Mesoscopic simulation for the structural change of a surfactant solution using dissipative particle dynamics

Ki Young Kim, Ki-Taek Byun, and Ho-Young Kwak†

Mechanical Engineering Department, Chung-Ang University, Seoul 156-756, Korea
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Abstract−With a simple model for a surfactant consisting of a hydrophilic head group and hydrophobic tail groups connected by harmonic springs, the structural change of the association structures of the surfactant in an aqueous solution was studied by using the dissipative particle dynamics (DPD) simulation. The effect of the interaction parameter of DPD particles on the structural change of the association structures was also studied. Simulations show that the proper relative values of these interaction parameters could yield desirable changes for the association structure depending on the concentration of the surfactant. That is, a spherical structure forms at $\phi=0.15$, structural change from a spherical to cylindrical one occurs at $\phi=0.26$, and a hexagonal structure appears at $\phi=0.30$, where ϕ is the volume fraction of surfactant SDS (sodium dodecyl sulfate), and they are in good agreement with observation.

Key words: Association Structure, Dissipative Particle Dynamics (DPD) Simulation, Sodium Dodecyl Sulfonate (SDS), Structural Transition, Surfactant Solution

INTRODUCTION

Surfactant molecules which possess a polar head and a nonpolar tail part are known as amphiphiles and they spontaneously aggregate to form association structures such as micelles, bilayers and vesicles in aqueous solution. At a concentration above the critical micelle concentration (CMC), a spherical micelle forms. It is also known that the shape of the micelle changes from spherical to cylindrical, hexagonal and also lamellar phases by increasing the concentration [1].

Determination of the phases and the structural transition of the micelles is very important in predicting the washing and cleaning mechanisms of surfactants. Also, a particular form of micelle, liposome, which is a vesicle formed from lipid molecules, can interact with biomembranes, and the liposomes play very important roles in many applications such as drug delivery and artificial oxygen carrier [2]. However, the measurement of phase behaviors and characterization of various micelle structures are difficult and time-consuming.

The elucidation of the surfactant mesostructures at atomic resolution is not currently possible because the time and length scales at which these phenomena occur are not accessible by molecular dynamics (MD) simulation [3,4]. An alternative approach is to simulate the surfactant system at mesoscopic scale using dissipative particle dynamics (DPD), which was introduced by Hoogerbragge and Koelman [5,6].

In the DPD simulation, two or three water molecules are lumped to a single coarse-grained particle so that one DPD particle represents a group of atoms. At present, the DPD technique is applied to dynamics of biological membranes [7] and vesicles [8], characterizing colloid systems, polymeric behavior [9-13] and multi-phase channel flow [14]. However, a fundamental problem of the DPD technique is that there are no general ingredients and procedures for the method to apply to a specific problem.

In this study, the structural change of the association structure in aqueous solution was studied using the DPD simulation. Especially, the effect of the interaction parameter of DPD particles on the structural change of the mesostructures of surfactant by changing the value of the parameters was studied.

DPD SIMULATION

In DPD simulation, a group of "fluid particles" is regarded as a DPD particle whose interaction with another particle is much softer than that between molecules in MD simulation. The motion of the cluster particles is governed by Newton's second law:

$$\frac{d\vec{r}_i}{dt} = \vec{v}_i \tag{1-1}$$

$$m_i \frac{d\vec{v}_i}{dt} = \vec{f}_i \tag{1-2}$$

where $\vec{r}_i$, $\vec{v}_i$, m_i and $\vec{f}_i$ are the position, velocity, mass and force of the ith particle, respectively. The force $\vec{f}_i$ on particle i includes conservative, dissipative and random forces, which is described as

$$\vec{f}_i = \sum_{j \neq i} (\vec{F}_{ij}^C + \vec{F}_{ij}^D + \vec{F}_{ij}^R) \tag{2}$$

The conservative force is the soft-core repulsive force, given by

$$\vec{F}_{ij}^C = \begin{cases} a_{in}(1 - r_{ij}/r_c)\hat{r}_{ij} & \text{if } r_{ij} < r_c \\ 0 & \text{if } r_{ij} \geq r_c \end{cases} \tag{3}$$

where a_{ij} is the maximum repulsion between particles i and j, $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$, $r_{ij} = |\vec{r}_{ij}|$, $\hat{r}_{ij} = \vec{r}_{ij}/|\vec{r}_{ij}|$, and r_c is the cut-off distance. The second

†To whom correspondence should be addressed.
E-mail: kwakhy@cau.ac.kr

and third forces in Eq. (2) are the dissipative and the random forces:

$$\mathbf{F}_{ij}^D = -\gamma\omega^D(\mathrm{r}_{ij})(\mathbf{r}_{ij}\cdot\mathbf{v}_{ij})\hat{\mathbf{r}}_{ij} \tag{4}$$

$$\mathbf{F}_{ij}^R = \sigma\omega^R(\mathrm{r}_{ij})\theta_{ij}\hat{\mathbf{r}}_{ij} \tag{5}$$

where $\mathbf{v}_{ij}=\mathbf{v}_i-\mathbf{v}_j$, $\omega(\mathrm{r}_{ij})$ is a weight function which tends to be zero $\mathrm{r}=\mathrm{r}_c$ for θ_{ij} and is a random number with zero mean and unit variance. The amplitudes σ and γ of the dissipative and random forces, respectively, and the weight function ω^D can be chosen arbitrarily, but the quantities should satisfy the following relations [15]:

$$\omega^D(\mathrm{r}_{ij})=[\omega^R(\mathrm{r}_{ij})]^2 \tag{6-1}$$

and

$$\sigma^2=2\gamma\mathrm{k}_B\mathrm{T} \tag{6-2}$$

with k_B is the Boltzmann constant. A simple choice for the weight function ω^D is given by

$$\omega^D(\mathrm{r}_{ij})=\begin{cases}(1-\mathrm{r}_{ij}/\mathrm{r}_c)^2 & \mathrm{r}<\mathrm{r}_c \\ 0 & \mathrm{r}\geq\mathrm{r}_c\end{cases} \tag{7}$$

A MODEL OF WATER AND SURFACTANT

In this study, the aggregation forms of the anionic surfactant sodium dodecyl sulfate (SDS), which is widely used in industry and science and its phase diagram is well-known [16,17], was simulated by DPD. The system simulated is composed of water beads and SDS particles. A water bead contains N_m water molecules where $N_m=3$ was taken. In this study, a new water bead including a sodium ion, which is represented by W+, was also considered because sodium ions dissociate from head groups when SDS molecules dissolve in water.

The SDS molecule is modeled as HT_4 as shown in Fig. 1. H and T represent a head group and butyl chains, respectively. Each bead of the SDS is assumed to be linearly connected by simple harmonic springs whose force is calculated by

$$\vec{\mathbf{F}}_{ij}^S = -C\vec{\mathbf{r}}_{ij} \tag{8}$$

where C is a spring constant and r_{ij} is the vector along the line connecting the center of i and j. The total force acting on the DPD particle is the combination of the spring force and the forces given in

Fig. 1. Simulation model of SDS and water bead.

Eq. (2)

$$\vec{\mathbf{f}}_i = \sum_{j\neq i}(\vec{\mathbf{F}}_{ij}^S+\vec{\mathbf{F}}_{ij}^C+\vec{\mathbf{F}}_{ij}^D+\vec{\mathbf{F}}_{ij}^R) \tag{9}$$

DETAILED DPD SIMULATION PROCEDURE

In the DPD method, the dissipative force of Eq. (4) is dependent on the particle velocity and the equation of motions are solved by a modified velocity-Verlet method [18]. This algorithm can be described as follows:

$$\mathbf{r}_i(\mathrm{t}+\Delta\mathrm{t})=\mathbf{r}(\mathrm{t})+\Delta\mathrm{t}\mathbf{v}_i(\mathrm{t})+\frac{1}{2}(\Delta\mathrm{t})^2\mathbf{f}_i(\mathrm{t}) \tag{10-1}$$

$$\tilde{\mathbf{v}}_i(\mathrm{t}+\Delta\mathrm{t})=\mathrm{t}\mathbf{v}_i(\mathrm{t})+\lambda\Delta\mathrm{t}\mathbf{f}_i(\mathrm{t}) \tag{10-2}$$

$$\mathbf{f}_i(\mathrm{t}+\Delta\mathrm{t})=\mathbf{f}_i(\mathbf{r}_i(\mathrm{t}+\Delta\mathrm{t}),\tilde{\mathbf{v}}_i(\mathrm{t}+\Delta\mathrm{t})) \tag{10-3}$$

$$\mathbf{v}_i(\mathrm{t}+\Delta\mathrm{t})=\mathbf{v}_i(\mathrm{t})+\frac{1}{2}\Delta\mathrm{t}[\mathbf{f}_i(\mathrm{t})+\mathbf{f}_i(\mathrm{t}+\Delta\mathrm{t})] \tag{10-4}$$

where ν is the intermediate velocity of particle i and λ has an arbitrary value. For $\Delta\mathrm{t}=0.06$ and $\rho=3$, $\lambda=0.65$ is the optimum value to accurately control the temperature [19]. In the simulations, the DPD particle density ρ was taken as 3 and the particle mass, cutoff distance, and temperature were chosen to be unity as follows:

$$\mathrm{m}=\mathrm{r}_c=\mathrm{k}_B\mathrm{T}=1 \tag{11}$$

To obtain the repulsion parameter for DPD particles, a relationship between the Flory-Huggins parameter χ and a_{ij}, which has been established by Groot and Warren [19], was used.

$$\mathrm{a}_{ij}=\mathrm{a}_{ii}+\frac{1}{0.231}\chi_{ij} \tag{12}$$

The interaction parameter between the identical DPD particles a_{ii} was derived from the compressibility of water at room temperature [7,19]:

$$\mathrm{a}_{ii}=\frac{(16N_m-1)}{0.2}\times\frac{\mathrm{k}_B\mathrm{T}}{\rho} \tag{13}$$

To study the effect of the interaction between DPD particles on the formation of association structures of the surfactant in aqueous solution, three cases of the combinations of the interaction parameters were considered. The FH parameters between hydrophobic beads of the same type were taken as zero. However, the FH parameters χ for the beads with repulsive interaction were taken to be positive, while for the beads with attractive interaction were taken to be negative. The FH parameters for the interaction between head (H) and tail (T) were taken as positive. For the case where three water molecules ($N_m=3$) are represented by one DPD particle, the FH parameter between the water bead and butyl chain (tail) was taken as 6.0 $\mathrm{k}_B\mathrm{T}$ [7]. Because this parameter scales linearly with bead volume, the FH parameter between head and head and head and the water bead having a sodium ion were taken as a reduced value, 2.0 $\mathrm{k}_B\mathrm{T}$ [7]. Furthermore, it was assumed that the head group has a strong affinity to water so that the FH parameter between the head and water bead having a sodium ion was taken as −2.0 $\mathrm{k}_B\mathrm{T}$. On the other hand, the FH parameter between the identical hydrophilic beads was taken as 2.0 $\mathrm{k}_B\mathrm{T}$. These sets of FH parameters and the repul-
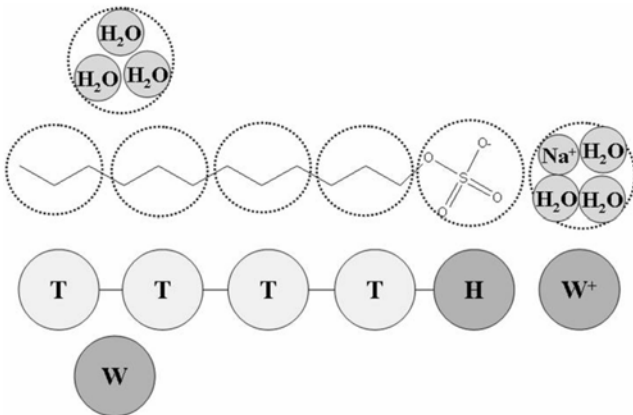
Table 1. The values of the Flory-Huggins parameters and the maximum repulsive forces between DPD particles used in DPD simulation. The unit used is k_BT

		Case 1					Case 2					Case 3			
		H	T	W$^+$	W		H	T	W$^+$	W		H	T	W$^+$	W
χ	H	2	6	-2	0	H	6	6	-6	0	H	2	3	-2	0
	T	6	0	6	6	T	6	0	6	6	T	3	0	6	6
	W$^+$	-2	6	2	0	W$^+$	-2	6	6	0	W$^+$	-2	6	2	0
	W	0	6	0	0	W	0	6	0	0	W	0	6	0	0
		H	T	W$^+$	W		H	T	W$^+$	W		H	T	W$^+$	W
a_{ij}	H	86.7	104	69.3	78	H	104	104	52	78	H	86.7	91	69.3	78
	T	104	78	104	104	T	104	78	104	104	T	91	78	104	104
	W$^+$	69.3	104	86.7	78	W$^+$	52	104	104	78	W$^+$	69.3	104	86.7	78
	W	78	104	78	78	W	78	104	78	78	W	78	104	78	78

sive parameters calculated by Eq. (12) are given in Table 1. The FH parameter $\chi_{i,j}$ may be obtained by calculation of the mixing energy of the fragments i and j [20].

In this simulation, the total number of DPD particles, N, employed was 24000 and the size of the simulation cell used was 20×20×20. Detailed simulation procedures are as follows:

(1) DPD simulation was started at the initial volume fraction of SDS, ϕ=0.15 in the aqueous solutions, at which the number of SDS molecules was 720. The initial positions of the water beads and SDS molecules were randomly distributed.

(2) After 100,000 time steps, the initial calculation was finished.

(3) After the initial run, 1.0% of SDS molecules (the number of SDS molecules is 48) were added randomly in a simulation box at each run while water beads were removed, correspondingly so that the total DPD particles density remained fixed.
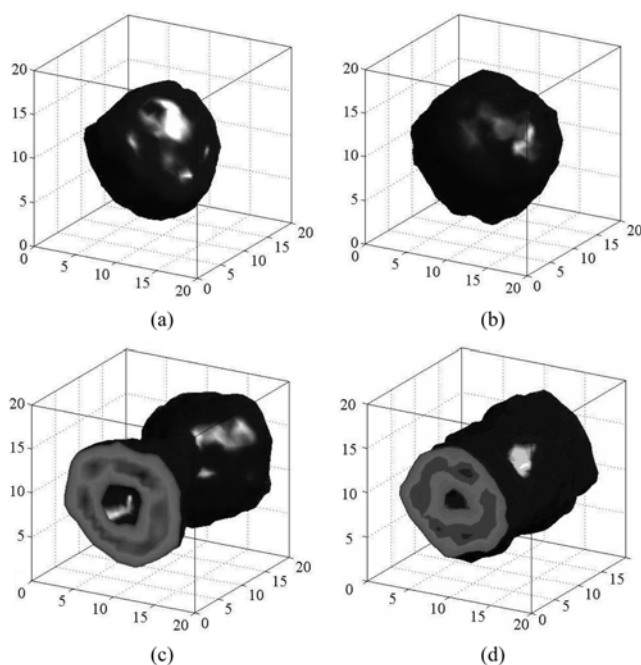
(4) After the removal and addition procedure of the DPD particles, the simulations were performed for 50,000 time steps.

The procedures of 3 and 4 were repeated until the volume fraction of SDS reached ϕ=0.3. All simulations were performed at the solution temperature of 27 °C.

RESULTS AND DISCUSSION

1. Case 1

The magnitude of FH parameters chosen for simulation in this case was discussed in Section 4. As shown in Fig. 2, the SDS surfactants at ϕ=0.15 aggregate spontaneously to form a spherical structure. With increasing SDS concentration, the spherical structure grows in its size without shape change until the concentration of SDS be-
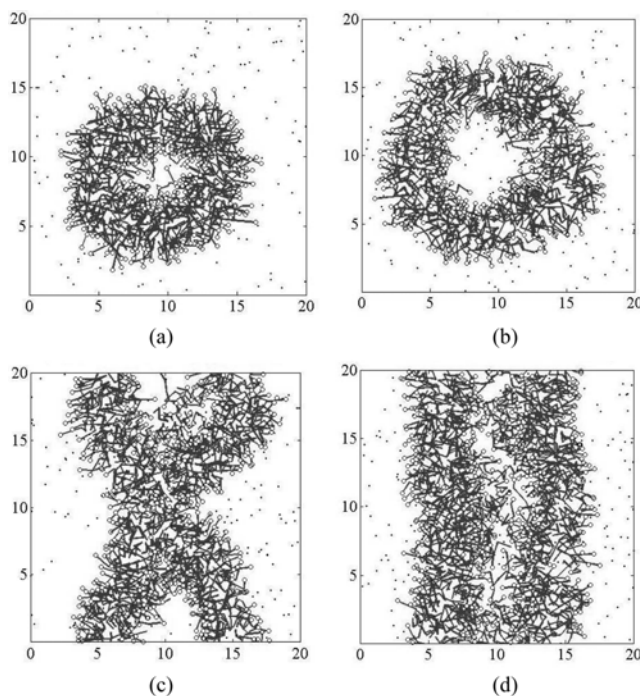

Fig. 2. Aggregation structures formed by SDS surfactant of case 1: volume fraction of SDS (a) ϕ=0.15, (b) ϕ=0.20, (c) ϕ=0.24, (d) ϕ=0.26.

Fig. 3. Slice images of Fig. 2: (a) ϕ=0.15, (b) ϕ=0.20, (c) ϕ=0.24, (d) ϕ=0.26; the head group (○), the hydrocarbon chain (—) and the water contained sodium ion (•).

comes 20% or so as shown in Fig. 2. The detailed structures of the self-assembly aggregates depending on concentration are shown in Fig. 3. The hydrophilic head groups of SDS particles are oriented to the water beads including a sodium ion, which are presented inside and outside the spherical aggregate. This structure seems like a vesicle. In fact, a typical vesicle has a multi-layer structure which encloses a water pool inside. However, the simulated structure, about 10 nm, which is the lower size limit of a micelle, is much smaller than the typical size of a vesicle.

The structural transition from spherical to cylindrical starts at volume fraction ϕ=0.24 and finishes at ϕ=0.26. At ϕ=0.24 two spherical structures join together to form a cylindrical structure as suggested by Kim and Lim [21]. Above a volume fraction of concentration ϕ=0.26 a structural change from spherical to cylindrical type (rod) occurs. These simulation results are in good agreement with the observed result, such that the transition from sphere to cylindrical type micelle occurs near at a solution temperature of 27 °C [16].

2. Case 2

The absolute magnitude of FH parameters for the repulsive interaction between H and H and W+ and W+ and for the attractive interaction between H and W+ was increased from 2 k_BT in case 1 to 6 k_BT in this case. As a consequence of this change, the interaction parameter a_{ij} between H and H and W+ and W+ increases and the interaction parameter between H and W+ decreases. As can be seen in Fig. 4, an ellipsoidal micelle rather than the spherical vesicle forms at ϕ=0.15. This indicates that a spherical vesicle forms when the value of the interaction parameter between H and W+ is comparable to the value between H and H and W+ and W+. Similar to case 1, the shape of the association structure becomes a cylindrical type at ϕ=0.22 even though the inclusion volume of water beads

having a sodium ion is very small, as shown in Fig. 4.

3. Case 3

In this case, the magnitude of FH parameters between T and T was reduced from 6 to 3, while the other FH parameters' values used in case 1 were unchanged. As shown in Fig. 5, a spherical micelle forms at ϕ=0.15. In this case, the repulsive interaction between hydrophobic T and hydrophilic H is smaller than the value in case 1, and the association structure cannot enclose water molecules. However, a structural change from spherical to cylindrical shape occurs at ϕ=0.30, which is certainly higher than the volume fraction of concentration where the structural transition occurs in case 1. Furthermore, the SDS molecules in the association structure formed at ϕ=0.30 are randomly distributed.

Finally, it is noted that the simulation results depend strongly on the initial condition of the volume fraction. For example, the association structure simulated with ϕ=0.30, as shown in Fig. 6, is quite different from the structure obtained at ϕ=0.30 by increasing ϕ from 0.15 to 0.30. The association structure shown in Fig. 6(b) is very similar to that obtained by Wang et al. [22] with the DPD simulation. We also note that the periodic boundary condition adopted in this DPD simulation allows a hexagonal structure for the aggregates, which is in good agreement with the observed results [16]. However, a systematic study to estimate proper magnitude of interaction parameters between DPD molecules is needed.

Fig. 7 gives a phase diagram of the SDS-water, which is drawn from literature data [23] below 25 °C and our results of simulation at 27 °C. Our calculation was done in the micellar region where the temperature dependence of the phase behavior is weak. In fact, the transition from sphere micelle to cylindrical micelle occurs near ϕ=0.20 at the solution temperature of 70 °C [16]. This figure shows
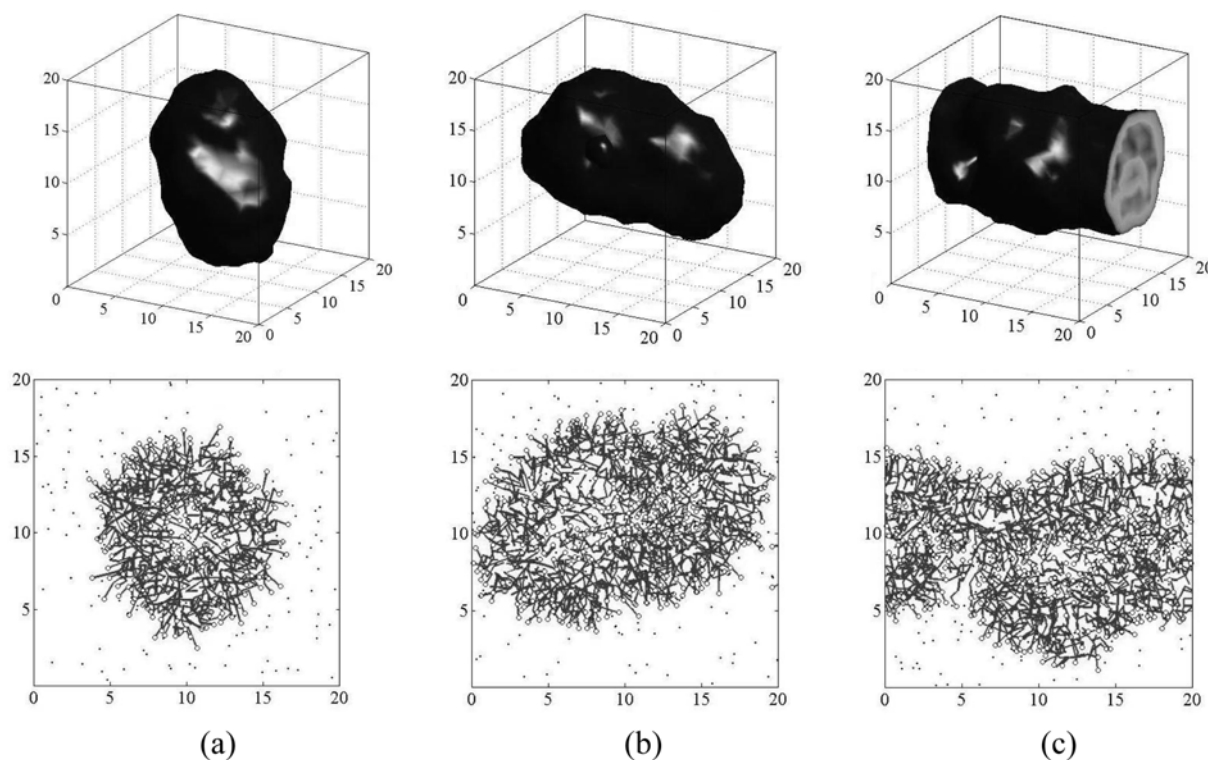

Fig. 4. Mesoscopic structures of case 2: volume fraction of SDS (a) ϕ=0.15, (b) ϕ=0.20, (c) ϕ=0.22.
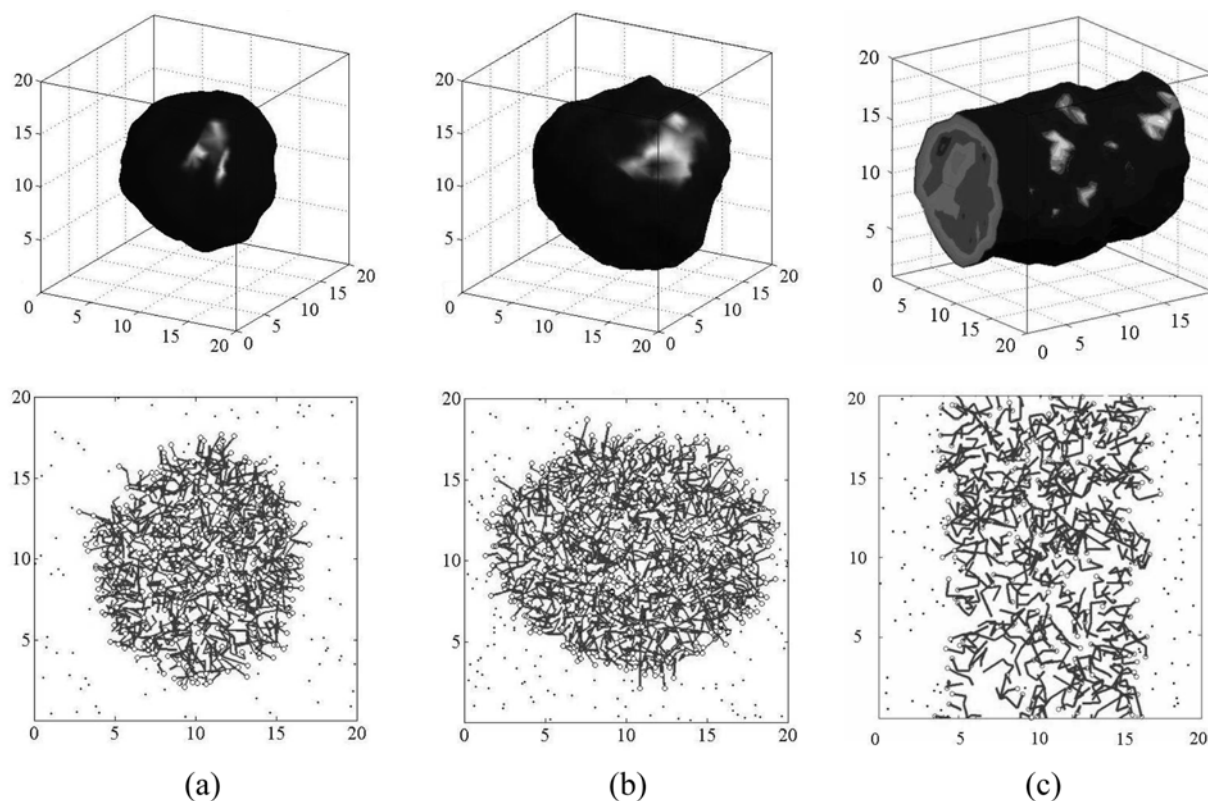
Fig. 5. Mesoscopic structures of case 3: volume fraction of SDS (a) ϕ=0.15, (b) ϕ=0.24, (c) ϕ=0.30.
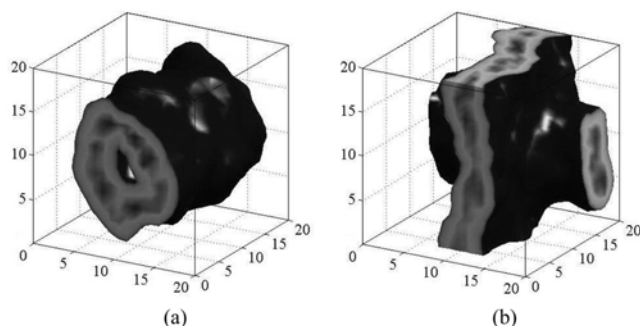

Fig. 6. The mesoscopic structures at ϕ=0.30: (a) is obtained by increasing from 15% to 30%, (b) is obtained at the initial volume fraction ϕ=0.30.

clearly how the phase transition of the SDS-water shifts with the change in the interaction parameter.

CONCLUSION

The structural change of the association structure for the anionic surfactant SDS was simulated by the DPD method, and the results were compared with the observed findings. The proper structural change of the association structure depending on the volume fraction of SDS concentration in aqueous solution was obtained with appropriate values for the interaction parameters between DPD particles. That is, a spherical structure forms at ϕ=0.15, structural change from a spherical to cylindrical one occurs at ϕ=0.26, and a hexagonal structure appears at ϕ=0.30, where ϕ is the volume fraction of
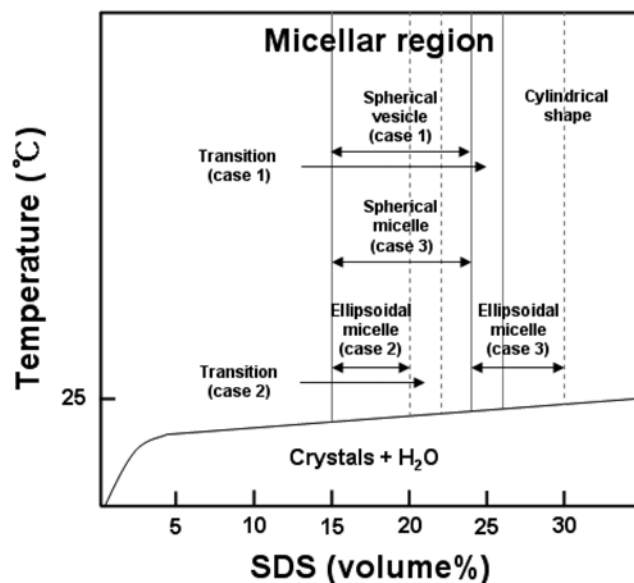

Fig. 7. Phase diagram of SDS-water system in micellar region. The phase behavior above 25 °C indicates the phase state and transition and 27 °C.

surfactant SDS (sodium dodecyl sulfate), and they are in good agreement with observation. Furthermore, DPD simulation yielded a process of structural transition from spherical to cylindrical shape. It was also found that the change in the value of the interaction parameters affects the internal structure of the association structures, and the concentration where phase change occurs, for example, a vesi-

cle type micelle can be formed provided that the interaction between hydrophilic and hydrophobic beads is greater than a certain value.

NOMENCLATURE

a_{ij} : the maximum repulsion between particle i and j
$\overset{\subset}{\supset}$: spring constant
$\vec{f}_i$: the force acting on particle i
$\vec{F}_{ij}$: the force between particle i and j
k_B : Boltzmann constant
N : total number of DPD particles
N_m : the number of water molecules in a DPD particle
r : the position vector
r_c : cut-off distance
T : temperature
v : the velocity
ṽ : intermediate velocity

Greek Letters
χ : Flory-Huggins parameter
ϕ : volume fraction of surfactant
γ : amplitude
λ : velocity-Verlet constant
θ : random number
ρ : particle density
σ : noise amplitude
ω : weight function

REFERENCES

1. E. Ryjkina, H. Kuhn, H. Rehage, F. Muller and J. Peggau, *J., Angew. Chem. Int. Ed.*, **41**, 983 (2002).

2. E. W. Kaler, A. K. Murthy, B. E. Rodriguez and J. A. N. Zasadzinski, *Science*, **245**, 1371 (1989).
3. R. Goetz, G. Gompper and R. Lipowsky, *Phys. Rev. Lett.*, **82**, 221 (1999).
4. E. Lindalh and O. Edholm, *Biophys. J.*, **79**, 426 (2000).
5. P. J. Hoogerbrugge and J. M. V. A. Koelman, *Europhys. Lett.*, **19**, 155 (1992).
6. J. M. V. A. Koelman and P. J. Hoogerbrugge, *Europhys. Lett.*, **21**, 363 (1993).
7. R. D. Groot and K. L. Rabone, *Biophys. J.*, **81**, 725 (2001).
8. S. Yamamoto and S. Hyodo, *J. Chem. Phys.*, **118**, 7937 (2003).
9. Y. Kong, C. W. Manke, W. G. Madden and A. G. Schlijper, *Int. J. Thermodynamics*, **15**, 1093 (1994).
10. A. G. Schlijper, P. J. Hoogerbrugge and C. W. Manke, *J. Rheology*, **39**, 567 (1995).
11. A. G. Schlijper, C. W. Manke, W. G. Madden and Y. Kong, *Int. J. Mod. Phys. C*, **8**, 919 (1997).
12. E. S. Boek, P. V. Coveney, H. N. W. Lekkerkerker and P. van der Schoot, *Phys. Rev. E*, **55**, 3124 (1997).
13. K. E. Novik and P. V. Covency, *Int. J. Mod. Phys. C*, **8**, 909 (1997).
14. F. Xijun, N. Phan-Thien, N. T. Yong, W. Xuhong and X. Diao, in Microfluidics and BioMEMS Applications, E. H. Tay ed. Kluwer Academic Publishers, Boston (2002).
15. P. Espanol and P. B. Warren, *Europhys. Lett.*, **30**, 191 (1995).
16. F. R-Husson and V. Luzzati, *J. Phys. Chem.*, **68**, 3504 (1964).
17. P. Kékicheff, *J. Colloid Interface Sci.*, **131**, 112 (1989).
18. M. P. Allen and D. J. Tildensley, *Computer simulation of liquids*, Oxford, Clarendon (1987).
19. R. D. Groot and P. B. Warren, *J. Chem. Phys.*, **107**, 4423 (1997).
20. E. Ryjkina, H. Kuhn, H. Rehage, F. Mueller and J. Peggau, *Angew. Chem. Int. Ed.*, **41**, 983 (2002).
21. H. U. Kim and K. H. Lim, *Bull. Korean Chem. Soc.*, **25**, 382 (2004).
22. B. Wang, Y. Shang, H. Liu and Y. Hu, *Fluid Phase Equilibia*, **228-229**, 109 (2005).
23. P. Kekicheff, C. Grabielle-Madelmont and M. Olivon, *J. Colloid Interface Sci.*, **131**, 112 (1989).