

MesoDyn Simulation Study on Phase Diagram of Aerosol OT/isooctane/water System

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Abstract: A simple model, *i.e.* sodium di(2-ethylhexyl) sulfosuccinate (AOT) represented by one-head and two-tail beads tied together by a harmonic spring and water or isooctane by one bead, was put forward *via* Dissipative Particles Dynamics (DPD) simulation method. Using the changes of interfacial tension between water and oil phase, a ternary phase diagram of AOT/water/isooctane system was drawn. From the simulation, one conclusion is shown that DPD simulation can be considered as an adjunct to experiments.

Keywords: Dissipative particles dynamics, interfacial tension, phase diagram, mesodyn simulation.

There is a growing interest in the study of surfactant self-assemble in oil/water/surfactant system because of their applications not only in traditional colloid chemistry but in analytical, synthetic, and medicinal chemistry as well^{1,2}. In these systems, one of the most commonly studied surfactants which can form reverse micelles is sodium bis(2-ethylhexyl) sulfosuccinate, *i.e.* Aerosol OT (AOT)³. The properties of the AOT reverse micelles have been discussed by some experimental methods⁴⁻⁷ including IR, NMR, light scattering, and so on. These experimental results enhance the understanding for the two-tail surfactant. At the same time, some molecular simulation methods have also gained a growing interest about reverse micelle in recent years⁸⁻¹⁰.

Dissipative Particle Dynamics (DPD) simulation method is an effective MesoDyn (Mesoscopic Dynamic) based on solving Newton's motion equation with Verlet algorithm¹¹. In this technique surfactant molecules are described by beads that act as centers of mass, and a series of beads are connected through harmonic springs. Using different parameters representing the liquid compressibility and mutual solubility, real surfactants molecules can be introduced into DPD model. In the model, the AOT molecule is represented by three beads, which divided into two tails and one head bead tied together by a harmonic spring. Using the molecular simulation, the interfacial tension between water and oil can be calculated. The phase diagram of water/oil/AOT system can be obtained by the changes of the interfacial tension.

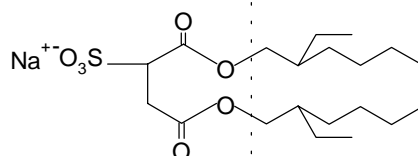
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Results and Discussions

Calculation of the interaction parameter

For the AOT surfactant structure, it is difficult to distinguish hydrophobic tails from a hydrophilic domain, because the COO ester groups (referred to as the “elbow” regions between the polar head and apolar tails) play an important role in the interaction with water molecules at the origins of the tails. In this letter, in term of our calculations, the $-\text{SO}_3\text{Na}$ group and the nearby $-\text{COO}-$ ester groups are considered as the hydrophilic group. In **Figure 1**, the structures on the left of the dashed line are selected as the hydrophilic group, in which we use the hydrogen atoms instead of the tails. Accordingly, the leavings, *i.e.* the structures on the right of the dashed line, are selected as the hydrophobic tails using the hydrogen atom instead of the head.

Figure 1 The structure of hydrophilic head and hydrophobic tails of AOT



When the head, the tail, isooctane and water are considered as the simulated objects, the interaction parameter, *i.e.* the Flory-Huggins parameter χ , between two simulated objects can be calculated using the computer simulation. And the parameters can be translated into the DPD interaction parameters depending on the calculation¹². These parameters are listed in the following **Table 1**.

Table 1 The interaction parameter among the molecules

		w	h	t	o			w	h	t	o
$a_{ij} =$	w	25.000	27.708	47.430	42.535	$\chi_{ij} =$	w	0.0001	0.8281	6.8592	5.3624
	h	27.708	24.744	31.288	27.622		h	0.8281	-0.0782	1.9047	0.8019
	t	47.430	31.288	25.675	28.997		t	6.8592	1.9047	0.2064	1.2222
	o	42.535	27.622	28.997	23.725		o	5.3624	0.8019	1.2222	-0.3899

Note: h represents the head group, t the tail group, w water molecule, and o isooctane.

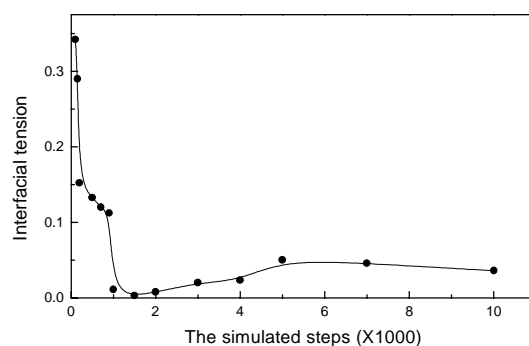
Dynamic interfacial tension in the process of phase separation

When these DPD parameters are used in the simulation, the interfacial tension between oil and water interface in isooctane/water/AOT system can be calculated using the Groot's result¹¹.

In **Figure 2**, the change of interfacial tension with the increase of simulated steps shows the change process of aggregates in the ternary system. For the fixed-concentration water/oil/surfactant system, the three components are dispersed in the solution at the beginning of simulation, so the value of interfacial tension is high. When small aggregates like water or oil drops begin to occur, surfactant molecules may arrange at the interface between small oil and water drops. This means that the interfacial tension decreases. Some bigger water or oil drops begin to form due to the collision

between small drops with the increase of simulated times. At last, interfacial tension reaches the lowest as soon as two incompatible discontinuous phases separate in the system. **Figure 2** also shows that the simulated system has already gotten equilibration state after 5000 steps, and additional simulated time does not affect the equilibration result. In order to average out all the thermal fluctuations in the interfacial region, the values of interfacial tension are calculated at 10000 simulated steps.

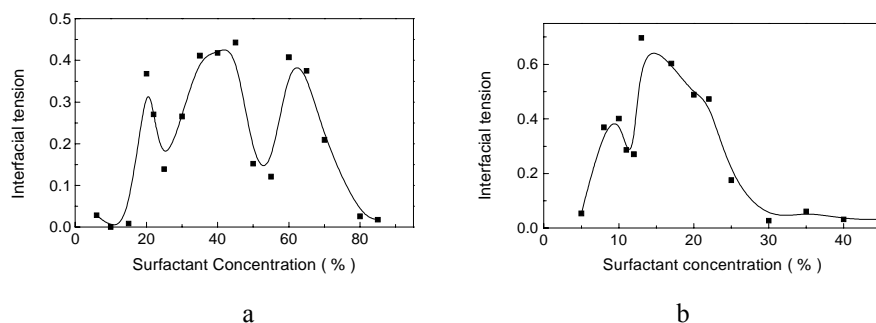
Figure 2 Simulated times dependence of interfacial tension for ternary system



Making phase diagram using the interfacial tension

In **Figure 3a**, three peaks are found in the curve of interfacial tension *via* surfactant concentration. It indicates that three phase transitions occur with the increase of the AOT concentration and three points are pointed out in the phase diagram of water/AOT/isooctane system at the 5% concentration of isooctane. Similar to this, it can be seen that two-phase transitions in the systems occur (see **Figure 3b**, at the 50% concentration of isooctane). Using this method, if many systems of fixed isooctane concentrations are provided, a whole ternary phase diagram can be drawn through the curves of the interfacial tension, as shown in **Figure 4**.

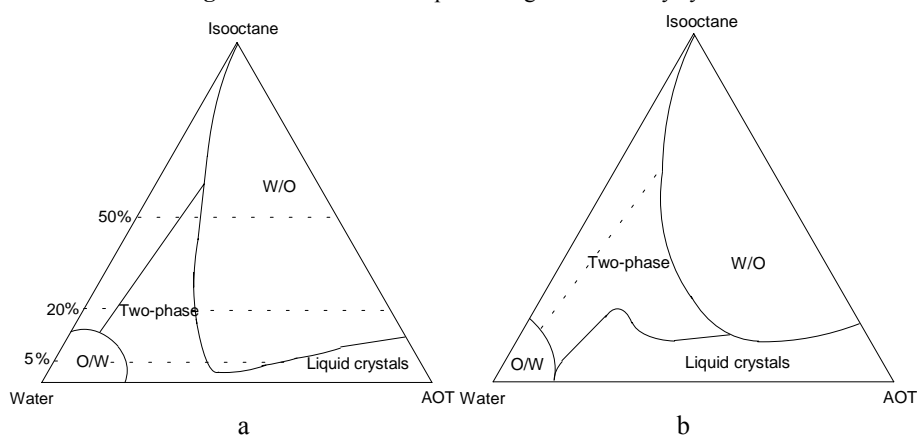
Figure 3 Interfacial tension in isooctane/water/AOT system. a, 5% isooctane; b, 50% isooctane



A typical phase diagram for the water/AOT/isooctane system (**Figure 4b**) was provided by Tamamushi¹³ using the experimental technique. The main difference

between our simulated phase diagram (**Figure 4a**) and his experimental result is that the former has bigger O/W and W/O micelle regions and a smaller liquid crystals region. The different results could be explained as follows. Firstly, the elbow regions, *i.e.* the COO ester groups, are assigned to the hydrophilic domain in our simulation. Although the spring constant is used between the head and tail in DPD simulation, maybe the COO ester groups have more important roles in the molecular structure. Secondly, in the partition of surfactant molecule (including the head and tails), H atom is used to substitute the leavings. Maybe this substitute is a little unfit to surfactant molecule in the theoretical calculations. Although there are some differences in the liquid crystals region, the main phase region is uniform, like W/O reverse micelle and the solution region. From the simulated phase diagram, one conclusion is shown that the ternary phase diagram can be drawn via the DPD simulation method.

Figure 4 The simulated phase diagram of ternary system



References

1. J. Faeder, B. M. Ladanyi, *J. Phys. Chem. B*, **2000**, *104*, 1033.
2. S. P. Moulik, B. K. Paul, *Adv. Colloid Interface Sci.*, **1998**, *78*, 99.
3. T. K. De, A. Maitra, *Adv. Colloid Interface Sci.*, **1995**, *59*, 95.
4. M. B. Temsamani, M. Maeck, I. El Hassani, *J. Phys. Chem. B*, **1998**, *102*, 3335.
5. O. A. El Seoud, *J. Mol. Liq.*, **1997**, *72*, 85.
6. E. Junquera, L. Pena, E. Aicart, *Langmuir*, **1997**, *13*, 219.
7. K. Karukstis, A. A. Frazier, D. S. Martula, *J. Phys. Chem.*, **1996**, *100*, 11133.
8. R. Bandyopadhyaya, R. Kumar, K. S. Gandhi, *Langmuir*, **2000**, *16*, 7139.
9. M. H. Alaimo, T. F. Kumosinski, *Langmuir*, **1997**, *13*, 2007.
10. B. Deresker, A. Derecskei-Kovacs, Z. A. Schelly, *Langmuir*, **1999**, *15*, 1981.
11. R. D. Groot, T. J. Madden, *J. Chem. Phys.*, **1998**, *108*, 8713.
12. R. D. Groot, *Langmuir*, **2000**, *16*, 7493.
13. B. Tamamushi, N. Watanabe, *Colloid Polym. Sci.*, **1980**, *258*, 174.

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