§28. Phase Behavior in a Bolaamphiphilic Solution: A Molecular Dynamics Study

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The self-organization of structures is a universal characteristic of nonequilibrium and nonlinear systems such as plasma syatems and soft matter systems. We investigate self-organization in amphiphilic systems in order to explore the universal self-organizing properties of nature. Amphiphilic molecules such as lipids and surfactants consist of both hydrophilic and hydrophobic parts. In aqueous solvents, these molecules often self-assemble into various structures such as hexagonal structures and bicontinuous structures[1]. The purpose of this study is to clarify the effect of hydrophilicity on phase behavior in a solution of bolaamphiphilic molecules, each of which consists of a hydrophobic stalk and two hydrophilic ends. To investigate the phase behavior in a 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 self-assembly processes.

The computational model is the same as the one used in our previous work[2]. A bolaamphiphilic molecule is modeled as a semiflexible chain that is composed of a hydrophobic stalk with three particles (denoted by B) and two hydrophilic ends (denoted by A and C), each of which consists of one particle. A solvent molecule is modeled as a hydrophilic particle (denoted by S). 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 the Lennard-Jones (LJ) potential. Numerical integrations of the equations of motion for all particles are carried out 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 at 0.75. The total number of particles is 5832. Initially, we provide homogeneous bolaamphiphilic solutions with various amphiphilic concentrations ($c_s = 0.1, 0.2, ..., 0.9$) at high temperature ($T^* = 10$) for various values of the hydrophilic interaction parameter ε^*_{CS} between a hydrophilic end particle C and a solvent particle S ($0.5 \leq \varepsilon^*_{CS} \leq 5.0$). The system is then quenched at $T^* = 1.3$ and MD simulations of $t^* = 2.5 \times 10^4$ (5.0×10^7 time steps) are carried out for each simulation run.

In Fig. 1, we pictorially show our simulated phase diagram. This diagram indicates that six types of self-assembled structures are obtained. Among them, four types of self-assembled structures are depicted in Fig. 2. These figures show that, at intermediate amphiphilic concentrations, the lamellar structure changes to a bicontinuous structure, and then to worm-like micelles or a hexagonal structure as the hydrophilic interaction parameter ε^*_{CS} increases.

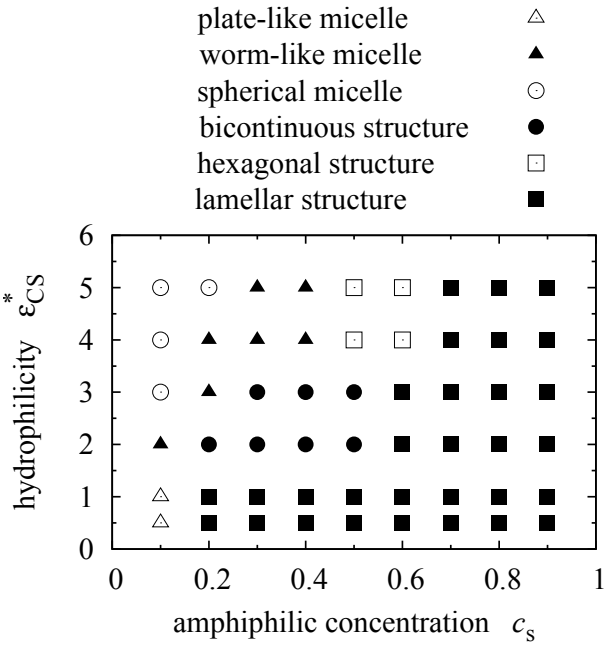

Fig. 1. Hydrophilic interaction parameter, ε^*_{CS}, vs. amphiphilic concentration, c_s, phase diagram of bolaamphiphilic molecules.

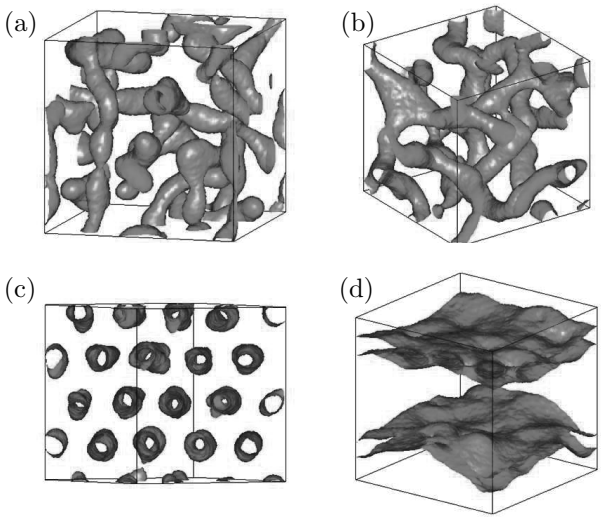

Fig. 2. Snapshots of self-assembled structures formed by bolaamphiphilic molecules: (a) the worm-like micelles, (b) the bicontinuous structure, (c) the hexagonal structure, and (d) the lamellar structure. Isosurfaces of the density of the hydrophobic particles, which are calculated by Gaussian splatting techniques, are shown.

1) Hamley, I.W., *Introduction to Soft Matter* (J. Wiley, Chichester, 2007) Rev. ed.
2) Fujiwara, S. et al.: Plasma Fusion Res. **10** (2015) 3401029.