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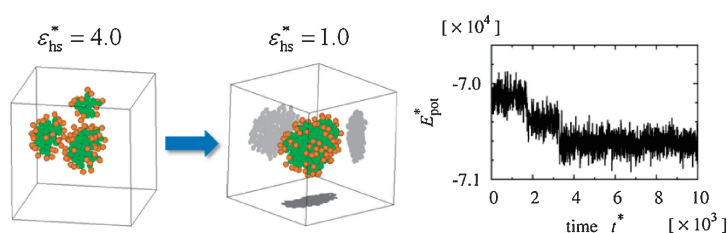
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When the intensity of the solvophilicity ε_{hs}^* decreases, the micellar shape change proceeds in a stepwise manner.

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Micellar shape change in amphiphilic solution after sudden change in the solvophilic interaction is studied by molecular dynamics simulations of coarse-grained, rigid amphiphiles. Our simulations demonstrate that, after sudden increase in intensity of the solvophilicity, the disc micelle transforms into cylindrical or spherical micelles immediately. In contrast, spherical micelles coalesce into a disc micelle in a stepwise manner after sudden decrease in intensity of the solvophilicity.

Amphiphilic molecules such as surfactants and lipids consist of two components: a solvophilic head and a solvophobic tail. In aqueous solvents, these molecules often spontaneously self-assemble into various structures such as micelles and mesophases.[1–3] Although several studies using computer simulation[4–6] and theoretical approaches[7,8] have been performed on micelle formation in amphiphilic solution, little is known about the detailed mechanism of formation at the molecular level. In our previous studies, we investigated micelle formation and the dynamic coexistence of micellar shapes in amphiphilic solution using molecular dynamics (MD) simulations of coarse-grained amphiphilic molecules with explicit solvent molecules.[9–11] We also studied the effect of molecular rigidity on micelle formation and micellar shape change.[12,13]

The purpose of this Letter is to clarify the molecular mechanism of micellar shape change in amphiphilic solution. Our particular intent was to investigate the effect of the solvophilic interaction on micellar shape change. With this goal in mind, we performed MD simulations of coarse-grained rigid amphiphilic molecules with explicit solvent molecules and analyzed the dynamic processes of micellar shape change by altering the solvophilic intensity.

The computational model is the same as that used in our previous work.[9–11] An amphiphilic molecule is modeled as a rigid rod which consists of one solvophilic particle and two solvophobic particles; while, a solvent molecule is a single particle. The interaction between a solvophobic particle and a solvent particle as well as between a solvophobic particle and a solvophilic particle is modeled by the repulsive soft core potential:

$$U_{SC}(r) = 4\varepsilon_{SC}\left(\frac{\sigma_{SC}}{r}\right)^9 \tag{1}$$

The interaction between a solvophilic head particle and a solvent particle is modeled by the Lennard–Jones potential:

$$U_{LJ\text{-}hs}(r) = 4\varepsilon_{hs}\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{2}$$

All other interactions are modeled by the general Lennard–Jones potential:

$$U_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{3}$$

where r is the interparticle distance, ε_{SC} is an interaction parameter for the intensity of the solvophobic interaction, and ε_{hs} is the intensity of the solvophilic interaction. The parameter σ_{SC} was set to be $\sigma_{SC} = 1.05\sigma$, as reported in ref. 4. To avoid discontinuities in both the potential energy and the force due to the potential energy cutoff, we used the shifted force variant of these nonbonded potentials:

$$V_X(r) = U_X(r) - U_X(r_c) - \left.\frac{\partial U_X}{\partial r}\right|_{r=r_c}(r - r_c) \tag{4}$$

where $X = SC$, LJ-hs, or LJ, and r_c is the cutoff distance, set to $r_c = 3.0\sigma$ here. In the following, the quantities with asterisks are reduced units, e.g., number density $\rho^* = \rho\sigma^3$, time $t^* = t\sqrt{\varepsilon/m\sigma^2}$, and temperature $T^* = k_B T/\varepsilon$, where k_B is the Boltzmann constant.

The equations of motion for all particles were solved numerically using the leap-frog algorithm at constant temperature with a time step of $\Delta t^* = 0.0025$ and the temperature was controlled every 10 time steps by ad hoc velocity scaling.[14] We applied periodic boundary conditions and the number density was set to $\rho^* = 0.75$.

Initially, we provided isolated micelles of 97 amphiphilic molecules in solution at $T^* = 1.3$ for various values of the interaction parameters ε_{SC}^* and ε_{hs}^* ($1.0 \leq \varepsilon_{SC}^*, \varepsilon_{hs}^* \leq 4.0$). The number of solvent particles was 5541, which corresponds to an amphiphilic concentration of 0.05. We then changed the value of the solvophilic interaction parameter ε_{hs}^* to various values suddenly and MD simulations of $t^* = 2.0 \times 10^4$ (8.0×10^6 time steps) were carried out for each simulation. In this Letter, we focused on the results for the sudden increase in ε_{hs}^* from 1.0 to 4.0 and those for the sudden decrease in ε_{hs}^* from 4.0 to 1.0 in the case of $\varepsilon_{SC}^* = 1.0$.

Simulation results in the case of the sudden increase in ε_{hs}^* from 1.0 to 4.0 are shown in Figures 1 and 2. We illustrate, in Figure 1, snapshots of micelles formed by amphiphilic molecules at $t^* = 0$ and 19000. Gray shadows of the amphiphilic molecules projected on three planes are also depicted in Figure 1a to show the micellar shape clearly. This figure indicated that the micellar shape changed from a disc to a cylinder or a sphere as the intensity of the solvophilic interaction ε_{hs}^* increased from 1.0 to 4.0. Figure 2 shows the time dependence of the total potential energy E_{pot}^*, the radius of gyration of the largest micelle R_g^*, the number of micelles n_m, and the fraction of various micellar shapes after the sudden increase in ε_{hs}^* from 1.0 to 4.0. As in our previous papers, we calculated the fractions of the micellar shapes on the basis of the
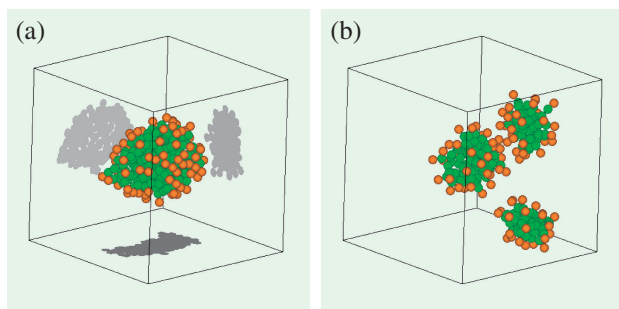
Figure 1. Snapshots of micelles formed by amphiphilic molecules after sudden increase of ε_{hs}^* from 1.0 to 4.0 in the case of $\varepsilon_{SC}^* = 1.0$. (a) at $t^* = 0$ and (b) at $t^* = 19000$. Orange and green particles denote solvophilic head particles and solvophobic tail particles, respectively. Gray shadows of the micelle projected on three planes are also depicted in (a) to illustrate its shape clearly. Note that, for clarity, solvent particles are not displayed.

orientational order parameters.[10–13] We realized the following features from Figure 2. (i) The potential energy E_{pot}^* and the radius of gyration R_g^* began to decrease and the number of micelles n_m began to increase immediately after the sudden increase in ε_{hs}^*, and these parameters reached equilibrium values at $t^* \approx 1000$ (Figures 2a–2c). (ii) Sharp increases and decreases in R_g^* and n_m were observed, which implied that coalescence and fragmentation of micelles occurred (Figures 2b and 2c). (iii) The dominant micellar shape after equilibration was a cylinder or a sphere; the fraction of cylindrical micelles was almost the same as spherical micelles (Figure 2d). These results indicated that the micellar shape started to change immediately after the sudden increase in ε_{hs}^*.

Simulation results in the case of the sudden decrease in ε_{hs}^* from 4.0 to 1.0 are shown in Figures 3 and 4. Figure 3 shows snapshots of micelles formed by amphiphilic molecules at $t^* = 0$ and 20000. This figure indicated that the spherical micelles coalesced into a disc micelle as the intensity of the solvophilic interaction ε_{hs}^* decreased from 4.0 to 1.0. Figure 4 shows the time dependence of the total potential energy E_{pot}^*, the radius of gyration of the largest micelle R_g^*, the number of micelles n_m, and the fraction of various micellar shapes after the sudden decrease in ε_{hs}^* from 4.0 to 1.0. The following characteristic features were identified from Figure 4. (i) The potential energy E_{pot}^* relaxed in a stepwise manner (Figure 4a). (ii) The radius of gyration R_g^* was found to increase in a stepwise manner in connection with the energy relaxation (Figures 4a and 4b). The sharp bumps in R_g^* occurred during coalescence of micelles (Figures 4b and 4c). (iii) The dominant micellar shape was a disc after coalescence of smaller micelles (Figure 4d). These results demonstrate that the spherical micelles coalesced into a disc micelle and the micellar shape change proceeded in a stepwise manner after sudden decrease in ε_{hs}^*.

In summary, we obtained the following new results by performing MD simulations of coarse-grained rigid amphiphilic molecules with explicit solvent molecules and analyzed the dynamic processes of micellar shape change by changing the intensity of solvophilicity. (i) After sudden increase in intensity of the solvophilic interaction, the micellar shape immediately started to change from a disc to a cylinder or a sphere. (ii) After a
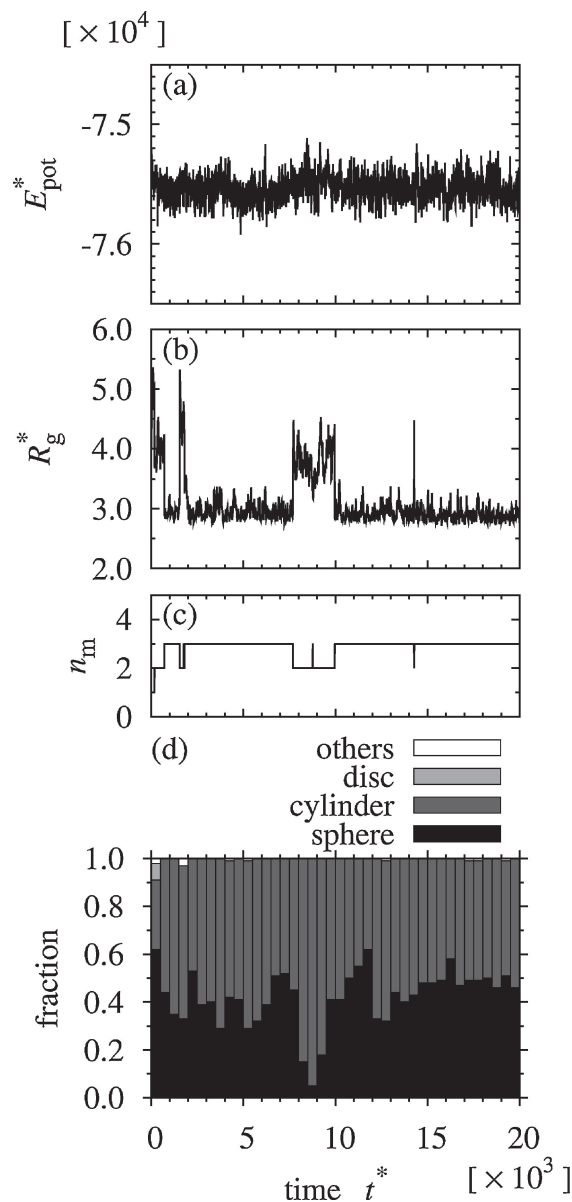

Figure 2. Time evolution of (a) the total potential energy E_{pot}^*, (b) the radius of gyration of the largest micelle R_g^*, (c) the number of micelles n_m, and (d) the fraction of various micellar shapes after sudden increase of ε_{hs}^* from 1.0 to 4.0 in the case of $\varepsilon_{SC}^* = 1.0$.

sudden decrease in intensity of the solvophilic interaction, the spherical micelles coalesced into a disc micelle in a stepwise manner.

It should be noted that the potential energy parameters between species can be changed by changing a condition of the solution such as the ionic strength. In reality, nonuniformity in the ionic strength occurs; thus, potential parameters were spatially distributed nonuniformly. In this study, we investigated the micellar shape change by the sudden uniform change of the potential parameters because we intended to understand the elementary processes of the micellar shape change in detail.
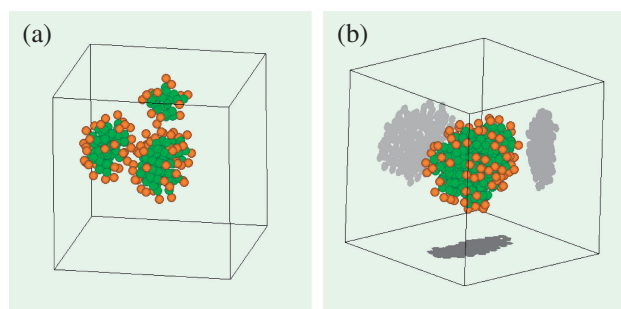
Figure 3. Snapshots of micelles formed by amphiphilic molecules after sudden decrease of ε_{hs}^* from 4.0 to 1.0 in the case of $\varepsilon_{SC}^* = 1.0$. (a) at $t^* = 0$ and (b) at $t^* = 20000$. Orange and green particles denote solvophilic head particles and solvophobic tail particles, respectively. Gray shadows of the micelle projected on three planes are also depicted in (b) to illustrate its shape clearly. Note that, for clarity, solvent particles are not displayed.

It is worth mentioning that the sphere-to-rod transitions of surfactant micelles in aqueous solution were recently investigated by coarse-grained MD simulations.[15,16]

For future work, we will study the micellar shape change from a disc to a cylinder or from a cylinder to a disc after sudden change in intensity of the solvophilic interaction.

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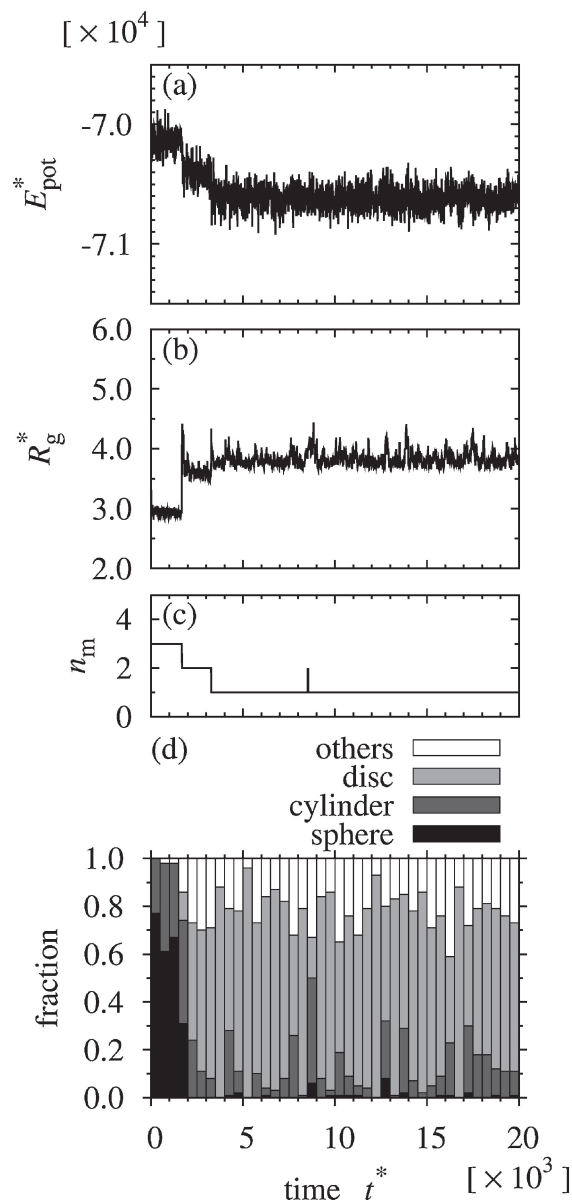9 S. Fujiwara, M. Hashimoto, T. Itoh, *J. Plasma Phys.* **2006**, *72*, 1011.

Figure 4. Time evolution of (a) the total potential energy E_{pot}^*, (b) the radius of gyration of the largest micelle R_g^*, (c) the number of micelles n_m, and (d) the fraction of various micellar shapes after sudden decrease of ε_{hs}^* from 4.0 to 1.0 in the case of $\varepsilon_{SC}^* = 1.0$.

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