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The cloud point phenomenon of ionic surfactants: A view from molecular dynamics and metadynamics simulation

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ABSTRACT

Molecular dynamics (MD) and metadynamics simulations were used to give an understanding on the cloud point phenomenon of ionic surfactants. Meanwhile, the differences between tetrabutylammonium interactions with dodecyl sulfate (DS^-) and alkyl carboxylate (C12) micelles are discussed. Micelle ionization degree (α), binding patterns between the counterions and micelle, potential of mean force (PMF), and intermicellar interactions were characterized to present a reasonable explanation on the different behaviors of tetrabutylammonium alkyl carboxylate (TBAC) and tetrabutylammonium dodecyl sulfate (TBADS). Free energy profiles indicate that three bridging models exist between TBADS micelles. This will be the fundamental intermicellar model to interpret the cloud point phenomenon of TBADS ionic surfactants and other analogous systems.

1. Introduction

The cloud point phenomenon is common in nonionic surfactants [1]. When the temperature is raised, the system becomes cloudy at a specific temperature. Nevertheless, previous experimental studies [2–8] showed that some ionic surfactants with large counterions also exhibited the behavior. The mechanism of the behavior in these ionic surfactant solutions has attracted a large amount of experimental research. However, different mechanisms have been proposed with many studies.

Most studies were focused on large organic counterions since their large hydrated radius and hydrophobic character. Hydrophobic counterions can cross-link different micelles in order to overcome the energy barrier between the micelles [5]. At the same time, the existence of hydrophobic counterions may be strongly binded to micelles that make the mixed micelle behave as a nonionic system [6]. However, also studies [7,8] thought that the cross-linked ionic micelle was due to a second layer of hydrophobic counterions. Meanwhile, some researches [9] just consider the first bound counterions. These experimental studies obtained about three bridging models between adjacent micelles. The models will be discussed detailed in the following.

Although large organic counterions will make some ionic surfactants have cloud point, Zana et al. [10] found tetrabutylammonium (TBA^+) dodecanoate shows no clouding in the range 0–100 °C while TBA^+ alkyl sulfates exist. They gave an interpretation that the cross-linked ionic micelle was due to a second layer of hydrophobic counterions. TBAC and TBADS belong to ionic surfactants, they hold similar aggregation behavior at room temperature. However, the aggregation behavior will be very different for TBAC and TBADS when the temperature is raised. They are different in micelle size and number of monomers in one micelle, chemical composition, partial charge and structure of head group. How these factors affect the aggregation behavior of these two micelle systems, especially the increasing temperature, need to be elaborated. The difference between TBAC and TBADS is vital and essential for understanding the cloud point phenomenon of ionic surfactants and deserved to be given more detailed studies.

MD simulation has been a powerful technique for obtaining a detailed microscopic understanding of the micelle properties at the molecular level. In a previous study [11], we propose a MD model for TBADS micelle, which is the elementary basis for understanding the cloud point phenomenon. Based on the experimental results [10], and our proposed MD micelle model, we performed this MD and metadynamics simulation study on the intermicellar interactions to give a reasonable explanation on the cloud point phenomenon of TBADS. The different intermicellar behaviors of TBAC and TBADS were discussed. More importantly, definite bridging models between adjacent TBADS micelles were obtained in this MD simulation.

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2. Simulation details

The original coordinates for C12, DS^- and TBA^+ surfactant monomer were obtained from the automated force field topology builder (ATB) [12,13]. The geometries were optimized at B3LYP/6-31G* level. Bonded and non-bonded parameters were generated with ATB that is compatible with the GROMOS 53A6 parameter set [14]. The electrostatic potential based method [15] was used to estimate the initial charges. Final charges and charge groups were obtained with the method described in the ATB paper. Additional bonded parameters were generated from the Hessian matrix. The detailed force field parameters can be seen in Tables S1–S4 and Fig. S1. Simple point charge (SPC) [16] model was used for water molecules.

The choice of a 36 monomer micelle for TBAC and a 58 monomer micelle for TBADS is according to the experimental results of Zana et al. [17] and Benrraou et al. [7], respectively. The initial spherical micelles of 36 C12 and 58 DS^- were constructed by the Packmol [18]. A cubic box of 8 nm sides was builded with randomly scattered counterions and water molecules. The numbers of water molecules for TBAC and TBADS are 16042 and 15191, respectively. The GROMACS 5.0.4 package [19] was used for all the simulations. Energy minimization was first carried out with the steepest descent method. In order to give a proper volume and density for the simulated system, 200 ps NPT ensemble at 1 atm and 298 K was performed. Temperature and pressure are controlled with the Berendsen weak-coupling method [20]. The time constants for temperature and pressure are 0.1 ps and 1.0 ps, respectively. After that, a NVT simulation with a 50 ns time length was executed at 298 K to get MD trajectories. All the data analyses were based on the MD trajectories of the last 30 ns, which was proven to reach equilibrium with the evolution of micelle ionization degree (Fig. 1) and total energy (Fig. S2). Bond lengths were constrained using the LINCS algorithm [21] in all the simulation. Periodic boundary conditions were applied for the three dimensional space, while a 2 fs time step was used throughout the simulations. The Particle Mesh Ewald (PME) [22] algorithm was adopted for the calculation of electrostatic interactions. Lennard—Jones interactions were used with a 1.4 nm distance cutoff.

As for the study of intermicellar interactions, the mixed micelle was based on the last MD snapshot of previous 50 ns trajectories. We then duplicated the micelle that obtained from the previous 50 ns MD run and placed the two micelles in a box of 10 nm × 10 nm × 22 nm. The NPT ensemble was performed to keep the system in the appropriate volume. All controlling parameters are same with the description in previous paragraph. Then, a ca. 10 ns NVT simulation was used to give a study on different intermicellar behaviors of TBAC-TBAC and TBADS-TBADS. According to the motions of TBAC and TBADS micelles, this time length is enough for the study on the distinctions of intermicellar behavior between TBAC and TBADS systems. The package *g_mmpbsa* [23] was used for the calculations of Coulomb interactions and van der Waals interactions without any cutoffs.

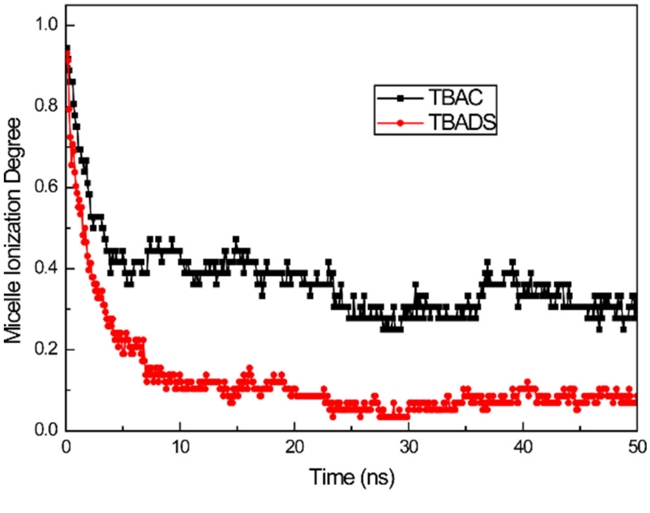

Fig. 1. Micelle ionization degree of TBAC and TBADS at different time.

To give more highlights on intermicellar interactions of TBADS micelles, well-tempered metadynamics simulation was performed with the Plumed 2.2 package [24] and GROMACS 5.0.4 package. The distance between micelle COM is defined as collective variables. Well-tempered metadynamics simulations with 40 ns were performed in the NVT ensemble at the temperature of 298 K. The Gaussian width was set to 0.35. The initial Gaussian deposition rate was 0.15 kcal mol^{-1} per ps, with a bias factor of 6.0. Meanwhile, three parallel simulations were used to prove the convergence and the correctness of the simulation result.

3. Results and discussion

3.1. Micelle ionization degree

The most relevant micelle property that affects the clouding behavior is micelle ionization degree (α). Zana et al. [17] mainly attributed the absence of phase separation of TBAC to its higher micelle ionization degree compared with that of TBADS. They pointed out that TBAC with high micelle ionization degree cannot form a second layer of the bound TBA^+ so that TBAC cannot present phase separation.

TBA^+ with DS^- or C12 can form mixed micelles. However, not all the randomly distributed counter ions aggregate onto the micelles. Since the experiments use the micelle ionization degree to study the counterions dissociate into the aqueous solution, we calculate the micelle ionization degree (Fig. 1). The criterion of distance between the N atom of counterion and the center of mass (COM) of the micelle was used. The counterion is supposed to be dissociated if the distance is greater than micelle radius (Rs) plus the radius of the counterion. The calculated α values change very much with the changing polar head. The α of TBAC is higher than that of TBADS, which is consist with the experimental results [17]. Meanwhile, the α fluctuation of TBAC is also greater than that of TBADS. This is mainly due to the fact that the affinity between the TBAC polar head and the counterions is less than that of TBADS. Result suggests the α value fluctuation is between 0.3 and 0.4. Longer time simulation is performed to affirm the fluctuation and convergence of α for TBAC.

Zana et al. [17] gave an explanation for the higher α value of TBAC than that of TBADS. They attribute the phenomenon to the different electrical charge distribution of ionic surfactants reported by Huibers [25]. Based on Huibers' calculated results, the charge on the sulfate headgroup (−1.13) is larger than that on the carboxylate headgroup (−0.92). Hence, Zana et al. [17] think that the alkyl sulfates micelles bind more TBA^+ counter ions than alkyl carboxylate micelles because of the higher charge per headgroup. And thus TBADS has a lower degree of ionization. In our force field parameters, the partial charge on sulfate headgroup and carboxylate headgroup are about −1.30 and −0.86, respectively. The differences of our used partial charge on the headgroup and Huibers' are mainly due to the different calculation methods. However, the trend is same. We agree that the different partial charge on the headgroups is one reason for the different α value. Meanwhile, we believe that the geometric configuration of the polar heads also plays an important role in the different α values. This will be discussed later.

Since the cloud point phenomenon occurs as the temperature is raised, micelle ionization degree (α) of TBAC and TBADS at different temperature was calculated (Fig. S3). When the temperature is raised, α values do not change very much. The phenomenon is in good accordance with the experimental results [7]. From this phenomenon, TBADS behaves like a nonionic surfactant micelle to show cloud point phenomenon. According to the definition of Raghavan et al. [6], TBADS micelle with low α values can be regarded as pseudo-nonionic micelle [6]. Due to high α value and high charge at the micellar surface, TBAC