§17. Micelle Formation in Bolaamphiphilic Solution: A Molecular Dynamics Study

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Amphiphilic molecules such as lipids and surfactants are composed of both a hydrophilic part and a hydrophobic part. In aqueous solutions, amphiphilic molecules often self-assemble into various structures such as micelles, mesophases, and bicontinuous structures[1]. Such self-assembly of amphiphilic molecules plays an important role in many biological and industrial processes. Although numerous computer simulation studies have so far been done on micelle formation of amphiphilic molecules, each of which consists of a hydrophilic head group and a hydrophobic tail group, there have been few theoretical and simulation studies on micelle formation of bolaamphiphilic molecules, each of which contains a hydrophobic stalk and two hydrophilic ends. The purpose of this study is to clarify the molecular mechanism of micelle formation in bolaamphiphilic solution. With a view to investigating the micelle formation process in bolaamphiphilic solution at the molecular level, we perform the molecular dynamics (MD) simulations of coarse-grained bolaamphiphilic molecules with explicit solvent molecules and analyze the micelle formation process.

The computational model is similar to that used in our previous work[2),3)]. A bolaamphiphilic molecule is modeled as a semiflexible chain which is composed of a hydrophobic stalk with three particles and two hydrophilic ends (H1 and H2), each of which consists of one particle. A solvent molecule is modeled as a hydrophilic particle. As bonded potentials, we consider a bond-stretching potential and a bond-bending potential. The interaction between a hydrophilic particle and a hydrophobic particle is modeled by a repulsive soft core potential and all other interactions are modeled by a Lennard-Jones (LJ) potential. Note that the LJ interaction parameter $\varepsilon^*_{\rm hs2}$ between a hydrophilic end particle (H2) and a solvent particle can be varied. The numerical integrations of the equations of motion for all particles are performed using the velocity Verlet algorithm at constant temperature with a time step of 0.0005. We apply the periodic boundary conditions and the number density is set to 0.75. The total number of particles is 5832. Initially, we provide homogeneous bolaamphiphilic solutions with the amphiphilic concentration of $c_{\rm s} = 0.1$ at high temperature ($T^* = 10$) for various values of the interaction parameter $\varepsilon^*_{\rm hs2}$ ($0.5 \leq \varepsilon^*_{\rm hs2} \leq 5.0$). The system is then quenched to $T^* = 1.3$ and MD simulations of 5.0×10^7 time steps are carried out for each simulation run.

We show, in Fig. 1, snapshots of micelles formed by bolaamphiphilic molecules for $\varepsilon^*_{\rm hs}$=1.0, 2.0 and 4.0 at $c_{\rm s} = 0.1$. Isosurfaces of the density of the hydrophobic particles, which are calculated by Gaussian splatting techniques, are depicted in this figure. This figure tells us that the platelike micelle changes into the wormlike micelles, and then into the spherical micelles at $c_{\rm s} = 0.1$ as the interaction parameter $\varepsilon^*_{\rm hs2}$ increases.

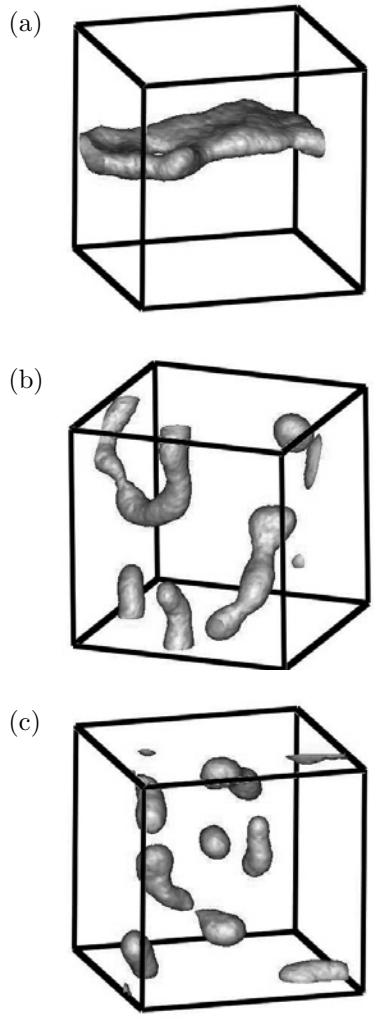

Fig. 1. Snapshots of micelles formed by bolaamphiphilic molecules at $c_{\rm s} = 0.1$: (a) the platelike micelle ($\varepsilon^*_{\rm hs2} = 1.0$), (b) the wormlike micelles ($\varepsilon^*_{\rm hs2} = 3.0$) and (c) the spherical micelles ($\varepsilon^*_{\rm hs2} = 5.0$). Isosurfaces of the density of the hydrophobic particles, which are calculated by Gaussian splatting techniques, are depicted to show the micellar shape clearly. Note that solvent molecules are not displayed for clarity.

1) Hamley, I.W., *Introduction to Soft Matter* (J. Wiley, Chichester, 2007) Rev. ed.
2) Fujiwara, S., Itoh, T., Hashimoto, M., Nakamura, H. and Tamura, Y.: Plasma Fusion Res. **5** (2010) S2114.
3) Fujiwara, S., Itoh, T., Hashimoto, M., Tamura, Y., Nakamura, H. and Horiuchi, R.: Plasma Fusion Res. **6** (2011) 2401040.