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Complete List of Authors:	Mandal, Taraknath; University of Michigan, Chemical Engineering Larson, Ronald G; University of Michigan, Chemical Engineering

Prediction of Striped Cylindrical Micelles (SCM) Formed by Dodecyl-β-D-maltoside (DDM) Surfactants

Taraknath Mandal and Ronald G. Larson*

Department of Chemical Engineering, University of Michigan, Ann Arbor, MI-48109, USA

Abstract: Using fully atomistic and coarse-grained (CG) molecular dynamics (MD) simulations, we report, for the first time, the self-assembly of initially randomly dispersed dodecyl-β-D-maltoside (DDM) surfactants into a striped cylindrical micelle (SCM) with lamellae of surfactant heads and of tails alternating along the cylindrical axis, with both heads and tails in contact with the water. By changing the interaction strength of the head group with water relative to itself, we find that such micelles are most likely for head groups with marginally solubility in the water solvent. Unlike the surfactants in a regular cylindrical micelle, whose tails are in the fluid micelle interior, the diffusion of DDM surfactants along the micelle body are blocked by the lamellar patterning. As a consequence, branches cannot slide along a micelle body and surfactant molecules cannot exchange between the micelle body and the branch, which should have a significant impact on the rheological properties of these micelles.

Keywords: Coarse-grained, Molecular dynamics, self-assembly, hierarchical-colloidal-polymer

*rlarson@umich.edu

Introduction: Surfactant molecules in aqueous solutions self-assemble into multiple aggregate geometries of varying length scale. The ability to design such solutions and optimize their rheological properties, which is determined by the structure of the aggregates, is of considerable importance in the design of consumer products such as shampoos and body washes, latex dispersions, foaming agents, oil-production fluids, medicines, and as drag-reduction agents for fluid transportation, among others.[1–4] Depending on the packing parameter of the constituent surfactant, the aggregate can adapt various structures such as small spheres, worm-like micelles (WLM), or vesicles. In a regular micelle, the hydrophilic heads remain at the outer surface, thus protecting the hydrophobic tails from the polar solvent. Recently, a self-assembled striped cylindrical structure with two repeating units, stacked in lamellar domains along the cylinder, has been observed in experiments and has potential applications in soft matter nanotechnology.[5–13] Recently Wang et al.[14] employed dissipative particle dynamics (DPD) simulation to investigate the self-assembly of a model surfactant-like amphiphiles consisting of a hydrophobic tail and hydrophilic head. By tuning the interaction between surfactant head and solvent and controlling the surfactant tail length and surfactant concentration, they obtained self-assembled structures of various morphologies including a striped cylinder structure which they named as hierarchical colloidal polymeric (HCP) structure.[14] The monomers of the self-assembled HCP structures reported in experiments, however, are usually nanoparticles such as nanospheres, nanorods and nanocubes tethered to polymers.[5–13] To date, formation of the HCP structure by experimental surfactants has not been reported.

In this paper, using coarse-grained simulations, we report the spontaneous self-assembly of structure analogues to the HCP structure from dodecyl-β-D-maltoside (DDM) surfactants and suggest conditions required for formation of such micelles. We name the structure a “striped cylindrical micelle” (SCM). The SCMs contain repeating blocks alternately composed of surfactant heads and surfactant tails, and thus both surfactant heads and tails are in contact with the water. We also performed atomistic simulations to support some of the results obtained from the coarse-grained simulations. Finally, we discuss about the consequence of such linear and branched SMS structures for the rheological properties of micelles.

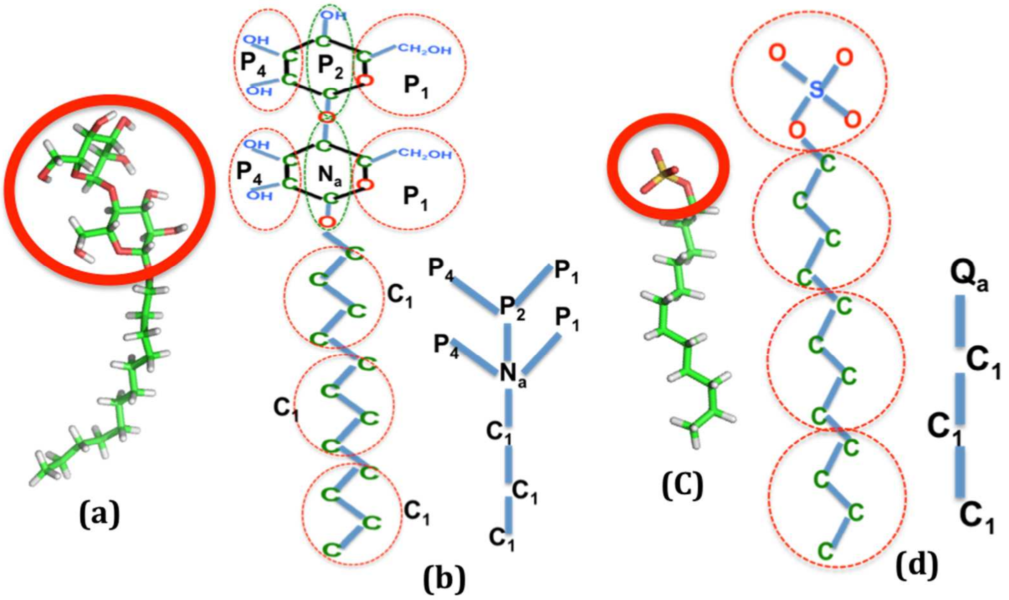


Figure 1: (a) Atomistic and (b) coarse-grained representations of DDM surfactant. (c) Atomistic and (d) coarse-grained representations of the SDS surfactant. Red, green, yellow and white colors in (a) and (c) represent oxygen, carbon, sulfur and hydrogen atoms, respectively. The head region of the surfactant is marked by red circle. In (b) and (d) black symbols represent the MARTINI bead types.

Methodology: We performed both atomistic and coarse-grained (CG) simulations to investigate the stability of the striped micelle structure formed by either DDM or SDS surfactants. The OPLS and CHARMM36[15] force fields were used to model the DDM[16] (https://lipidbook.bioch.ox.ac.uk/lipid/show/id/35.html) and the SDS surfactant, respectively in the atomistic model. The atomistic structures of the DDM and SDS surfactants are shown in **figure 1(a)** and **(c)**, respectively. The extended simple point charge (SPC/E)[17] water was used as solvent in both cases. Periodic boundary conditions were enforced in all three directions. The long-range electrostatic interactions were computed using the Particle Mesh Ewald (PME)[18] method. A time step of 2 fs was used for the numerical integrations. All initially built structures were first energy minimized using the conjugate gradient method followed by a short NVT simulation to relax the system. All equilibrium simulations were performed using NPT simulations. The pressure and temperature of the system were maintained using a Parrinello-Rahman barostat[19] with a time constant of 2 ps and a velocity-rescale thermostat[20] with a time constant of 0.5 ps, respectively. The MARTINI force field was used for all CG simulations. **Figure 1** shows the CG representation of the atomistic structures of the surfactants based on the MARTINI coarse-grained model. The CG parameters for the DDM and SDS surfactants were taken from the MARTINI[21] webpage (http://cgmartini.nl/) and are also presented in **Table S1** of the Supporting Information (SI). In the CG simulations, the time constants for the barostat and thermostat were 12 ps and 1 ps, respectively. The potential of mean force (PMF) simulations were calculated using an Umbrella Sampling method. The water/vacuum interface was created along the Z direction of the simulation box, and a single surfactant head was pulled from water to the vacuum. Steered molecular dynamics (SMD) simulations were performed to generate the initial configurations for equal spaced (0.1 nm) "windows" of the Umbrella Sampling simulations. In each window, the system was equilibrated for 200 ns. The weighted histogram analysis method (WHAM) was used to calculate the PMF from the Umbrella Sampling simulations. All simulations were performed using the GROMACS-4.6.7 package.[22]

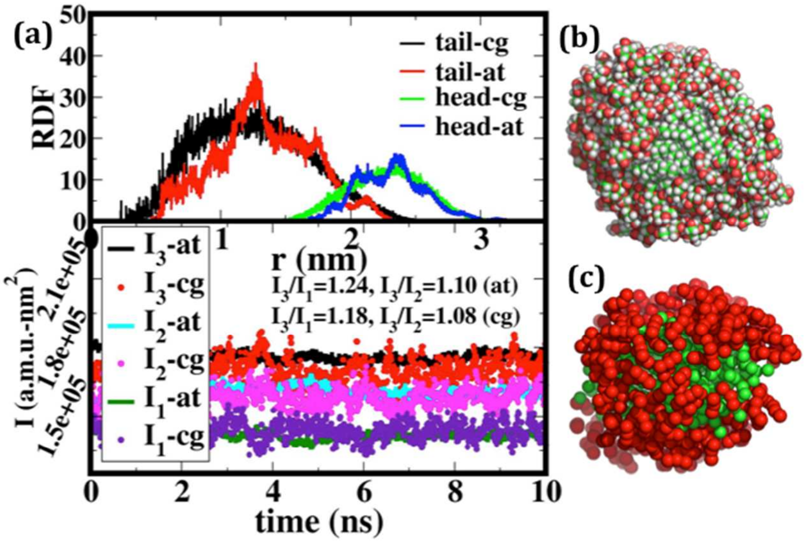


Figure 2: (a) *Upper panel*: RDFs of the DDM surfactant heads and tails relative to the center of mass of the micelle in both atomistic and CG simulations and *Lower panel*: Principal components of moment of inertia tensor obtained from last 10 ns of the atomistic and CG simulations. Snapshot of the equilibrated micelle structure from (b) atomistic (Red, green and white are oxygen, carbon and hydrogen, respectively) and (c) CG simulations (Red and green are surfactant heads and tails, respectively).

Results and Discussions: First, to validate the CG force field of the DDM surfactant, we compare several properties of a single spherical micelle calculated from atomistic and CG simulations. Note that the MARTINI CG parameters have been used extensively to model SDS surfactants and have been shown to reproduce correct structural properties.[23–28] Thus, here we validate the CG parameters for the DDM surfactant only. A prebuilt spherical micelle containing 98 DDM surfactants was solvated in a cubic box and equilibrated for 50 and 1000 ns in the atomistic and CG model respectively. We find that the micelle preserves its spherical geometry (**figure 2**) in both atomistic and CG simulations, perhaps not surprisingly since the micelle does not have enough surfactants to form more extended structures, such as cylinders. **Figure 2** compares the radial distribution functions (RDFs) of the micelle head and tails with respect to the center of mass of the micelle and the ratios of the principal components of the moment of inertia tensor obtained from the atomistic and CG simulations. In **figure 2**, I_3 and I_1 are the largest and smallest principal components of inertia tensor, respectively. The radius of gyration of the micelle is 2.171+-0.014 and 2.188 +- 0.009 nm obtained from CG and atomistic simulations, respectively, in good agreement with each other. This agreement, and the similarity between atomistic and CG values of the ratios of principal components of the moment of inertia tensor shown in **figure 2(a)**, help validate the accuracy of the CG parameters of the DDM surfactant.

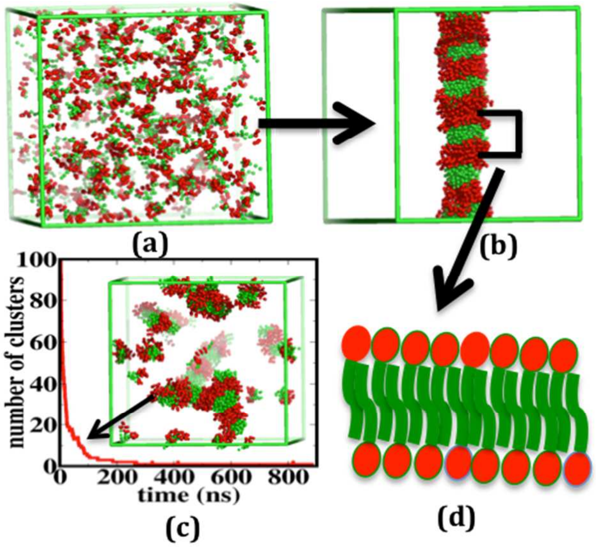


Figure 3: (a) Initial randomly dispersed CG DDM surfactants. (b) Final self-assembled striped micelle structure. The size of the simulation box is 20 × 20 × 20 nm^3. (c) Number of clusters as a function of simulation time. Inset shows the simulation box after a 70 ns simulation. (d) Schematic drawing of a block. Water beads are removed for clarity.

We next performed self-assembly simulations using the CG model of a larger number of surfactant molecules, namely 480 DDM surfactants, which were randomly dispersed in a cubic box 20 nm on a side (**figure 3(a)**). The box was then solvated using regular MARTINI water with 10% anti-freeze beads as was originally suggested by Marrinck et al.[21] The surfactant concentration in this system is ~100mM. Upon equilibration of the simulation box at room temperature and atmospheric pressure, the surfactants spontaneously self assembled into a linear striped micelle as shown in **figure 3(b)**. **Figure 3(c)** presents the number of clusters as a function of simulation time along with a snapshot of the simulation box showing an intermediate stage prior to complete re-arrangement into the striped micelle. The striped micelle is a linear aggregate with lamellar structure in which the surfactant tails are interdigitated within each tail lamella. A schematic diagram of a constituent lamella of the micelle is shown in **figure 3(d)**. There are approximately 96 DDM surfactants in each lamella of the striped structure. In a regular micelle, the hydrophobic surfactant tails are usually covered roughly uniformly by the hydrophilic surfactant heads, which shield the tails from contact with water. However, in a striped micelle, both the heads and tails of the surfactants are exposed along the perimeter of the micelle to water, as shown in **figure 3(b)**.

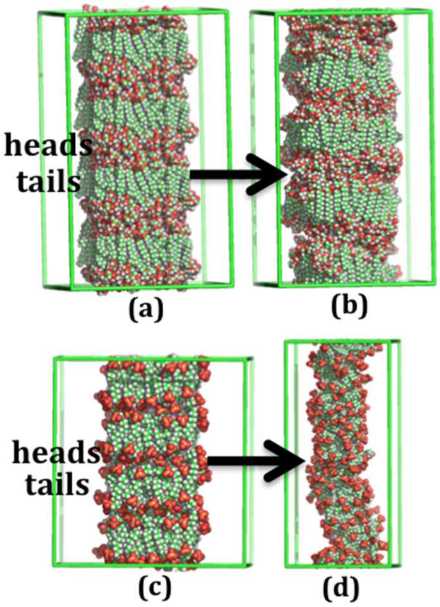


Figure 4: (a) Initially built and (b) final structure after a 40-ns long simulation of the striped micelle with atomistic DDM surfactants. (c) Initially built SCM with SDS surfactants and (d) the structure after a 2 ns-long simulation. Water beads are removed for clarity. The size of the simulation box in (a) and (b) is 8.1 × 8.1 × 14.2 nm^3. The sizes of the simulation box in (c) and (d) are 8.0 × 8.0 × 9.0 nm^3 and 6.5 × 6.5 × 13.9 nm^3.

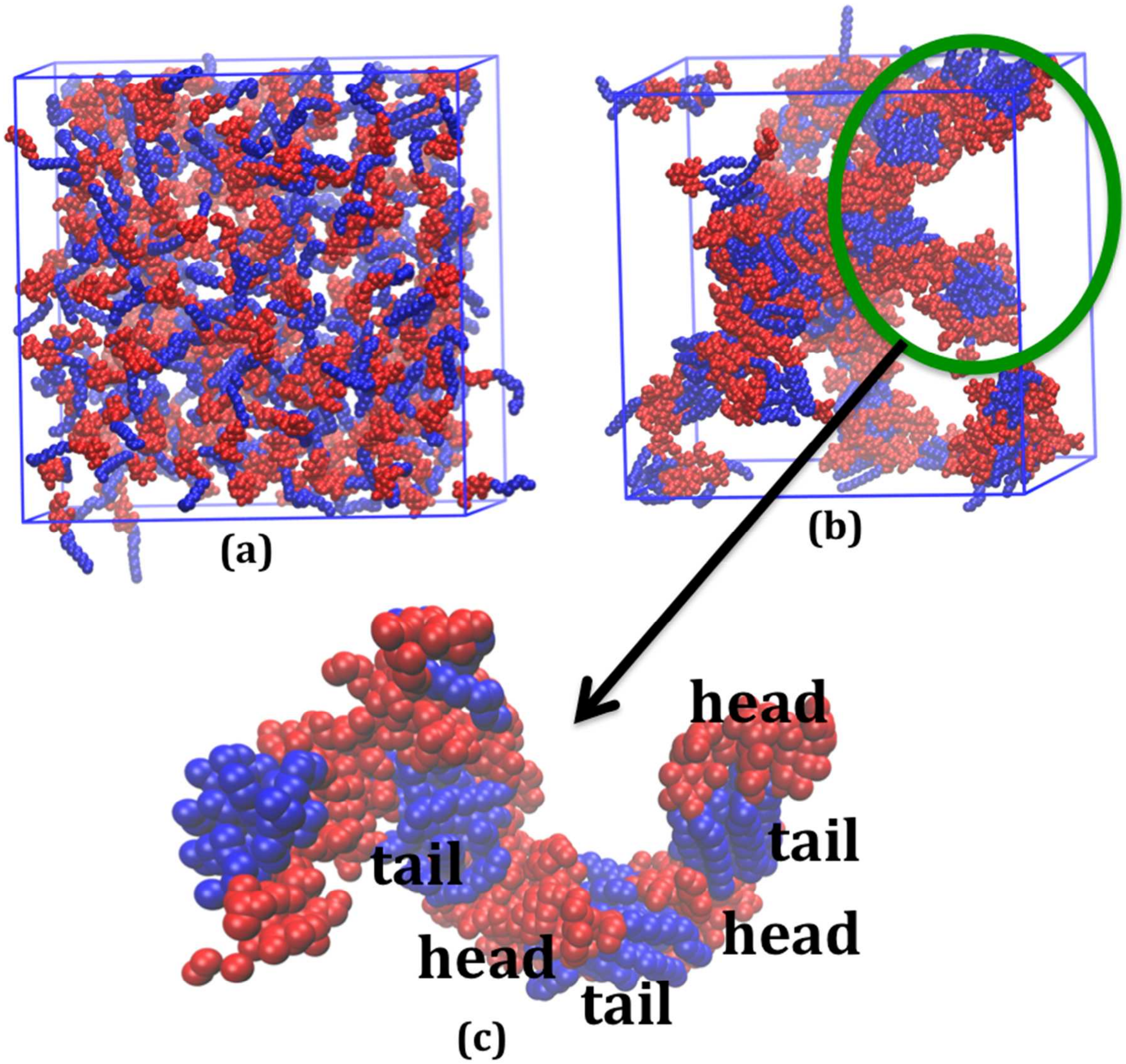


Figure 5: Self-assembly simulation of DDM surfactants with atomistic model: (a) initial configuration and (b) configuration after 30 ns long MD simulation. The size of the simulation box is 12 × 12 × 12 nm^3. Water and hydrogen atoms are removed for clarity. Head and tail atoms are marked by red and blue colors, respectively. (c) A zoomed version of a part of the assembled structure showing the signature of the formation of striped micelle structure.

To confirm the stability of such a striped linear micelle, we built an initially striped micelle structure with DDM surfactants using an atomistic model as shown in **figure 4(a)**. The atomistic striped micelle structure was built using *Packmol* software (http://m3g.iqm.unicamp.br/packmol/home.shtml). We put 100 DDM surfactants in each lamella, which is close to the number of surfactants in each lamella (~96) of the corresponding CG SCM structure. This prebuilt structure was then solvated using SPC/E water and energy minimized, followed by a 40 ns-long equilibration at atmospheric pressure and room temperature. As shown in **figure 4(b)**, the striped structure remained stable throughout the simulation run, confirming its stability and validating the formation of these structures found in coarse-grained simulations. To confirm that this simulation run was long enough to dissolve the striped structure, if it were unstable, we followed a similar protocol for SDS surfactants, and showed that after only a 2 ns-long equilibration, the lamellae in the initial SCM structure disintegrated, as the SDS molecules reoriented to put the head groups into contact with the water, forming a regular cylinder like structure as shown in the **figure 4(d)**. Thus, the SCM structure is a special characteristic of the DDM surfactants and is not a stable structure for SDS surfactants. To further confirm the formation of SCM structure by the DDM surfactants, we also performed self-assembly simulations of DDM surfactants using the atomistic model. 300 surfactants were randomly dispersed in a cubic simulation box of 12 nm per each side. Since the system size is much bigger and the atomistic simulations are computationally expensive, we were able to run only a 30 ns-long MD simulation. However, even in this short equilibration, the surfactants clearly show a tendency to form the SCM structure as shown in the **figure 5.**

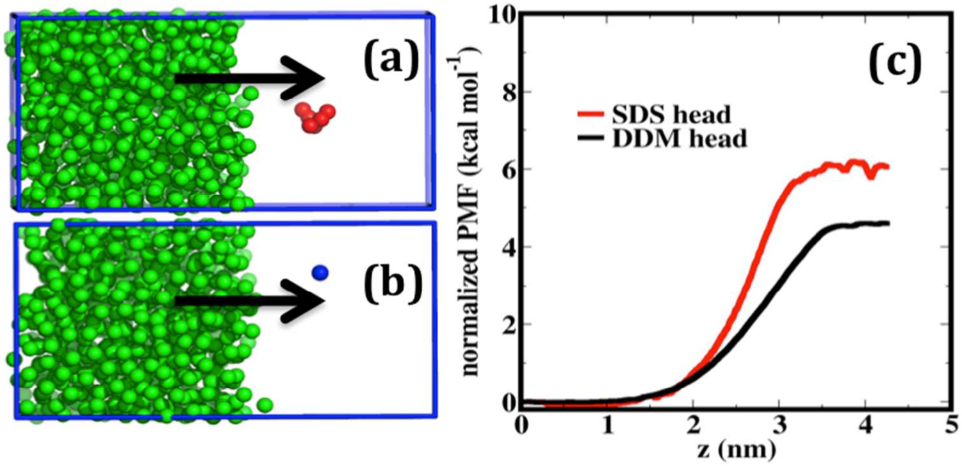


Figure 6: Simulation box set up for calculating PMF of a single (a) DDM and (b) SDS head pulled from water solvent to vacuum. Green, red and blue are water, DDM head and

SDS head, respectively. (c) PMF, normalized by the number of beads used to represent the head group (i.e., six for DDM, and one for SDS) for extraction of a single SDS and DDM head group from water solvent to vacuum. The size of the simulation box in (a) and (b) is $4.5 \times 4.5 \times 11.0\ \mathrm{nm}^3$.

Recently, Wang et al.[14] employed dissipative molecular dynamics (DPD) simulations with a surfactant-like amphiphilic object (toy model) to show that the striped micelle can be formed over a wide range of parameter space by tuning various parameters such as the size of the head group, the length of the tail, and the interaction strength between the surfactant head and water. They named the structure a "hierarchical colloidal polymeric (HCP)" structure. They observed that one condition for formation of the striped micelle structures is that the surfactant head is large, relative to the tail diameter. This is consistent with our result, since the head of the DDM is much bigger than the head of the SDS (**figure 1**), which may partly explain why the former forms the striped micelle. Wang et al. also found another condition is that the interaction between head and solvent be unfavorable, relative to the head-head and solvent-solvent interactions.[14] To investigate the relative strength of the head-solvent interaction of DDM and SDS surfactant, we used an umbrella sampling method to calculate the potential of mean force (PMF) for a single DDM and SDS head to move from bulk water solvent to vacuum. The simulation box setups for calculating these two solvation free energies are shown in **figure 6(a)** and **(b),** respectively. The DDM head group is approximately six times bigger than the head of the SDS since the DDM and SDS heads are modeled by six and one MARTINI beads, respectively, and in each case each CG bead represents four "heavy" atoms, i.e., atoms other than hydrogen. As shown in **figure 6(c)**, the PMF between a DDM head and water, divided by the number of head beads (6), is ~4.5 Kcal/mol. However, the normalized PMF between an SDS head and water, namely ~6.2 Kcal/mol, is ~1.7 Kcal/mol higher than the normalized PMF between a DDM head and water solvent. Thus, the interaction between the DDM head and water is relatively weak compared to that between an SDS head and water. And hence, according to Wang et al., a DDM surfactant is more likely to form the SCM structure than is the SDS surfactant, which is consistent with our simulation results. We note that there are several hydroxyl groups present in the DDM head. Thus because of these hydroxyl functional groups, DDM heads can form hydrogen bonds amongst themselves as well as with the water. (Note that in the CG model the hydrogen interactions are implicitly included through the assigned interaction parameters of the beads.) The radius and width of the head-head interface of a single repeat block of head groups are approximately 2.5 and 1.8 nm, respectively (**figure 7(a)**). The heads, which are at the periphery of the block, are in contact with other heads as well as with water. The average number of hydrogen bonds per unit area in the head-head interface is larger than the average number of hydrogen bonds in the head-water interface, calculated in the atomistic structure as shown in **figure 7(b).** This energy gain in the head-head interface helps overcome the energy cost in the tail-water interface and hence stabilize the SCM structure. It remains somewhat a mystery why the structure has the radius of around 2.5 nm, rather than expanding laterally into a lamellar phase that separates from the water phase. Presumably it has something to do with interface curvature, the packing of head groups along the micelle surface, and entropy favoring dispersed micelles rather than phase separation.

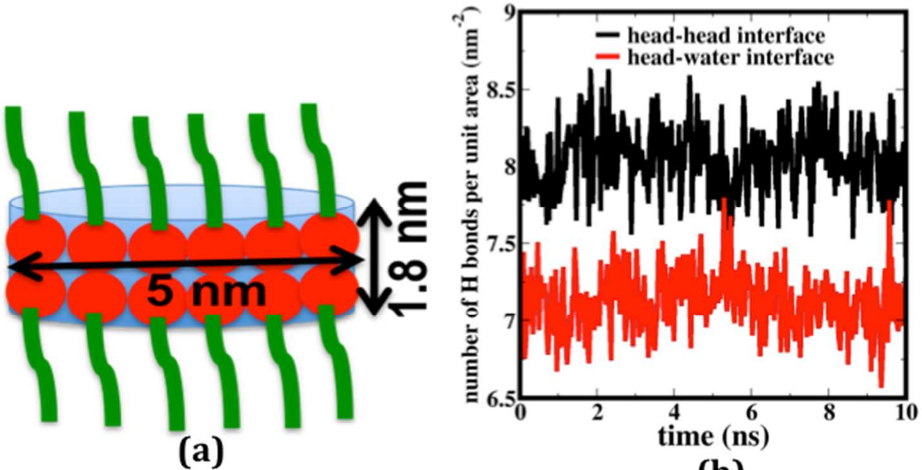


Figure 7: (a) A schematic representation of the DDM-DDM interface in a block of the SCM. Heads and Tails are shown by red and green colors, respectively. (b) Number of hydrogen bonds per unit area as a function of simulation time (last 10 ns).

Here we note, however, that, in a recent study, Schmalhorst et al[29] reported that the Martini force field overestimates the aggregation propensity of polysaccharides including maltose. As a remedy, they suggested scaling down the interaction strength amongst the polysaccharides beads following the equation $\epsilon_{ij,scaled} = 2KJ/mol + \lambda(\epsilon_{ij,original} - 2KJ/mol)$, while keeping polysaccharide-solvent interaction strength unchanged. Here 2KJ/mol is the lowest value of ϵ_{ij} for any pair of Martini beads, and λ is a scaling parameter, which when equal to unity recovers the original Martini value $\epsilon_{ij,original}$. Schmalhorst et al.[29] showed that a value of $\lambda = 0.5$ prevents the aggregation of polysaccharides. We observed, however, that the interaction strength of the head beads with $\lambda = 0.5$ was too weak to maintain the prebuilt micelle structure. Upon equilibration, a spherical micelle with 98 DDM surfactants broke into several small spherical micelles while the atomistic spherical structure remained intact. Thus we gradually increased the value of λ until the CG micelle remained stable and its structural properties were close to those of the atomistic simulations. We found that a minimum value of $\lambda = 0.7$ is required to prevent the micelle from breaking up. **Figure S1** shows that the radius of gyration (Rg) of the micelle and the radial distribution function (RDF) of the micelle heads and tails with respect to the micelle center for the coarse-grained structure agree well with those of the atomistic structure for $\lambda = 1$, i.e. with the original MARTINI force field. But, for $\lambda = 1$, we also observed that maltose molecules unphysically aggregate in water as shown in **figure S2 (a)**. However, for $\lambda = 0.9$, maltose molecules do not aggregate, remaining well dispersed in the solution (**figure S2 (b)**). Also, with $\lambda = 0.9$, the structural properties of DDM micelles compares reasonably well the atomistic structure (**figure S1**). By repeating the self-assembly simulation with randomly dispersed DDM surfactants, we confirmed in **figure S3** that the SCM structure also forms for $\lambda = 0.9$, showing that the appearance of the SCM structure is not an artifact due to the overestimated aggregation propensity of the maltose by the MARTINI force field. Moreover, the atomistic structure of the SCM shown in **figure 4 (b)** also confirms the SCM structure. The results are consistent with the DPD simulations of Wang et al., who show that when interactions between head groups are roughly as favorable, or significantly more favorable, with each other than with the solvent, the SCM structure appears. In a situation wherein both heads and tails prefer interactions with each other than with the solvent, a clumped structure would probably appear when the surfactant concentration is very high. However, at relatively low surfactant concentration when the average distance between micelles is large, entropy would favor the cylindrical micelles. To confirm this further, we also performed two more simulations: one with 100mM surfactant concentration in a box of twice the volume, containing 960 surfactants (twice as many as in **figure 3**) and another system with 125mM surfactant concentration containing total 600 surfactants. In both cases, the initially dispersed surfactants again aggregated into striped cylinders, and did not form phase-separated clumps. The corresponding SCM structures are shown in the **figure S4** and **S5** of the SI, respectively.

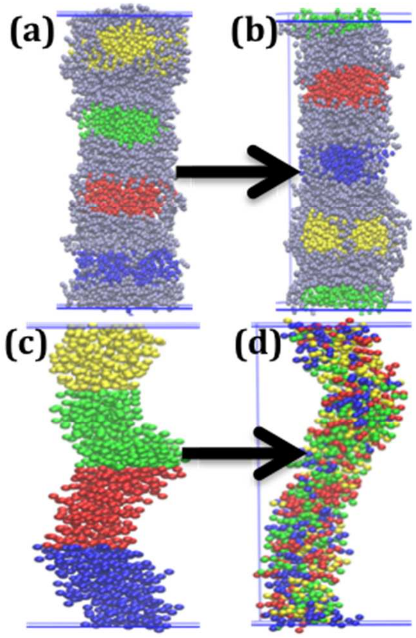
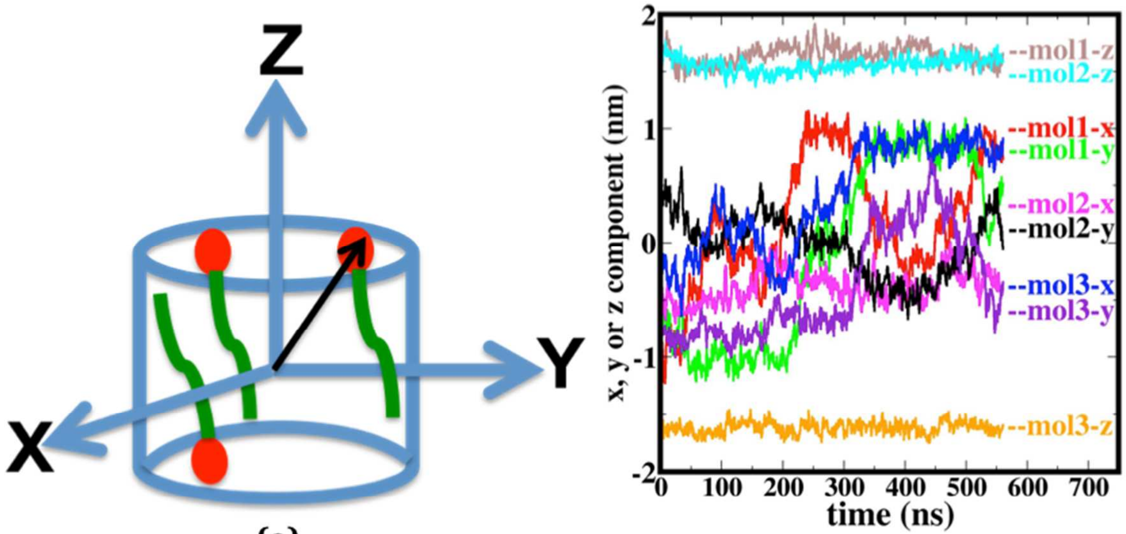


Figure 8: *Upper panel*: (a) Image of a striped micelle at time zero with heads (grey) and tails (colored blue, red, green and yellow, distinguishing each lamella) of the CG DDM SCM and (b) the same molecules, each retaining its color, after a 500 ns simulation. *Lower panel*: (c) Blue, red, green and yellow colors are arbitrarily assigned to different portions of a regular SDS micelle at time zero, which mix to form image (d) after a 40 ns simulation.

Now we discuss the dynamics of the surfactants within a striped micelle structure. Surfactants in ordinary cylindrical micelles are labile and can easily diffuse along the micelle. However, a striped cylindrical micelle structure is periodically structured and the surfactants of a particular block cannot readily move along the micelle body. Color-marking the tails of surfactants in different lamellae as shown in **figure 8(a)** at time 0, **Figure 8(b)** shows that after 500 ns (see **video1** in the Supporting Information (**SI**)) the different tail colors do not mix, showing that the surfactants are not able to move along the micelle body. A similar behavior was also observed with the force field for $\lambda = 0.9$ as well. In contrast, in a regular cylindrical micelle formed by SDS, the colors initially assigned to surfactants of different lamellae in **figure 8(c)** are readily mixed in only 40 ns, as shown in **Figure 8(d)** and **video2** in the **SI**. To probe the interlocked motion of the surfactants in a particular block of the SCM structure, we calculated the time dependence of the x, y and z components of the surfactant head group position of three randomly chosen surfactants of a particular block as shown in the schematic diagram of **figure 9(a)**. The components of the position vector were computed with respect to the center of the block. As shown in **figure 9(b)**, the z components of the vector do not change with time although both the x and y components do change suggesting that while the surfactants cannot move along the micelle length, they can diffuse along the radial direction.



(a) (b)

Figure 9: (a) Schematic diagram for calculating the components of the position vector of the surfactant head groups in a particular lamellar block. Blue arrows represent the X, Y and Z directions. The micelle axis is along the Z direction. The black arrow shows the position vector of a surfactant head relative to the center of the block. Red and green are the surfactant heads and tails, respectively. (b) x, y and z components of the position vectors of three randomly chosen surfactant heads as a function of simulation time. 'mol1-x', 'mol1-y' and 'mol1-z' are the x, y and z components of the position vector of molecule 1, respectively. Analogous notations are used for other two molecules.

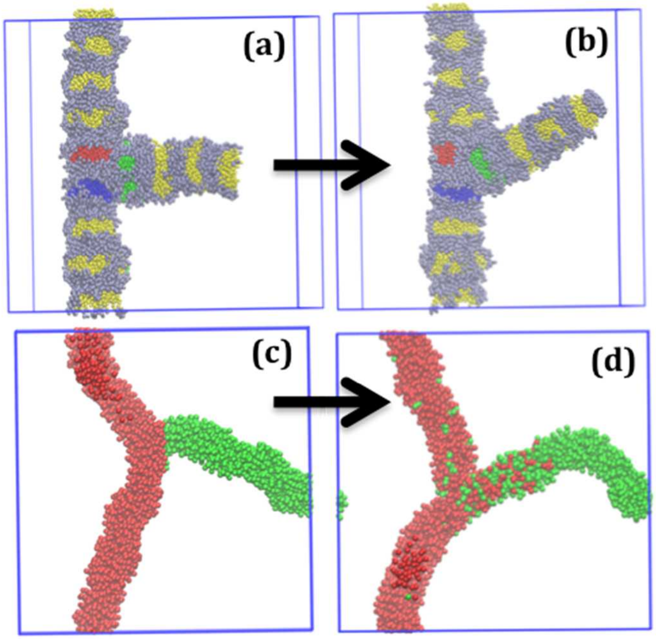


Figure 10: Branched micelle as (a) initially built and (b) after a 500 ns simulation containing DDM surfactants, with blue, red and green showing surfactant tails at the branch junction. A branched CTAC micelle (c) as initially color labeled and (d) after a 90 ns simulation showing migration of surfactants between micelle body and branch. Water, sodium, chlorine and salicylates are left invisible for clarity.

This interdigitation of the surfactants in the striped micelle has also a strong impact on the motion of the branches of the micelles. Branches are known to slide along the body of regular micelles, which gives an extra degree of freedom by which a micellar solution can relax its stress, thus decreasing its viscosity.[30] To investigate the motion of a branch of the striped micelle, a prebuilt branched micelle (**figure 10(a)**) was solvated, energy minimized and equilibrated for 500 ns at atmospheric pressure and temperature. As shown in the **figure 10(b)** and **video 3** in the **SI**, the branch cannot slide along the micelle body, as the surfactants in the micelle body are immobilized by the striped structure. Also, since the surfactants are interdigitated within the blocks, there is no exchange of surfactants between the micelle body and branch and hence the branch can neither grow nor shrink, which contrasts with the behavior of a regular branched micelle. To confirm the surfactant exchange between the micelle body and branch, we simulated a branched micelle composed of cetyltrimethylammonium chloride (CTAC) surfactant in the presence of sodium salicylate (NaSal) salt using the MARTINI coarse-grained force field. We considered this system, because it is well known to form branched micelles[31–33] and moreover, MARTINI force field parameters are available for both the surfactant and organic salt. The diffusion of surfactants between the micelle body and branch and the movement of the branch are shown in **figure 10(c)** and **(d)**. The sliding motion of the branches along micelle body is believed to reduce the viscosity of a micellar solution.[31] Thus, the immobility of the branches of the DDM micelle should significantly impact their viscosity and other rheological properties.

Conclusions: In summary, here we have reported for the first time the formation of a striped cylindrical micelle (SCM) by a specific simple surfactant, namely dodecyl-β-D-maltoside or DDM. The interaction strength between the large head group of DDM surfactant and water is relatively week compared to the interaction of the SDS head with the water. Thus while SDS forms a regular micelle, the DDM surfactants form a striped cylindrical micelle containing lamellar repeats wherein both surfactant heads and tails are in contact with water. Unlike a regular micelle, in a striped micelle the surfactants are locked within the lamellae and hence they cannot diffuse along the micelle body. As a consequence, a branch also cannot slide along the micelle body, which should strongly impact the viscosity of the micellar solutions. Since, unlike a regular micelle, the SCM is inhomogeneous along its length, it would be interesting to know how (in which part) a striped micelle breaks. We plan to consider this in a future study.

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