Mesoscopic Simulation of Aggregates in Surfactant/Oil/Water Systems

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The aggregates in sodium dedecylsulphate (SDS)/dimethylbenzene/water systems have been investigated using dissipative particles dynamic (DPD) simulation method. Through analyzing three-dimensional structures of aggregates, three simulated results are found. One is the phase separation, which is clearly observed by water density and the aggregates in the simulated cell; another is the water morphology in reverse micelle, which can be found through the isodensity slice of water including bound water, trapped water and bulky water; the third is about the water/oil interface, *i.e.*, ionic surfactant molecules, SDS, prefer to exist in the interface between water and oil phase at the low concentration.

Introduction

One important application of surfactants is that their aqueous solutions are able to dissolve substantial amounts of compounds which have very low solubility in water. Similarly, surfactants can also greatly increase the solubility of water and other polar compounds in hydrocarbons and other liquids of low polarity.[1] Some experimental methods[2-7] and computer simulation[8] have been devoted to the spreading of surfactant/water/oil system. Especially for reverse micelle or w/o microemulsion of these ternary systems, different experimental techniques[9-14] and molecular dynamics (MD) methods[15] were concentrated on investigating the water morphology in these systems. Moreover, for vapor/liquid interface of three-dimensional Lennard-Jones fluids, both MD and Monte Carlo (MC) methods[16-18] have been reported, but few simulations have considered the liquid/liquid interface, because it is difficult to investigate the liquid/liquid interface of Lennard-Jones fluids in three components systems containing several thousands particles using MD or MC methods.

In this paper, we study water morphology and liquid/liquid interfacial properties in surfactant/oil/water system using mesoscopic simulation method. The different surfactant systems through dissipative particles dynamics (DPD) simula-

tion have been investigated.[19,20] This method is an effective coarse-grained molecular dynamics simulation method for simulating complex fluids, such as surfactant solutions and polymer melts. In this technique, surfactant molecules are described by particles that act as centers of mass, and each particle represents a large number of atoms. The aggregation properties of different systems can be investigated using the mesoscopic simulation method.

Simulation model

DPD technique is a mesoscopic simulation method for complex fluids. A modified velocity-Verlet algorithm[21] is used to integrate the Newton's equations of motion. The position r_i and momentum p_i of particles at the next position can be obtained using the following equations:[22,23]

$$dr_i = \left(\frac{p_i}{m} \right) dt \tag{1}$$

$$dp_i = \sum_j \Omega_{ij} \hat{r}_{ij} dt \tag{2}$$

$$\Omega_{ij} = w(r_{ij}) [\alpha + \sigma\theta_{ij} - \frac{\sigma^2}{2kT} w(r_{ij}) \hat{r}_{ij} \nu_{ij}] \tag{3}$$

where w is r-dependent weight function vanishing for the distance r between the particles and $w(r) = (1 - r)$ for $r < 1$ and $w(r) = 0$ for $r > 1$. Three forces are conservative force, dissipative force and random force in the square brackets of the equation (3). The detailed methods have been depicted in the former papers.[19,20] In the DPD method, two properties must be considered, one is the liquid compressibility, and the other is the mutual solubility. These parameters can be used to show the properties of surfactant systems.

For the present application, we used the simplest possible model, *i.e.*, the surfactant molecules are represented by two beads tied together by a harmonic spring; the water

molecule and the oil molecule are represented by one bead respectively. The interaction parameters among the head, the tail, water and oil can be obtained via Blend program in Cerius^2 package. The system that we selected includes ionic surfactant, SDS, water and oil, dimethylbenzene.

In the simulation, the calculated interaction parameters are listed in the following table in the matrix form (Table 1). When these interaction parameters are used in DPD simulation, the mesoscopic properties of surfactant/oil/water system can be obtained, such as the micelle shape, the density distribution of water in the micelle, and so on.

All computational works were performed on the SGI workstation, and the software programs Cerius^2 and DPD from MSI (Molecular Simulations Inc.), San Diego. The simulations comprised of a total of 3000 beads including surfactant, water and oil beads in a cubic cell of size $10 \times 10 \times 10R_C^3$, where R_C is a cut-off radius. The spring constant between different beads in the surfactant molecule is equal to 4 according to the paper reported.[24] The DPD times are usually equal to

10000 in order to obtain the steady and balanceable results.

Results and discussion

Microphase separation using the isodensity slice of water

Fig. 1 shows the process of microphase separation of the simulated system (including 5% surfactant, 20% water and 75% oil) using the isodensity slice of water. The different colors represent the different density of water in the simulated cell. The black means high-density water, while the blank is low-density. For the black region, the water density is above 0.97 DPD units, which indicates the distribution of bulky water molecules, while the blank region represents the aggregates of the oil molecules. Obviously, at the beginning of simulation (Fig. 1a), water molecules as small liquid drops are dispersed in the surfactant/oil/water system, and the distribution of oil and water is well proportioned in the simulated cell. With the increase of simulated time, the flocculation

Table 1 The interaction parameters in DPD simulation[a]

		w	- h	t	o		w	h	t	o
	w	25.00	25.33	61.12	80.85		0.000	0.100	11.047	17.079
$a_{ij} =$	h	25.33	25.11	53.57	71.16	$\chi_{ij} =$	0.100	0.033	8.737	14.116
	t	61.12	53.57	24.90	43.26		11.047	8.737	-0.030	5.585
	o	80.85	71.16	43.26	23.98		17.079	14.116	5.585	-0.313

[a] w represents water, h, the head of surfactant, t, the tail of surfactant and o, oil.
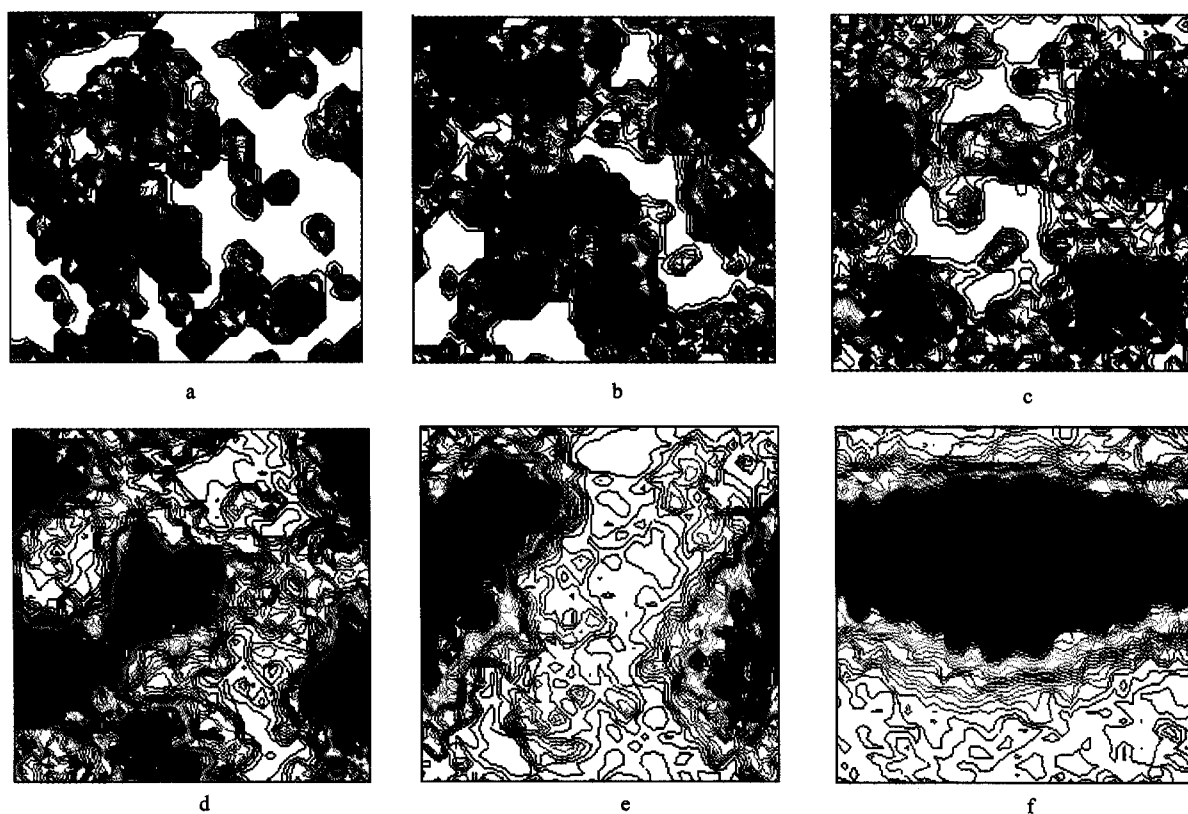

Fig. 1 Microphase separation in surfactant/oil/water system at different simulated steps. From a to f, the aggregates after 100, 200, 500, 1000, 2000, 10000 simulated steps respectively.

and aggregation of aqueous drops occur followed by the collision among different drops, then the small liquid drops are replaced by bigger drops (Fig. 1b, 1c and 1d). At last, the phase separation is finally observed (Fig. 1e) in ternary system, and the oil/water separated system is formed (Fig. 1f). From Fig. 1, one can see that the changes of water density in the simulation cell can show the dynamic process in the surfactant/water/oil system. Firstly, water molecules are in existence as little liquid-drops (from Fig. 1a to 1c); then under the surfactant interaction, dispersive liquid-drops begin to aggregate; and at the final equilibrium (Fig. 1f), a whole oil/water interface can be shown by the water density.

The above figures are shown using the water density slice. The final state of the system can also be shown using the coarse grain model in the DPD method, and the interfacial properties between water and oil phases can easily be observed. As we assumed in Fig. 2, surfactant molecules distribute mostly in the interface between oil and water at the lower concentration of surfactant, not in the oil or water phase. Since the apolar oil molecule, dimethylbenzene, is used in the simulated system, the solubility between oil and water is very low. Thus, only little water molecules can dissolve in the oil phase in the presence of surfactant molecules. In the other words, surfactant molecules always exist in the interface between water and oil phase especially at the low surfactant concentration.

Fig. 2 The final state of system after 10000 simulated steps (5% Surfactant, 20% water and 75% oil. Oil molecules removed, and the long rod represents surfactant molecule).

Different systems have different aggregates, and different microphase separation of these systems can be shown using DPD method. Other techniques, such as TEM, can only be used to see the final states, while DPD simulation technique can be used to investigate the continuous dynamic process of aggregated morphology at the mesoscopic level.

Distribution of water in reverse micelles

According to the different ratio of water and oil, different types of microemulsions (w/o or o/w) or micelles are found in surfactant/oil/water system. The water solubilized in reverse micelles is divided into three different types, such as

bound water, trapped water and bulky water. In the last several years, some molecular simulation methods are used to research the water structures in surfactant/oil/water system too,[15] but mesoscopic simulation technique is not found to investigate the water morphology in micelles. Because the interaction parameters used in the DPD simulation depend on the calculations about molecular structures at the atomic level using the Blend program, in which several types of energies including the electrostatic, hydrogen bond, non-bond and van der Waals interactions are present, which indicates that the DPD parameters can represent the interaction between different molecules at the atomic level. When these DPD parameters are used, some mesoscopic properties can be obtained. In Fig. 3a, we can clearly observe the reverse micelle aggregate, in which some beads representing water molecules are surrounded by surfactant molecules. Fig. 3b is the isodensity slice of water in the reverse micelle. There are bulky water in the center of micelle, i.e., the red section in the isodensity slice (A), trapped water during the palisade of micelle, i.e., the green section (C) in Fig. 3b, and bound water around polar beads of surfactant molecules, i.e., the yellow section (B) which is between the red and green sections. In Fig. 3b, we can clearly found the middle section between bulky water and trapped water. At the same time, water aggregates can easily be understood that trapped water locates the hydrophobic section among surfactant molecules; bound water is around the polar beads of surfactant molecules; and bulky water is in the center of micelles. From Fig. 3, it can be concluded that the water isodensity slice can be used to research the morphology of water in reverse micelles.
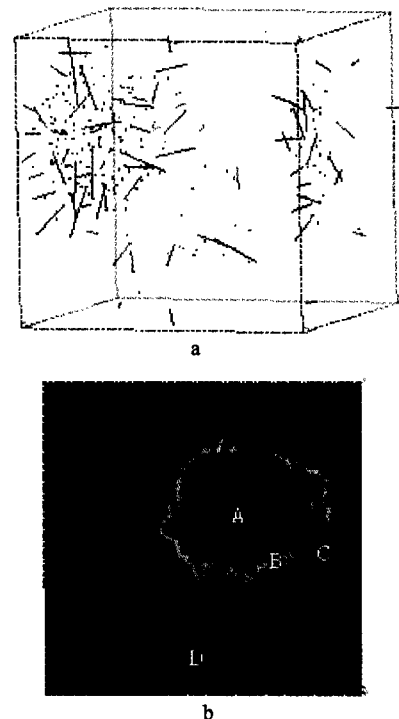

a

b

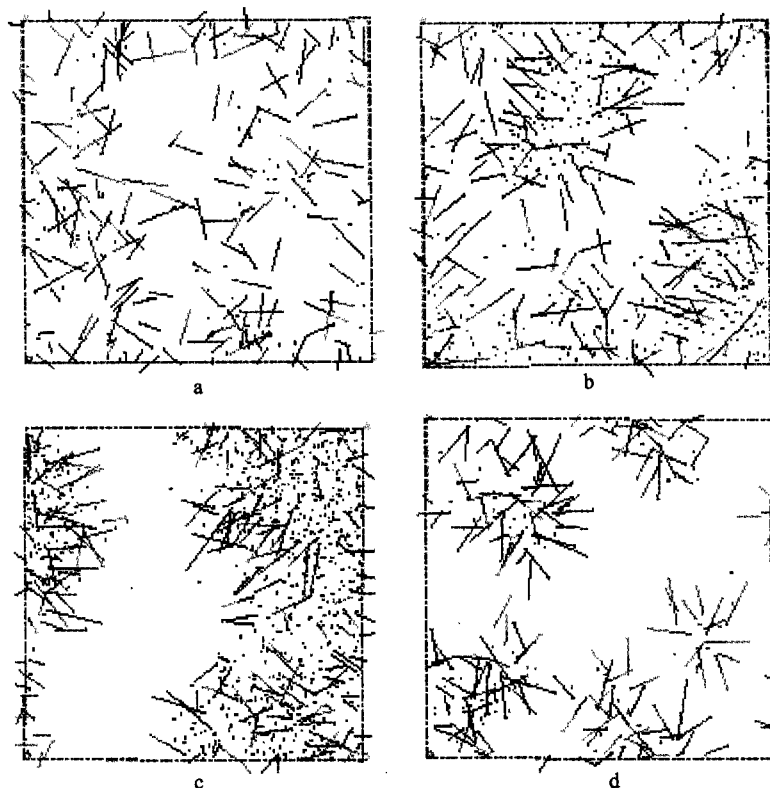**Fig. 3** Distribution of water in reverse micelles.

Fig. 4 Effect of water content on aggregates in simulated system (Oil molecules removed in Fig. 4a and Fig. 4b, water molecules removed in Fig. 4c and Fig. 4d). For the systems, the concentration of surfactant is 10%, the system a includes 86% oil and 4% water; b, 76% oil and 14% water; c, 45% oil and 45% water; d, 4% oil and 86% water.

Effect of water content on the aggregates

Since the interaction parameters between the head and water are smaller than those between the tail and water (see Table 1), this means that the head of ionic surfactant molecule SDS is easier to interact with water than with oil, and it also indicates that the interaction between water and surfactant molecules may easily form spherical micelles in water phase when the oil concentration is low. Fig. 4 shows the aggregates in surfactant/oil/water systems at different water contents. In the different systems, the fixed concentration of surfactant is equal to 10%, while the total concentration of the water and oil is 90%, and the water and oil concentration are changed from 4% to 86% in the simulated systems, respectively. The simulated results show that no micelles are observed in the simulated system at lower concentration of water (below 4%), while water exists as small liquid drops, and surfactant molecules as single-dispersed forms attach water molecules in the oil phase (Fig. 4a). With the increase of water content, reverse micelles begin to form and solubilized water in these reverse micelles is found (Fig. 4b). Then a clear oil/water interface appears, and surfactant molecules which are represented by rod-like line arrange at the interface (Fig. 4c); when oil contents are low in the simulated system, normal micelles are found to solubilize oil phase(Fig. 4d). From Fig. 4, we can get the following information, surfactant molecules are single-dispersed in the

system at the lower concentration of water (Fig. 4a), while surfactant molecules are in existence as normal micelles at the lower concentration of oil (Fig. 4d). From Fig. 3b to Fig. 4d, one can see that hydrophilic heads of surfactant molecule locate in the center of reverse micelles at the beginning; then arrange at oil/water interface, at high water concentration, lie in the outside of normal micelles. All the changing processes of aggregates in oil/water/surfactant system can be found by the coarse grain model using DPD simulation method, and these dynamic processes can help to understand the properties of surfactant/oil/water system.

Conclusion

DPD simulation method can be used to investigate the surfactant/oil/water system. The dynamic change of microphase separation can be found by DPD method, while other techniques such as TEM photograph can provide the final states. A very clear isodensity slice of water can also distinguish three morphology of water including bound water, trapped water and bulky water in reverse micelle, and the interfacial properties between water and oil can be shown using the coarse grain cell. These simulated phenomena show that DPD simulation method can be considered as adjuncts to experiments and provide otherwise inaccessible mesoscopic information at the mesoscopic level.

Acknowledgement

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