



## Atomic level and coarse-grained simulation of long chain alkyl sulfonate: Micelle self-assembly



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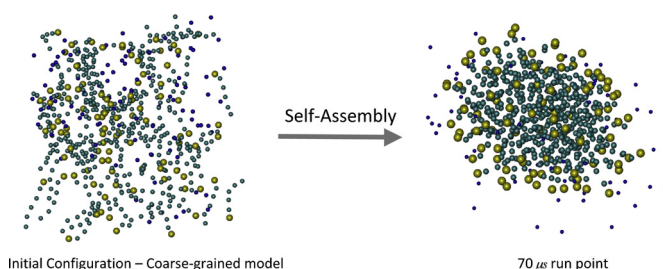
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### HIGHLIGHTS

- Surfactant micelle fission was observed via coarse-grained approach.
- The growth of micelles occurs by gradually coalescence of micellar aggregates.
- The long chain alkyl sulfonate micelle formation time is within order of  $10^{-4}$  s.

### GRAPHICAL ABSTRACT



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### ABSTRACT

A series of long runs were performed on pentadecyl sulfonate/water systems using both atomic level and coarse-grained approaches. Surfactant micelle fusion was observed with coarse-grained approach; however, the atomic scale study did not reach the equilibrium even at long timescales. The shape of micellar aggregate appeared as to be prolate spheroidal rather than spherical. The aggregation number, hydrocarbon tails and water properties were also examined. The comparison data obtained from atomic level and coarse-grained are in agreement with previous reports. In this report self-assembly of micelle formation is discussed. We state that the growth of micelles occurs by gradually coalescence of micellar aggregates. We suggest that with coarse-grained approach equilibrium is achieved at dispersed initial configuration and therefore, the model is ideally suited to describe the dynamical nature of the self-assembly of surfactants.

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### 1. Introduction

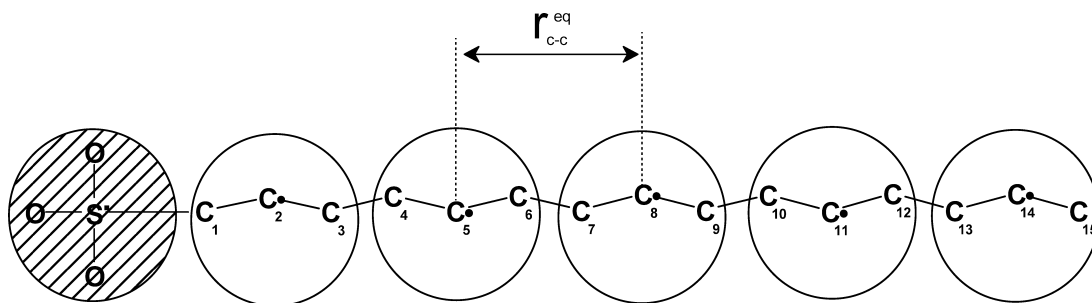
Self-assembly of surfactant molecules is important in a variety of areas ranging from medicine to the industry [1,2]. The dual chemical nature of these molecules assumes that they have both hydrophilic and hydrophobic segments, and when dissolved in water solution, they self-organize into various structures. The surfactant systems were studied using theoretical, real-time and computer experiments [3–8]. Traditionally the computational

studies of surfactant self-organization were conducted mainly by molecular dynamics (MD) simulations [6,7,9–12]. It is noteworthy that different levels of molecular dynamics simulations were previously used, i.e. atomistic scale with explicit and implicit solution and CPU-time-consumable coarse-grained level [13–22]. That is why MD is considered to be a unique method to compute dynamical features of many classical body systems.

A number of simulation studies, with either short or long timescales [8,11,12,23], were performed on variety of surfactants, such as sodium octanoate [24,25], dodecyl and hexyl sulfates [26–28], dodecylphosphocholine [29,30]. In these simulations a wide range of micelle sizes was used. However, if the initial configuration is randomly distributed, equilibrium is hard to reach, as the

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**Fig. 1.** The conceptual coarse-grained model of SPDS molecule, where specific 3:1 mapping is applied. The SPDS molecule has long alkyl chain with 15 carbon atoms represented by 5 Martini beads. The interaction centers are marked as asterisks.

experimental observations claim that the timescale of micellar formation is typically  $10^{-6}$ – $10^{-3}$  s; therefore, long time simulations are required to mimic the equilibrium nature of those systems.

Despite some limitations the granular (so-called coarse-grained level) approach has been recently used to reduce the computational time and achieve longer timescales. The concept of “granular” presentation was originally developed by Marrink et al. [31] for GROMACS software [32,33]. The suggested simplification of the model enables faster computations, i.e. large systems can be simulated for longer periods of time.

These computational studies typically include sulfate based detergents; however there is a lack of reports on self-organization of long chain primary alkyl sulfonates (PAS). We have recently reported the mechanism of self-assembly of long chain alkyl sodium pentadecyl sulfonate/water systems at lamellar phases [34].

Here, we describe long chain alkyl sulfonate self-organization mechanism using both classic atomic scale and coarse-grained level MD method. First we looked at the self-assembly of sulfonate micelle on atomistic scale, starting from both randomly distributed and preassembled configuration and then, we conducted two independent long simulations with various system sizes using coarse-grained models. The purpose of this study was to investigate the mechanism of self-assembly of long chain alkyl sulfonate with various approaches. We also investigated the surfactant micelle fusion behavior at atomistic and coarse-grained. To verify the obtained MD results we defined the structural parameters with further comparison to the existing experimental observations.

## 2. Simulation construction details

### 2.1. Atomistic level

Sodium pentadecyl sulfonate ( $C_{15}H_{31}SO_3Na$ ) (SPDS) was used as a detergent. A single SPDS molecule .pdb file was extracted from our previous simulation [34]. We set up two systems (AT-I and AT-II) with different initial configurations: randomly dispersed and preassembled.

The initial configuration of AT-I was randomized by randomly positioning 95 molecules in the  $8.7 \text{ nm} \times 8.7 \text{ nm} \times 8.7 \text{ nm}$  cell using GROMACS software package modules (*genbox* module). We added 95 sodium counter-ions to the system using GROMACS *genion* module, where the counterions were modeled closely at about 0.3 nm from the headgroups’ sulfurs of surfactant molecules. The system was minimized and solvated by means of GROMACS [32,33] *genbox* module with corresponding 20,086 water molecules (much higher than CMC). After the construction, the energy was minimized using steepest descent method for 5000 steps to remove high-energy contacts that might have formed during the construction process.

For AT-II system a preassembled micelle with 95 PDS molecules was chosen. The initial configuration was build using our own code. Then, we added 95 sodium ions to neutralize the system (GROMACS

*genion* module). Further, the system was minimized and solvated using GROMACS *genbox* module. Note that the number of water molecules was 20,160, i.e. we set up the same SPDS/water ratio as in the case of AT-I. The total system was subjected to minimization in order to avoid bad contacts.

The force field parameters were previously discussed [34]. The partial charge distribution was estimated according to Huibers [35], where the semi-empirical calculations (MINDO, PM3, and AM1) were carried out to define charges on sulfonate headgroup ( $SO_3^-$ ), first methylene ( $CH_2$ ) group of alkyl chain ( $\alpha$ -methylene) and remaining alkyl tail. In particular, we were interested in the charge distribution as the proper choice of partial charges can influence surfactant self-assembly and its physical properties. Both  $CH_2$  and methyl ( $CH_3$ ) groups were set as unified atoms. The simple point-charge (SPC) molecules were used as a water model [36]. The LINCS algorithm was used to impose the constraints on the bond lengths [37]. The temperature was set at 323 K and fixed using V-rescale algorithm with the time constant  $\tau = 0.1$  ps, where the temperatures of surfactants, counterions and solvent were controlled independently. The pressure coupling Berendsen algorithm was used with  $\tau = 0.1$  ps time constant [38]. The Particle Mesh Ewald (PME) method was used for long range electrostatic interactions [39], and the van der Waals interactions were truncated at 1.2 nm. The equations of motion are integrated using leapfrog Verlet integrator with timestep of 2 fs [40]. Three-dimensional periodic boundary conditions were applied. Coordinates and velocities were saved every 0.1 ns and the visualization of the molecular configurations of the system was produced with VMD package [41].

Both systems were subsequently subjected to the small simulation ( $\sim 100$  ps) in NVT ensemble. Further, the 300 ns (0.3  $\mu$ s) and 200 ns (0.2  $\mu$ s) parallel MD runs were conducted (correspondingly AT-I and AT-II). The parallel MD simulations were performed on Hungarian Szeged<sup>1</sup> supercomputer.

### 2.2. Coarse-grained level

For the coarse-grained approach we used a SPDS molecule back mapped from an atomistic simulation in accordance with MARTINI force field [31,42]. In principal, MARTINI force field uses a 4:1 mapping to represent molecules by suggesting four main types (also some subtypes) of interaction centers (beads): polar (P), nonpolar (N), apolar (C) and charged (Q).

To interpret the geometry of SPDS surfactant molecule, three carbons and their associated hydrogen atoms are represented by one coarse-grained bead (3:1 mapping), i.e. the atomistic simulations are converted into coarse-grained simulations to identify the center of mass of corresponding atoms as the coarse-grained bead (Fig. 1). The random initial configuration from 95 molecules

<sup>1</sup> Hungarian Szeged supercomputing Center, <http://www.niif.hu>.

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