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Dependence of a self-assembled amphiphile structure on the interaction between hydrophilic groups

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Abstract. In a previous study (2005 *Comput. Phys. Commun.* **169**, 139–143), we clarified the dependence of the phase structure on the hydrophilicity of an amphiphilic molecule by varying the interaction potential between the hydrophilic molecule and water (a_{AW}) in a dissipative particle dynamics (DPD) simulation using the Jury model. In the present paper, we perform another DPD simulation using the previous model to investigate the dependence of the interaction potential between adjacent hydrophilic groups on the phase structure. By varying the coefficient of the interaction potential between adjacent hydrophilic groups a_{AA} ($a_{\mathrm{AA}} = 15, 25, 40$ and 250) at a dimensionless temperature of $T = 0.5$ and a concentration of amphiphilic molecules in water of $\phi = 50\%$, hexagonal ($a_{\mathrm{AA}} = 14, 25, 40$) and micellar ($a_{\mathrm{AA}} = 250$) phases were observed. In comparison with the previous results, the dependence of the A–B dimer's shape on a_{AA} was determined to be weaker than that on a_{AW}. Therefore, it is concluded that the solvent water W plays an important role in aggregation of the A–B dimers.

1. Introduction

Amphiphilic molecules have many degrees of freedom in the structures they adopt. However, when the temperature and concentration of an aqueous solution of the amphiphilic molecules are fixed, the molecules are restricted to a certain molecular shape and aggregate to form a variety of mesoscopic structures, for example, micellar, lamellar and hexagonal phases.

In previous papers [1, 2], we have investigated the amphiphilic molecule hexaethylene glycol dodecyl ether ($C_{12}E_6$), a popular surfactant in water that forms a variety of self-assembled structures. The phase structure of $C_{12}E_6$ was investigated by Mitchell [3] in 1983. In our work, we clarified [2] the dependence of the phase structure on hydrophilicity by varying the interaction potential (a_{AW}) between the hydrophilic molecules and water in a dissipative particle dynamics (DPD) simulation using the Jury model [4].

In the present paper, to determine the relative dominance of different microscopic interaction potentials in determining the mesoscopic phase structure, we investigated the dependence of the phase structure on the interaction potential between adjacent hydrophilic groups a_{AA}. The details of the DPD simulation algorithm and models cannot be included due to lack of space but are the same as reported previously [2] with the exception of the interaction potentials a_{AW} and a_{AA}. The differences with the previous simulation are described in Sec. 2.

Table 1. Table of coefficients a_{ij} showing dependence on particle type for particles i and j, where W is a water particle, A is a hydrophilic particle and B is a hydrophobic particle. By varying the coefficient a_{AA} between adjacent particles A and A, $a_{\mathrm{AA}} = 15, 25, 40$ and 250, the dependence of the phase structure on the A–A interaction potential can be clarified.

	W	A	B
W	25	0	50
A	0	a_{AA}	30
B	50	30	25

2. Simulation method

We used the same DPD model and algorithm [4, 5] as described previously [1, 2], with a modification of the conservative force $\mathbf{F}_{ij}^{\mathrm{C}}$ between particles i and j, given in the present paper by

$$\mathbf{F}_{ij}^{\mathrm{C}} \equiv \begin{cases} a_{ij}(1 - r_{ij})\mathbf{n}_{ij} & \text{if } r_{ij} < 1, \\ 0 & \text{if } r_{ij} \geqslant 1, \end{cases} \tag{2.1}$$

where $\mathbf{n}_{ij} \equiv (\mathbf{r}_i - \mathbf{r}_j)/|\mathbf{r}_i - \mathbf{r}_j|$, and $\mathbf{r}_i$ is a position vector for particle i. Coefficients a_{ij} in (2.1) denote the coupling constants between particles i and j. The numerical values of a_{ij} are given by Table 1.

3. Simulation results and discussion

To demonstrate the dependence of the mesoscopic phase structure on the interaction potential between adjacent hydrophilic groups, we varied the A–A interaction potential coefficient such that $a_{\mathrm{AA}} = 15, 25, 40$ and 250.

The aggregation structure for each value of a_{AA} is shown in Fig. 1. To quantitatively classify the phase structure, we also plot the radial distribution function of the solute particles for each a_{AA} in Fig. 2. The figures show that hexagonal ($a_{\mathrm{AA}} = 15, 25, 40$) and micellar ($a_{\mathrm{AA}} = 250$) phases are formed depending on the coefficient a_{AA} of the A–A interaction potential.

The distance R between a hydrophilic group in an A–B dimer and another group in the nearest A–B dimer (Fig. 3) is shown as the first peak $R(a_{\mathrm{AA}})$ of $g_{\mathrm{AA}}(r)$ in Fig. 2(a). On the other hand, the intramolecular distance between A and B, that is l in Fig. 3, is shown as the first peak in Fig. 2(b). We plotted the dependence of the distance R and the length l on the interaction potential a_{AA} in Fig. 4(a). Figure 4(a) indicates that the dependence of the length $l(a_{\mathrm{AA}})$ on a_{AA} is weaker than that for R. We also plotted the dependence of $1/(R^2 l)$ on the interaction potential a_{AA} in Fig. 4(b).

Here we consider the packing parameter introduced by Israelachvili [6, 7] (see also [2]). According to this description, the hexagonal and micellar phases correspond to $\frac{1}{3} \leqslant p \leqslant \frac{1}{2}$ and $p \leqslant \frac{1}{3}$, respectively. The packing parameter p is considered to be proportional to $1/(R^2 l)$. From Fig. 4(b), $p \propto 1/(R^2 l)$ decreases as a_{AA} increases. Therefore, it is found that A–B dimers form cylinders for small a_{AA} values, and that A–B dimers modify their shape from cylinders to cones by increasing the distance between the neighboring head groups as a_{AA} increases.

Finally, we compares the present results with our previous work [2], which investigated the dependence of the phase structure on a_{AW}. In that previous work, we showed that the A–B dimer modifies its shape with changing hydrophilicity a_{AW}. It is intuitively expected that the shape of the A–B dimer would depend more strongly on the parameter a_{AA} than the parameter a_{AW}, because a_{AA} affects the distance

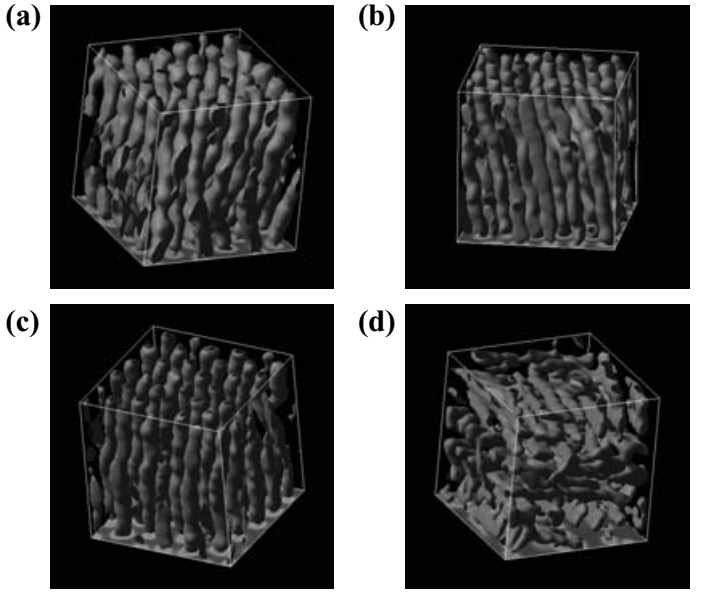

Figure 1. Structures formed for each potential coefficient, where a_{AA} is equal to (a) 15, (b) 25, (c) 40 and (d) 250. We set $T = 0.5$ and $\phi = 50\%$ during simulation.

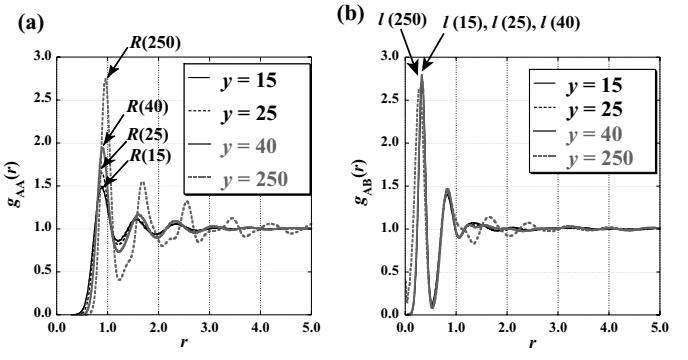

Figure 2. Radial distribution functions for the solute particles versus distance between the two particles r for $a_{\mathrm{AA}} = 15, 25, 40$ and 250. (a) The A–A radial distribution function $g_{\mathrm{AA}}(r)$. The first peak $R(a_{\mathrm{AA}})$ of each curve corresponds to the A–A distance between two adjacent A–B dimers. $R(15) = 0.889, R(25) = 0.889, R(40) = 0.904, R(250) = 0.963$. (b) The A–B radial distribution function $g_{\mathrm{AB}}(r)$. The first peaks correspond to the length of the A–B dimer l in Fig. 3. $l(15) = 0.326, l(25) = 0.326, l(40) = 0.326, l(250) = 0.296$.

between the hydrophilic groups more directly than a_{AW}. However, in contrast to our expectation, the present simulation results show that the dependence of the A–B dimer's shape on a_{AA} is weaker than that on a_{AW}. Based on this result, we conclude that the solvent water W plays an important role in determining the phase structure of the A–B dimers in aggregation.

4. Conclusion

We have demonstrated the dependence of the A–B dimer's aggregated structure in solvent water W by varying the A–A interaction potential a_{AA} in a dissipative

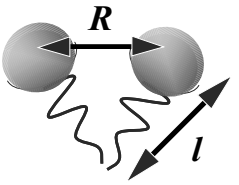

Figure 3. Schematic diagram of two adjacent molecules. A gray ball and a twisting black line are used to denote the hydrophilic and hydrophobic parts, respectively, of an amphiphilic molecule. The parameter R is the distance between the hydrophilic groups, and l is the 'maximum effective length' of the hydrophobic tail.

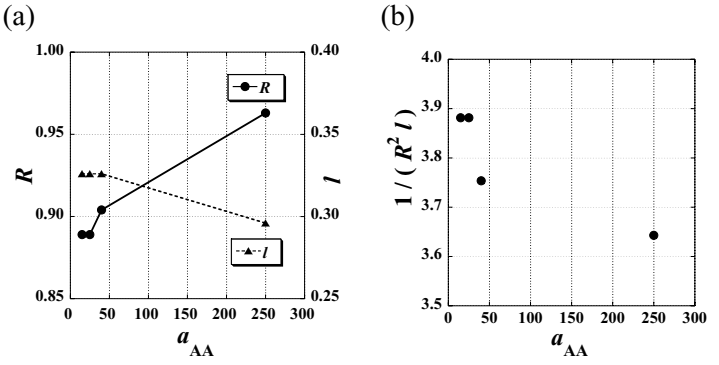

Figure 4. Shape parameters of two adjacent molecules versus the A–A interaction potential coefficient a_{AA}. (a) The A–A distance between two adjacent A–B dimers R and the length of the hydrophobic tail l are shown. (b) The inverse of $R^2 l$, which is proportional to the packing parameter p, is plotted.

particle dynamics simulation. The present simulation and the previous results [2] show that the a_{AA}-dependence of the A–B dimer's shape is weaker than the a_{AW}-dependence. Therefore, it is concluded that the solvent water W plays an important role in forming the phase structure of the A–B dimers in aggregation.

Acknowledgments

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