

Dynamic Study of Gemini Surfactant and Single-chain Surfactant at Air/Water Interface

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Abstract: Molecular dynamics (MD) simulation are used to study the properties of gemini surfactant of ethyl- α,ω -bis(dodecyldimethylammonium bromide) ($C_{12}C_2C_{12}$) and dodecyl-trimethylammonium bromide (DTAB) at the air/water interface, respectively. In the two systems, the surfactant concentrations are both 28 wt. %, and other conditions are also the same. After reaching the thermodynamic equilibrium, the concentration profiles, the radial distributions functions (RDF) and the mean squared displacement (MSD) are investigated. The results reveal that the surface activity of $C_{12}C_2C_{12}$ surfactant is higher than DTAB surfactant.

Keywords: Molecular dynamics simulation, gemini surfactant, air/water interface.

The structure of surfactants at interfaces is of great importance in industrial processes¹. Gemini surfactants have become a topic of scientific interest due to their effectiveness in the modification of interfacial properties and their molecular geometries lead to interesting aggregate structures at interface². They are considerably interested in the present due to the low critical micelle concentration and high efficiency in reducing the surface tension compared with the conventional single-chain surfactants³. Aqueous solutions of some dimeric surfactants with short spacers have very high viscosity at relatively low concentration of surfactant whereas the solution of the corresponding monomer remains to be low viscous⁴.

Gemini surfactant is *superior to* single-chain surfactant in many properties, and there are many studies on gemini surfactant systems in experiments, but it is only few in molecular simulations⁵⁻⁷. Molecular dynamics (MD) simulation is an effective method to investigate surfactant systems, and there is a growing interest in the studies of surfactant aggregate at interface with MD method. In this letter, we have studied and compared the microscopic dynamics properties of monolayers of $C_{12}C_2C_{12}$ and DTAB adsorbed at the air/water interface using MD simulation method.

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Results and Discussions

In **Figure 1**, the z -dependent concentration profiles show the location of water molecules and surfactant molecules after reaching the thermodynamic equilibrium. It shows that the range of the distribution of $C_{12}C_2C_{12}$ is wider than that of DTAB. This means that the interaction between DTAB molecule and water molecule is strong, and the DTAB molecules locate mostly at the water surface. To further quantify the difference from the concentration profiles, the ratio of the area per surfactant molecule is calculated, and the ratio is 2: 1 for $C_{12}C_2C_{12}$ with DTAB, it means that one $C_{12}C_2C_{12}$ molecule corresponds to two DTAB molecules.

RDF - $g(r)$ may be regarded as the ratio of local density and bulk density, the local density and bulk density are different near the site of one atom, but they are the same at the position far from the atom. $g(r)$ also can give the frequency information of the appearance of the atom. The RDF of the Br^- with the nitrogen is shown in **Figure 2**.

Figure 2 shows that the value of $g(r)$ is zero when the r is less than 4.0 Å, it means that the Br^- can not appear around the nitrogen atom when their distance is less than 4.0 Å; the peak of RDF appears when the r equals about 5.0 Å, where the local density is maximal. But the peak heights are different, and it is about 32 for $C_{12}C_2C_{12}$ system and 25 for DTAB system, which means that the frequency of the appearance of Br^- around 5 Å of the nitrogen atom is higher in $C_{12}C_2C_{12}$ system than that in DTAB system, because the $C_{12}C_2C_{12}$ molecules ionize difficultly, while the DTAB molecules ionize easily, so there are more Br^- near the nitrogen atom in $C_{12}C_2C_{12}$ system than in DTAB system.

Figure 1 The z -dependent concentration profile of water, $C_{12}C_2C_{12}$ and DTAB, the left (A) and right (B) figures correspond to $C_{12}C_2C_{12}$ and DTAB system, respectively.

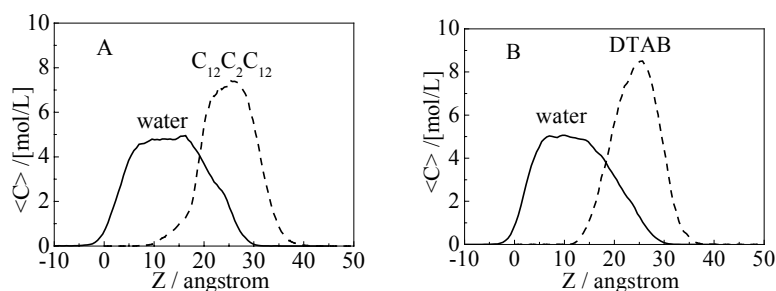


Figure 2 The radial distributions functions of Br^- with the nitrogen atom.

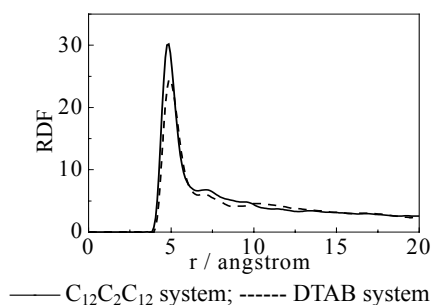
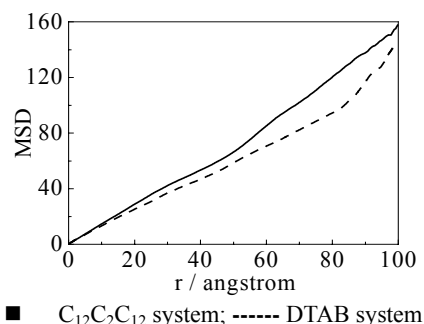


Figure 3 The mean squared displacement of Br⁻.

The MSD for the Br⁻ is shown in **Figure 3**. The MSD obey the equation for three dimensions (valid for long times):

$$D = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle |r_j(t) - r_j(0)|^2 \rangle \quad (1)$$

The diffusion coefficient (D) is determined, where, $r_j(t)$ is the particle position at the time t . Using this relation the D values of Br⁻ (D_{Br}) for the systems can be calculated. It can be obtained that the value of D_{Br} is $2.57 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ in C₁₂C₂C₁₂ system and $2.13 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ in DTAB system (**Figure 3**). It is obvious that D_{Br} in C₁₂C₂C₁₂ system is greater than that in DTAB system. The reason is the interfacial activity of C₁₂C₂C₁₂ is higher than that of DTAB, so the former moves more easily than the latter.

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