Supporting Information for

Coarse-Grained Molecular Dynamics Simulation of Self-Assembly and Surface Adsorption of Ionic Surfactants Using an Implicit Water Model

Shihu Wang and Ronald G. Larson*

Department of Chemical Engineering, University of Michigan

2800 Plymouth Avenue, Ann Arbor, Michigan 48109

*rlarson@umich.edu

1. Comparison of Micelle Structures

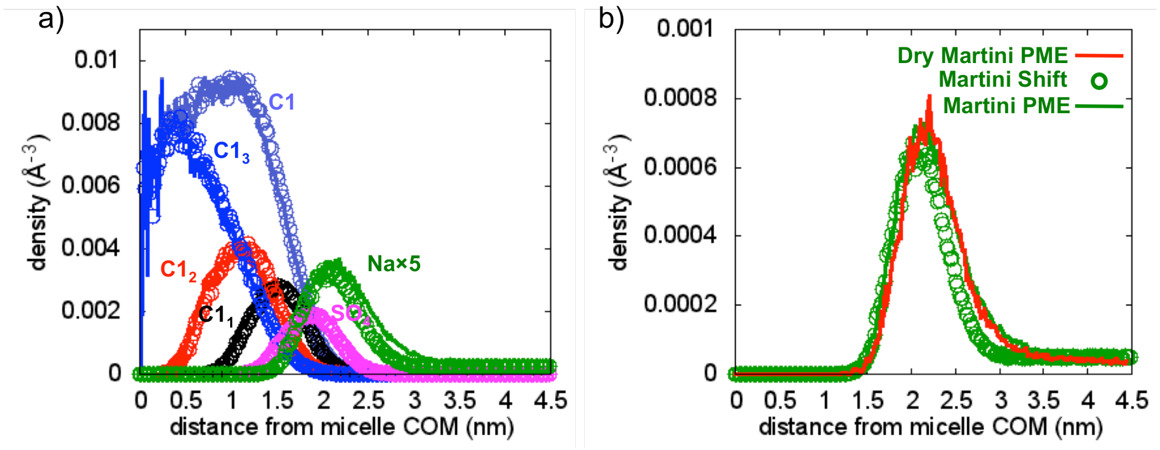

Figure S1. (a) Radial number density as a function of distance from micelle center of mass (COM) of various CG beads, including three C1 (alkane tail) beads as designated in Figure 1a, all C1 beads, and sulfate bead, in a micelle composed of 60 SDS surfactants. The radial density of hydrated sodium ions (Na) beads is multiplied by 5 for clarity. Lines represent calculations using Martini FF with shifted cutoff (1.2nm) and relative permittivity of ε_r=15 and open circles are for standard Martini FF with PME and relative permittivity of ε_r=80. (b) Radial number density of hydrated sodium ions for Dry Martini FF with PME and relative permittivity of

ε_r=150, Martini FF with shifted cutoff (1.2nm) and relative permittivity of ε_r=15, and Martini FF with PME and relative permittivity of ε_r=80. The simulation is performed at 300K.

Shown in Figure S1 are the comparisons of radial number density of different CG beads in an SDS micelle composed of 60 surfactants in a box of 9nm×9nm×9nm at 300K using Martini FF with shifted cutoff (the Coulomb potential is shifted smoothly to zero between 0 and 12Å) and relative permittivity (ε_r) of 15, Martini FF with particle-mesh Ewald (PME) and ε_r=80 and Dry Martini FF with PME and ε_r=150. Combining with the results in Figure 2, we find that in all three cases, the distributions of coarse-grained beads in dodecyl sulfate anion are almost identical. There is only a small difference in ion distribution between the Martini FF with shifted cutoff and the other two cases as shown in Figure S1b: even though the maximum ion density is very similar, its width is slightly smaller due to the shorter cutoff distance and smaller relative permittivity.

2. Effect of Electrostatics On Self-Assembly of Surfactants

2.1 when no salts are added

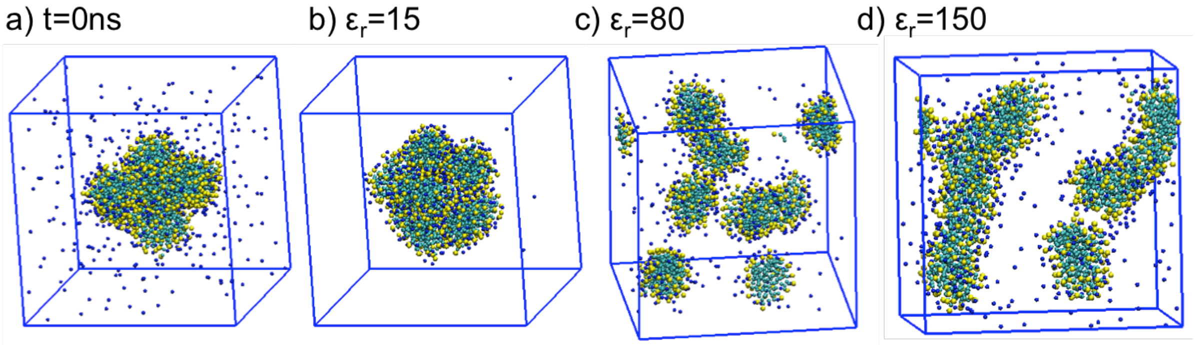

Figure S2. Simulation snapshots for 500 SDS in a box of 16.6nm×16.6nm×16.6nm at (a) t=0ns and (b-d) t=100ns using PME with different relative permittivity (ε_r): (b) ε_r=15; (c) ε_r=80; (d) ε_r=150. SO4 beads are shown in yellow; C1 in cyan; and Na+ in blue. The temperature is 300K.

We performed several different simulations to study the influence of relative permittivity (ε_r) on the clustering of SDS micelles. Shown in Figure S2a is the initial conformation of the simulation that is taken from Figure 6a, i.e. a snapshot from simulation with ε_r=15 and the Columbic interaction shifted to zero from 0 to 1.2 nm. In Figure S2b-d corresponds to 100 ns simulations with PME and different dielectric constants. From the above simulations snapshots, we can see that using PME and ε_r=15 results in clustering of SDS aggregates, even though the conformation of clustered aggregates is different from its initial conformation. Using PME and ε_r=80 does break some clustering, but the micelle size is relatively smaller at this high SDS concentration. As shown below in Figure S3, it causes strong clustering in the presence of salts or very high surfactant concentrations. Using ε_r=150 results in more reasonable results with co-existence of long cylindrical micelles and spherical micelles.

2.2 when salts are added

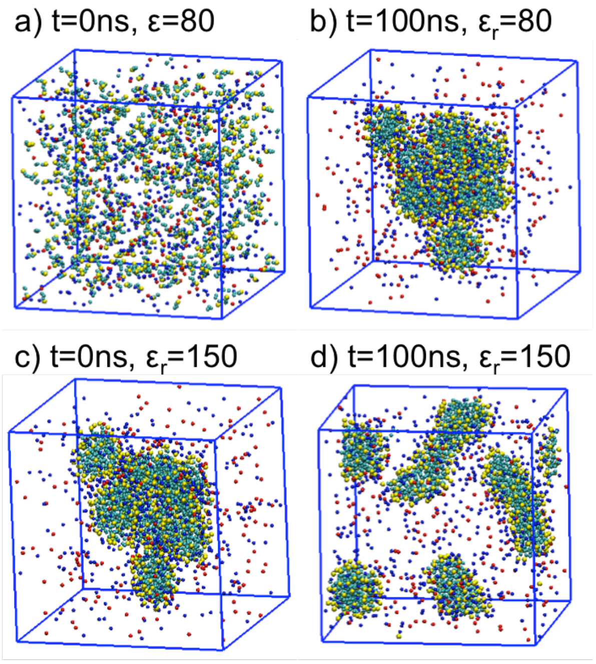

Figure S3. Simulation snapshots for 500 SDS and 200 NaCl in a box of 16.6nm×16.6nm×16.6nm at t=0ns (a) and (c) and t=100ns (b) and (d) using PME with two different relative permittivity (ε_r): part a and b ε_r=80; part c and d ε_r=150. SO4 beads are shown in yellow; C1 in cyan; Na+ in blue and Cl- in red. The simulations are performed at 300K.

Shown in Figure S3 are different scenarios of SDS self-assembly in the presence of salts. All systems are charge neutral. Using PME and a relative permittivity of 80 leads to clustering of SDS aggregates at t=100ns. For the same system, if a relative permittivity of 150 is used, the big cluster of SDS aggregates at t=0ns in Figure S3c breaks after 100ns and both spherical and cylindrical micelles form as seen in Figure S3d.

2. Adsorption of SDS onto Hydrocarbon Slab

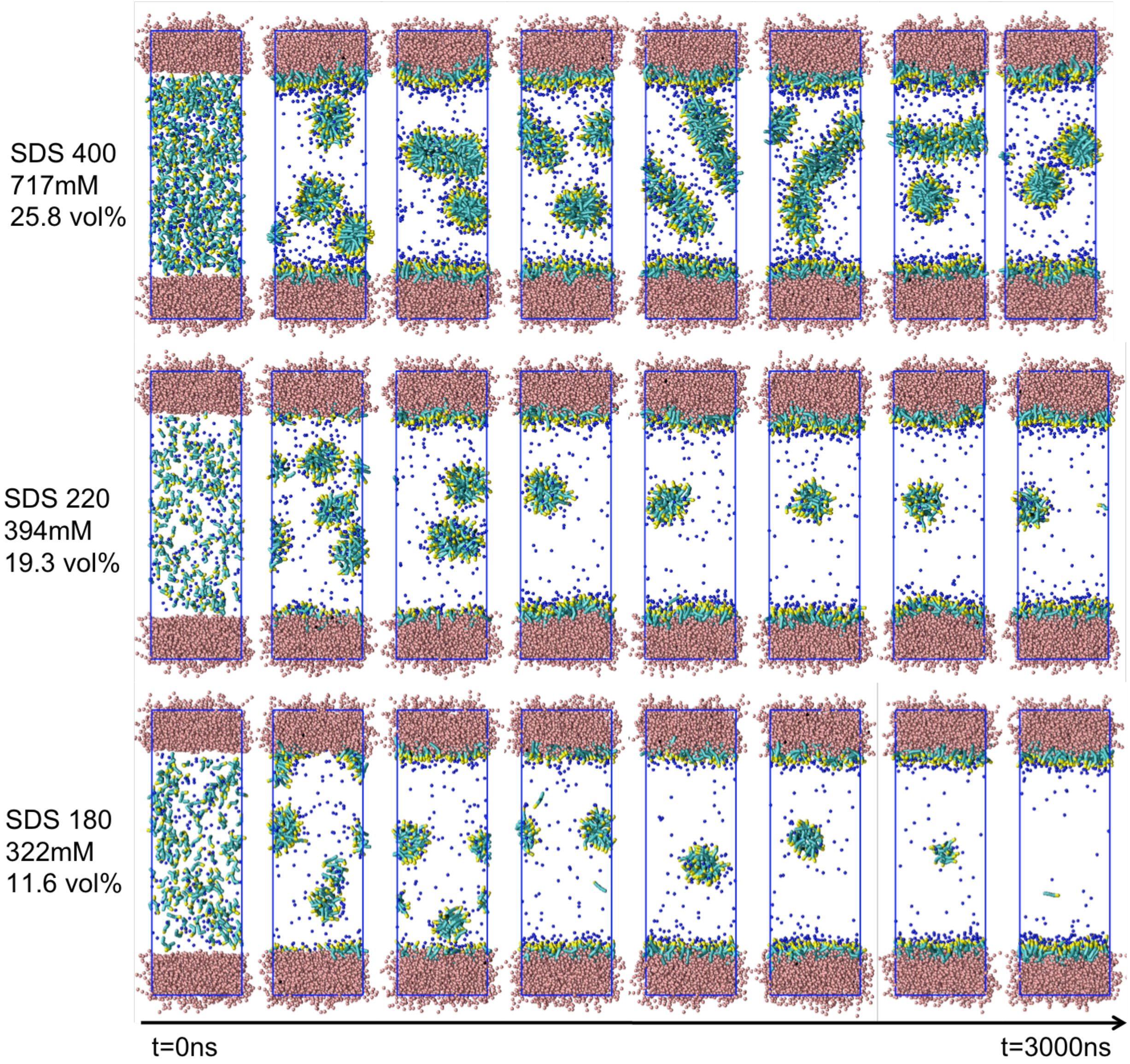

Figure S4. Snapshots from adsorption simulations for three different SDS concentrations. From top to bottom, the numbers of SDS molecules in the system are 400, 220 and 180, corresponding to initial surfactant concentrations in the gallery of 717mM, 394 mM and 322mM and volume fractions in the gallery of 25.8 vol%, 19.3 vol% and11.6 vol%. The hydrocarbon slab is shown in pink. The SDS head groups are shown in yellow and tails in cyan. The sodium ions are shown in blue. The temperature is 323K. Simulation time increases from left to right.

Shown in Figure S4 are simulation snapshots for three different SDS concentrations. For a high SDS concentration (717mM), we observe the formation of spherical and cylindrical micelles in the gallery. They break and reform dynamically. The long cylindrical micelles can sometimes span the periodic box. For an intermediate concentration (394mM), multiple spherical micelles form in the gallery at the beginning of simulation and they gradually fuse into one micelle. At a later time, one micelle is left in the solution while the rest of surfactants are adsorbed on the surfaces. For a relatively low concentration (322mM), we also observe multiple spherical micelles at the beginning of simulation, and again these micelles are either adsorbed by the two surfaces or fuse into one micelle at later time. But with further increase in simulation time, individual surfactants leave the micelle in the gallery and are absorbed on the surfaces. This shrinks the size of the micelle in the gallery until essentially all surfactants are adsorbed, although some surfactants can still leave the surface from time to time and become free in the gallery before they are adsorbed again.

3. Amount of Adsorbed Surfactants

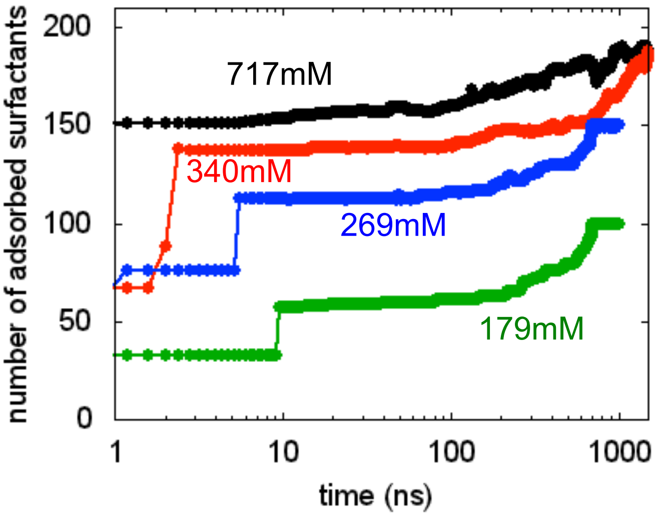

Figure S5. Number of adsorbed surfactants as a function of time for several initial surfactant concentrations. The temperature is 323K.

The number of sulfate dodecyl anions adsorbed onto the hydrocarbon slab surface as a function of time is plotted in Figure S5 for different initial surfactant concentrations. As seen, some sulfate dodecyl anions are adsorbed onto the surface almost immediately. The rest of surfactants in the gallery space form aggregates. For low initial concentrations, such as 179mM or 269mM, this initial adsorption is almost constant for several nanoseconds before a sharp increase in the number of adsorbed surfactants is seen. This sharp increase is caused by the adsorption of a micelle onto the surface. For example, at 179mM, a small micelle with a size of 24 (and at 269mM a slightly large micelle with a size of 37) is adsorbed onto the hydrocarbon surface. For a high initial concentration at 538mM, a larger number of surfactants are absorbed very quickly so that the surface becomes almost saturated. In this case, no big micelles can be further absorbed onto hydrocarbon surface. The gradual increase in the number of adsorbed surfactants (at later time for low surfactant concentration) corresponds to another adsorption process: some surfactants escape their micelles formed in the gallery and are then adsorbed onto the hydrocarbon surfaces. For low surfactant concentrations, such as 179mM or 269mM, we observe that only one single micelle is left in the gallery at a later time. The size of this micelle decreases gradually with time until all surfactants are adsorbed onto surfaces. Snapshots of this process are shown in Figure S4.

4. Interfacial Tension

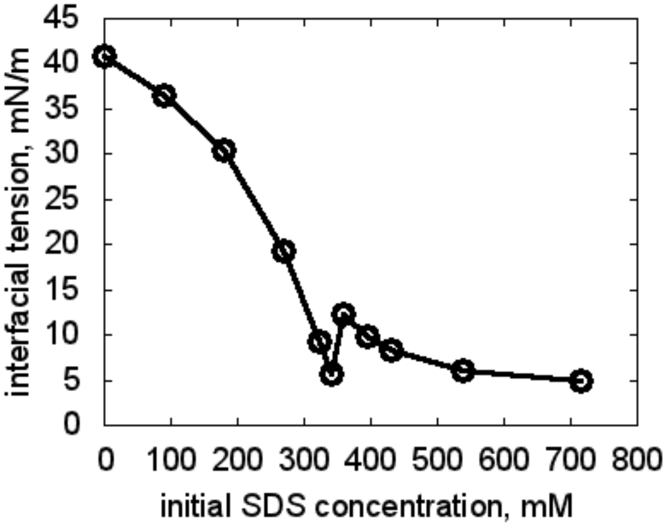

Figure S6. Surface tension as a function of initial SDS surfactant concentration

Shown in Figure S6 is the interfacial tension as a function of initial SDS concentration in the gallery. The interfacial tension of C36/water is 41mN/m at 323K. Upon adsorption of SDS surfactants, interfacial tension decreases quickly. It reaches a minimum around 5mN/m when the surface is saturated by SDS surfactant. A sharp increase in interfacial tension is seen when the surface coverage decrease as seen in Figure 8a due to the formation of a single micelle. Further increase in SDS concentration leads to a continuous decrease in interfacial tension until it reaches the minimum level around 5mN/m.