§26. Molecular Dynamics Simulation of Micelle Formation in Amphiphilic Solution: Effect of Molecular Rigidity

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Amphiphilic molecules such as lipids and surfactants consist of a hydrophilic head group and a hydrophobic tail group. In aqueous solutions, these molecules spontaneously self-assemble into various structures ranging from micelles and bilayers to bicontinuous cubic structures[1]. Such self-assembly of amphiphilic molecules is of great importance in many biological and industrial processes. Although several computer simulations have so far been performed in relation to the effect of molecular rigidity on structure formation in polymeric systems, few simulation studies have been done with respect to the effect of molecular rigidity on micelle formation in amphiphilic solution. With a view to investigating the self-assembling processes of amphiphilic molecules in solution *at the molecular level*, we carry out the molecular dynamics (MD) simulations of coarse-grained amphiphilic molecules with explicit solvent molecules and analyze the dynamical processes of micelle formation systematically[2),3)]. Our particular concern is to investigate the effect of molecular rigidity on the micelle formation process[4].

The computational model is the same as that used in our previous work[4]. An amphiphilic molecule is modeled as a semiflexible chain which is composed of one hydrophilic head particle and three hydrophobic tail particles. A solvent molecule is modeled as a hydrophilic particle. Particles interact via the non-bonded potentials and the bonded potentials. As for non-bonded potentials, 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 potential. Here, the interaction parameter between a hydrophilic head particle and a solvent molecule represents the intensity of the hydrophilic interaction. As bonded potentials, we consider a bond-stretching potential and a bond-bending potential. The molecular rigidity is controlled by the bending modulus k_3 of the bond-bending potential. The equations of motion for all particles are solved numerically using the velocity Verlet algorithm at constant temperature with a time step of $\Delta t^* = 0.0005$. We apply the periodic boundary conditions and the number density is set to $\rho^* = 0.75$. Initially, we prepare an isolated micelle of 120 flexible amphiphilic molecules with $k_3^* = 0.0$ in solution at $T^* = 1.3$. The number of solvent molecules is 7520, which leads to the amphiphilic concentration of 0.06. The bending modulus k_3^* is then changed to various values (k_3^*=1.0, 2.0, 4.0, 8.0, 16.0) and MD simulations of $t^* = 5.0 \times 10^3$ (1.0×10^7 time steps) are performed for each simulation run.

We show, in Fig. 1, snapshots of self-assembled structures formed by amphiphilic molecules for $k_3^* = 4.0$ and $k_3^* = 16.0$. Gray shadows of the micelle projected on three planes are also depicted to show the micellar shape clearly. This figure tells us that the micellar structure formed for $k_3^* = 4.0$ is *cylindrical* and that for $k_3^* = 16.0$ is *disclike*. Our simulations indicate that the micellar shape changes from a cylinder into a disc as the intensity of the molecular rigidity increases. It is also ascertained that a cylindrical micelle and a disc micelle coexist dynamically in a certain range of molecular rigidity.
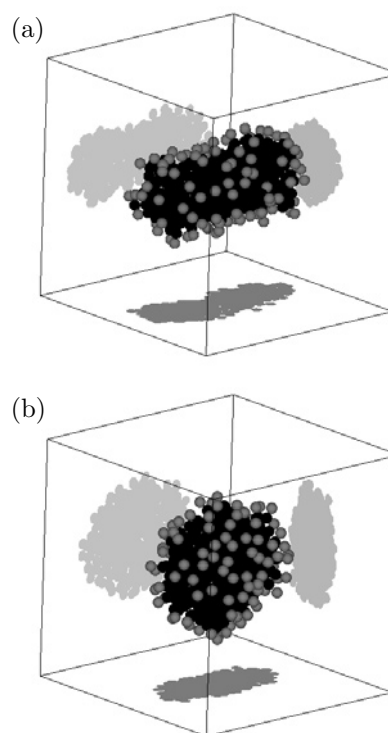

Fig. 1. Snapshots of self-assembled structures formed by amphiphilic molecules for various values of the bending modulus k_3^*. (a) A cylindrical micelle for $k_3^* = 4.0$ and (b) a disc micelle for $k_3^* = 16.0$. Light gray and dark gray particles denote hydrophilic head particles and hydrophobic tail particles, respectively. Gray shadows of the micelle projected on three planes are also depicted to make the micellar shape understandable.

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