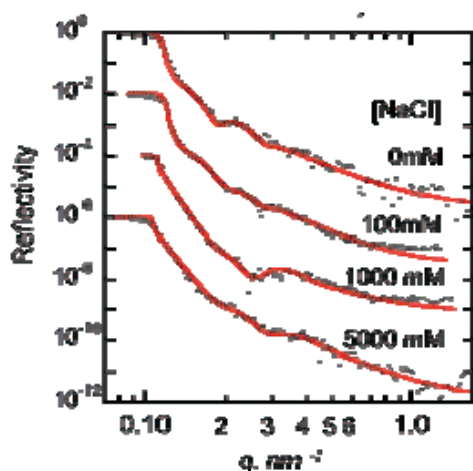


Fig. 8 Neutron reflectivity profiles of poly(MTAC) in contact with NaCl aqueous solutions.

unique behavior of the poly(MPC) brush in an aqueous solution of NaCl might result in the unique properties in tribology, anti-fouling, and wettability.

References

- K. Mitamura et al., J. Phys.: Conf. Ser., **272** (2011) 012017.
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6-8 Surface reorganization of poly(methyl methacrylate) films by water

It is well-known that water is a typical non-solvent of poly(methyl methacrylate) (PMMA). According to neutron reflectometry results, PMMA thin films, however, slightly swelled water and the interface with water was diffuse in comparison with the pristine surface. This is probably due to the partial dissolution of segments into the water. If this is the case, the

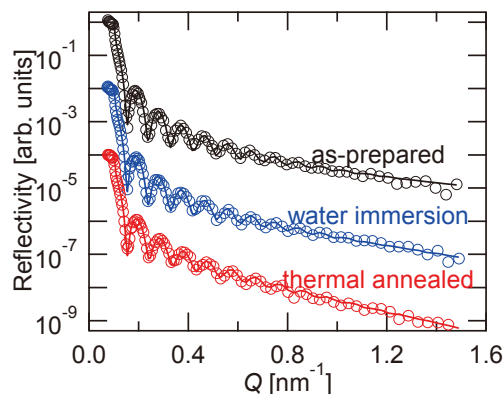


Fig. 9 Neutron reflectivity profiles for dPMMA/PMMA bilayer films before and after water immersion or thermal annealing.

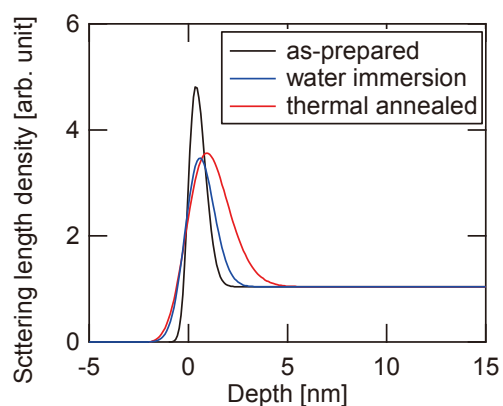


Fig. 10 Neutron scattering length density profiles at the surface dPMMA layer.

surface aggregation states of PMMA should be changed on a relatively large scale by water.

In this study, we experimentally demonstrated the partial dissolution of PMMA segments using the neutron reflectometer ARISA-II at J-PARC/MLF with a deuterium labeling method. A very thin deuterated PMMA (dPMMA) layer was deposited on a thick hydrated PMMA film spin-coated on a Si wafer. Figure 9 shows neutron reflectivity profiles for the dPMMA/PMMA bilayer films before and after the water immersion or thermal annealing. We performed the fitting for the reflectivity profiles and evaluated the scattering length density profiles as shown in Fig. 10. The peak at the surface corresponding to a dPMMA layer became broader not only after the thermal annealing but also after the water immersion. This is because water molecules could penetrate into the PMMA film.

Reference

- A. Horinouchi et al., Chem. Lett., **39** (2010) 810-811.