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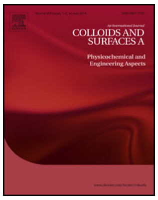

Molecular dynamics simulation of shape and structure evolution of preassembled cylindrical cetyltrimethylammonium bromide micelles induced by octanol

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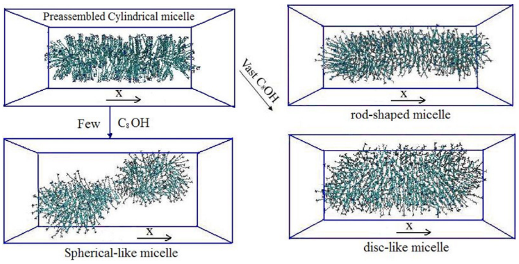
HIGHLIGHTS

- The evolution of CTAB aggregates was simulated.
- At low $r = C_8OH/CTAB \leq 1/3$, the cylindrical CTAB micelles were unstable.
- At $r \geq 2/3$, the rod-like and disc-like micelles with a bilayer structure coexist.
- Octanol can modify the arrangement of CTAB in aggregates.

GRAPHICAL ABSTRACT



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ABSTRACT

United-atomic molecular dynamics simulation was performed to probe the shape and structure evolution of the preassembled cylindrical cetyltrimethylammonium bromide (CTAB) micelles at constant CTAB content with an addition of octanol (C_8OH). Without or at low amount of C_8OH, e.g., $r = C_8OH/CTAB \leq 1/3$, the simulation results indicate that the cylindrical CTAB micelles are unstable and apt to split into smaller spherical-like micelles, which is dominated by CTAB content in terms of the principle of the lowest Gibbs free energy. Specifically, although C_8OH and CTAB may form molecule pairs by electrostatic attraction because of the positive charge of CTA^+ and the partial negative charge of O in C_8OH (the O atom having $-0.700\ e$ in our MD simulation) and there are no additional interactions existing between these pairs because the C_8OH content is too low. While in the case of $r \geq 2/3$, the micelles become stable and is transformed into rod-like and then disc-like micelles with bilayers. The situation has been changed at the high content of C_8OH, a quasi-2D lattice structures begin to form by the electrostatic attraction and the hydrogen bonds. According to the simulation results, this phenomenon can be explained by the distribution of CTAB induced by C_8OH. In other words, C_8OH as cosurfactants can modify the arrangement of CTAB in aggregates, which result in closer distance between CTAB molecules and lead to the smaller average equilibrium head-group area (a) of the surfactant. Meanwhile, the C_8OH molecules embed into the hydrophobic chains of CTAB and increase the average volume (v_0) of the hydrophobic chains, but do not cause the change of the length (l_0) of the hydrophobic chains. Therefore, a larger packing parameter ($P = v_0/a \cdot l_0$) can be obtained, which gives rise to the formation of the stable rod-like and disc-like micelles at high C_8OH content.

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1. Introduction

Surfactants in solution can self-assemble into various aggregates with unique morphologies and microstructures [1–3] such as micelles, vesicles, lamellar phases, and lyotropic liquid crystalline phases [4–8]. Commonly, in terms of the lowest Gibbs free energy, spherical micelles with a given radius and monodisperse state can be obtained when the concentration of surfactant is higher than the critical micelle concentration (CMC). However, once the composition of surfactant or thermodynamic conditions including surfactant concentration, pH, the ionic strength, and temperature are changed, the evolution of the micelle morphology can occur [9–11]. It is well-known that co-surfactant such as alkyl alcohols C_nOH (with $n = 3–8$, generally) or/and counterions are the two most popular ways to change compositions of surfactant solution, which have been widely used to induce the transition of surfactant aggregates [12–28]. Both experimental and theoretical researches on this aspect have attached more and more attentions.

Alkyl alcohols are considered as typical co-surfactants which have been applied to evolve the transition of the shape and structure of CTAB micelles [16–24]. Generally, it is well accepted that the alkyl alcohols (C_nOH with $n = 4–8$, generally) can intercalate into the ionic surfactant headgroups and decrease the micellar surface charge density [19–22]. Whereas the longer alkyl alcohols (C_nOH, $n \geq 8$) can increase the aggregation number of CTAB and produce large mixed alkyl alcohol–surfactant micelles [23,24]. In the studies performed by Kumar et al. [25] and Desai et al. [26], the alkyl alcohols were more effective in promoting the growth of cationic micelles and finally leaded to the sphere-to-rod transition. Sreejith et al. [27] investigated the formation of gel-phase in CTAB/KBr aqueous solution, and recently they also found a micelle–vesicle transition [28] induced by KBr. In the transition process, the C_8OH was considered to be embedded into the surfactant monomers, which can induce shape transition by increasing the volume of the micelles. They considered that C_8OH molecules were excellent candidate in tuning phase behaviors and aggregates of surfactants in solution.

Molecular dynamics (MD) simulation is a powerful tool in analyzing the microstructures of aggregates at atomic level, which is expected to set up a bridge between experimental results and theoretical considerations. Over the past decades, MD simulations have been performed on surfactant systems to probe the aggregation behaviors of surfactant on the interface [29,30] or bulk solution [31–34]. These simulation results have lighted new views on the understanding of surfactant aggregates and their aggregation transition at a molecular-level. In fact, a few atomistic MD simulations have already contributed to understand the structural and dynamic properties of micelles formed by CTAC [35,36]. Larson et al. demonstrated that NaCl and sodium salicylate salts can drive spherical-to-threadlike micelle shape transition in CTAC aqueous solutions [35]. Vanin et al. [36] estimated the spherical and cylindrical micelle sizes and surface area per surfactant polar head in the CTAC micelles with the different additives including 2-propanol, acetone, and sodium benzoate. Unfortunately, to the best of our knowledge, the researches about the effects of alkyl alcohols on the structural and dynamic properties of CTAB micelles are barely reported by MD simulations.

Herein, united-atomic MD simulations are performed to probe the effect of C_8OH on the evolution of the structure and shape of the preassembled cylindrical CTAB micelles at constant CTAB content with varying C_8OH content. First, the stability and shape evolution of the preassembled cylindrical C_8OH/CTAB micelles are simulated and described. The structure evolution of preassembled cylindrical C_8OH/CTAB micelles was illustrated by analyzing the radial distribution function (RDF), hydrogen bonds, and the area of per headgroups of CTAB during the simulation periods. Finally, based on simulations and calculation results, the reason for shape and structure evolution of micelles was also discussed and the interaction model of C_8OH and CTAB was proposed.

2. Theoretical simulations

2.1. Tools for MD simulations

All the simulations in this paper were performed by Gromacs 4.5.4 simulation package with the united-atomic model. The surfactant, CTAB, was parameterized by a force field used in our previous literature [37], which had been proved to be validated in simulating CTAB self-assembly. Similarly, the force field parameters for C_8OH were also taken from the previous papers [38–40]. In this model, four types of interaction sites were considered in C_8OH: the oxygen (O) atom, the hydroxyl proton (H) of the hydroxyl group, the united methylene group (CH_2), and the united methyl group (CH_3), respectively. In order to illustrate the electrostatic interaction of CTAB and C_8OH, the partial charge of CTA^+ and C_8OH used in the MD simulations was listed in Table 1 [35,37,40], where the three methyl groups in headgroup and methylene group (C_1) adjacent to nitrogen atom carry $+0.25e$, the central nitrogen atom is neutral, and the charges of H, O and methylene group (C_O) in C_8OH are set to be $+0.435$, -0.700 and $+0.265e$, respectively. The simple point charge (SPC) water model was adopted for water molecules [41]. All simulations were conducted in the NpT ensemble with pressure of $p = 1$ bar and temperature of 323 K by Berendsen bath coupling scheme [41]. A semi-isotropic pressure coupling was applied because of its convenience of simulating thread-like and cylindrical micelles. Specifically, we performed our simulations based on the simulation cells in the *X*- and *Y*-directions, but independently rescaled in the *Z*-direction. To integrate the Newtonian equations of motion for all atoms, the Verlet leapfrog algorithm with a time-step of 5 fs is used. The trajectories are saved every 1 ps. The electrostatic interactions are treated by particle mesh Ewald (PME) technique [42]. Visualizations of all molecular configurations are done in molecular graphics software, VMD [43].

2.2. Detail simulations

Owing to the limit of the current computational power and algorithm, no more than hundreds of surfactants and less than thousands of explicit water are used in most simulations, and most of their equilibrium times are 100–200 ns [44,45]. It is very time-consuming to obtain the spontaneous surfactant aggregates from random initial configuration. Our simulations start from the preassembled cylindrical micelles, which have been taken in other MD simulations of surfactant thread-like micelles [35,36,45–48]. The equilibrium time is limited within tens of nanoseconds for all the simulation systems in our research. The preassembling process was conducted in the Packmol [49,50], a code package for arranging molecules in defined regions of space. The distance between the artificial surfactant aggregates and the box borders is first adjusted to 1.40 nm, and then explicit water and the counter ion, Br^-, are added, respectively. Fig. 1 gives the snapshot of preassembled cylindrical micelles along *x*-axial view (a) and the molecule models of CTA^+ and C_8OH (b).

As shown in Table 2, the detailed composition, simulation time (t_{run}) and the duration time (t_{ana}) for data analysis at the end of MD simulation are listed for the systems *I–V*. The preassembled cylindrical micelles are composed of 300 CTAB and different numbers of C_8OH (0–300). In addition, 26,981 to 27,398 water molecules are included. The equilibrium time is 10 ns for CTAB system I but 20 ns for CTAB/C_8OH systems II, III and 30 ns for IV and V, the time for data analysis of systems for II–V are the last 10 ns besides 5 ns for system I.