

## Supporting Information

### Scission Energy and Topology of The Micelles Controlled by Molecular Structure of The Additives

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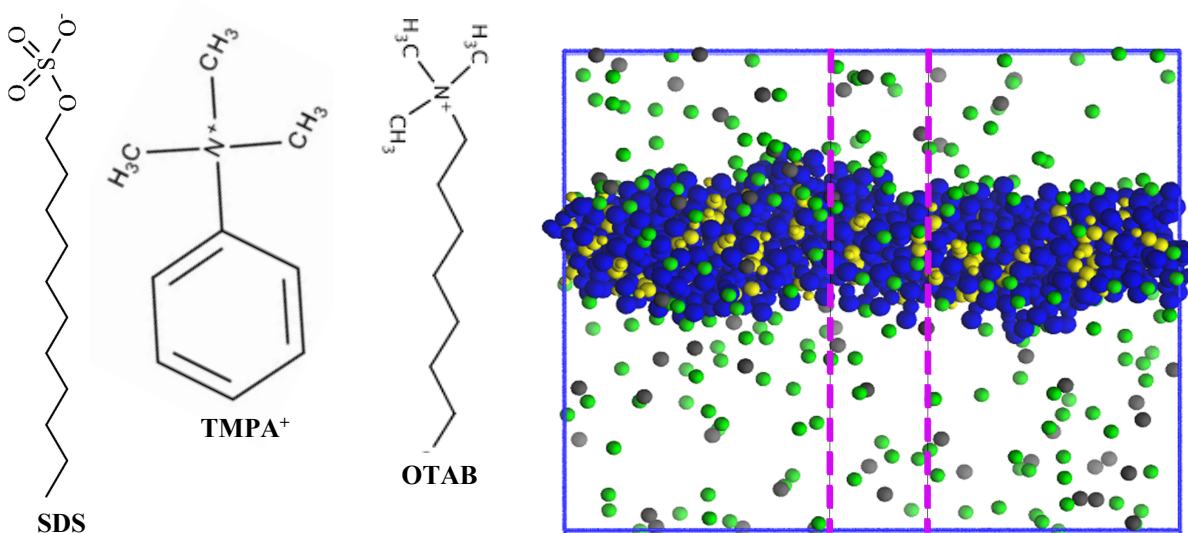


Figure S1: (left panel) Schematic drawing of the chemical structures of SDS, TMPA<sup>+</sup>, and OTAB molecule. (Right panel) an equilibrated SDS/OTAB worm-like micelle structure at  $R = 0.24$ . The micelle is spanning the simulation box along the Z direction. Blue and yellow color represent the SDS surfactant and OTAB additive, respectively. Green and gray color represent the  $\text{Na}^+$  and  $\text{Cl}^-$  ions, respectively. Pink dotted lines represent the scission region. Width of the scission region is 3 nm.

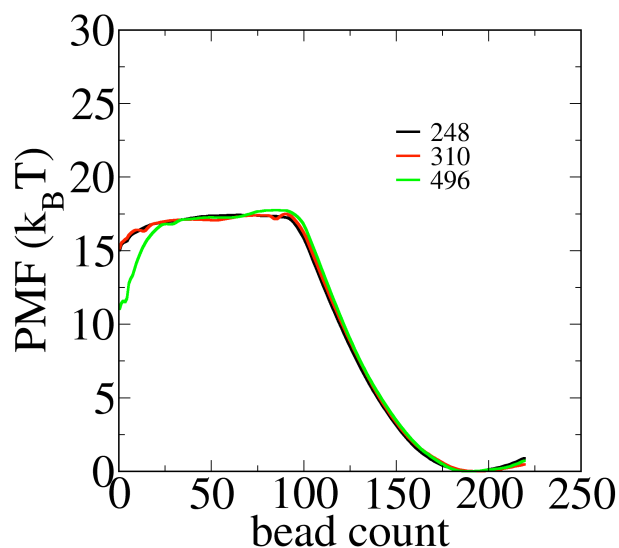


Figure S2: PMF profiles for breaking a worm-like micelle of different length containing 248, 310 and 496 surfactants. The PMFs are calculated at TMPAC to SDS concentration ratio ( $R$ ) = 0.2.

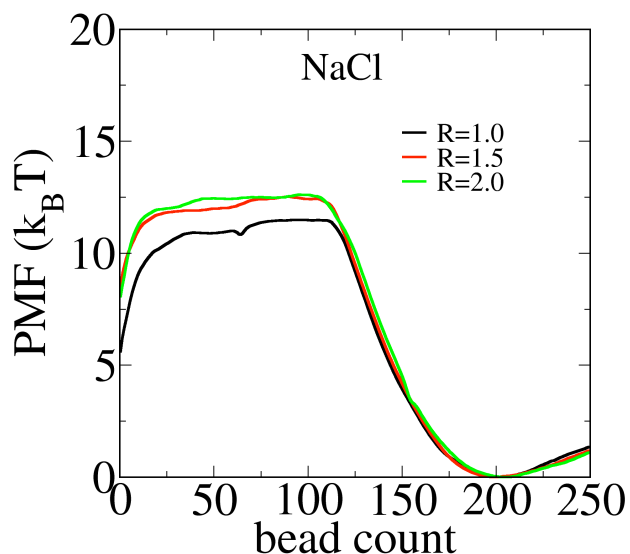


Figure S3: PMF profiles for breaking a worm-like micelle at different NaCl to SDS concentration ratio ( $R$ ). There is no hydrotrope (TMPA<sup>+</sup>) present in the system. Scission energy increases by only  $\sim 1 k_B T$  when  $R$  is increased from 1.0 to 2.0. This is consistent with recent experimental results (see main text) suggesting micelle length and viscosity are weakly affected by the inorganic salt. However, since the effect of the inorganic salts on the micelle scission energy is much weaker, the changes in the scission energy with the concentration of inorganic salt may not be accurately captured using our method.

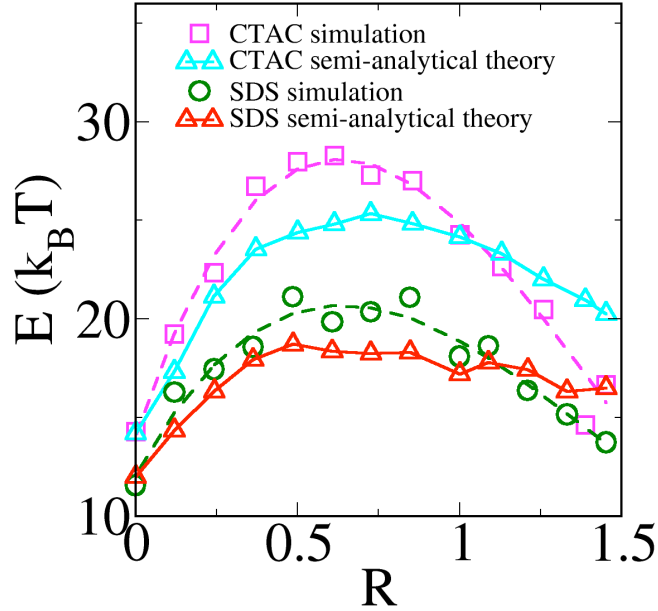


Figure S4: Comparison between the simulated scission energy profile and that obtained from the semi-analytical expression,  $E(n, Q) = An - BQ^2$ .<sup>†</sup> Results are shown for both SDS/TMPAC and CTAC/NaSal micelles. Two constants  $A$  and  $B$  of the semi-analytical expression are calculated in the following way. First,  $A$  is obtained by putting  $Q = 0$  for  $R = 1.14$  and using corresponding  $n = 50$  and  $E(n, Q) = 17.5 K_B T$  from **figure 3** for the SDS/TMPAC case. Value of the constant  $A = 0.35 \text{ nm} \cdot K_B T$ . Using this  $A$  value and  $Q = -16.75e$  and  $n = 67$  for  $R = 0$ , we obtain the value of constant  $B$  to be  $0.041 \text{ nm}^2 \cdot K_B T \cdot e^{-2}$ . Using the values of these constants, we can obtain the scission energy from the expression  $E(n, Q) = An - BQ^2$  at all values of  $R$  with the known  $n$  and  $Q$ . Scission energy obtained from simulations and semi-analytical expression are shown in green and red color, respectively for the SDS/TMPAC micelles. Following similar calculations, we obtain  $A = 0.324 \text{ nm} \cdot K_B T$  and  $B = 0.045 \text{ nm}^2 \cdot K_B T \cdot e^{-2}$  for CTAC/NaSal micelles. Scission energy obtained from simulations and semi-analytical expression are shown in pink and cyan color, respectively for the CTAC/NaSal micelles. We note that the simulation results do not follow the semi-analytical expression exactly because the surfactant density is not likely to be uniform throughout the micelle.

<sup>†</sup>The first term indicates micelle scission energy increases with the micelle cross section. Total number of surfactant beads in the scission region which can be approximate as a small cylindrical of length  $l$ , can be written as  $N = \rho\pi r^2 l$ , assuming surfactant density  $\rho$  is uniform throughout the micelle of radius  $r$ . This suggest micelle cross-section ( $\pi r^2$ ) is proportional to number of surfactants per unit length,  $n (= N/l)$ .

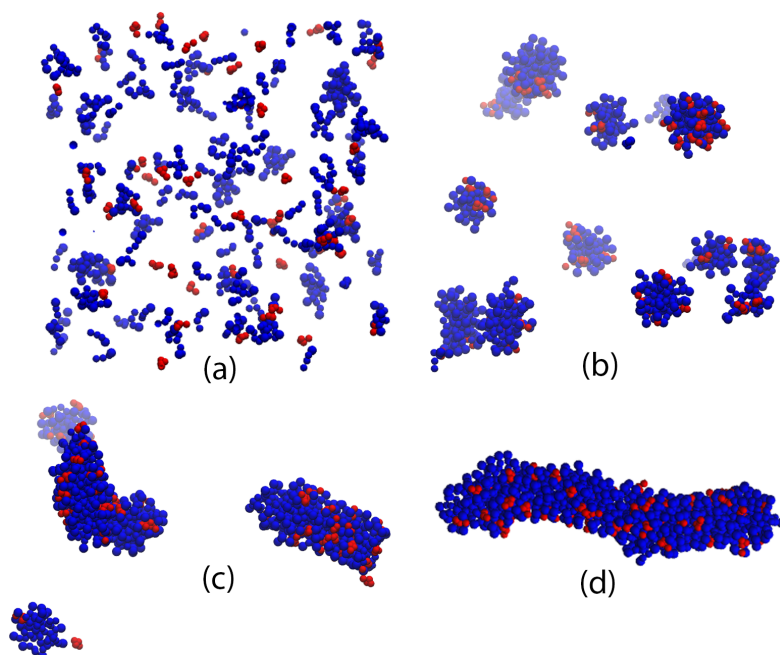


Figure S5: Different stages of the self-assembly of the SDS/TMPAC system for  $R = 0.2$  at (a) the beginning of the simulation (b) 80 ns (c) 500 ns and (d) 1000 ns. Blue and red color represent SDS and TMPAC respectively.  $\text{NA}^+$ ,  $\text{CL}^-$  ions and water beads are removed for clarity.

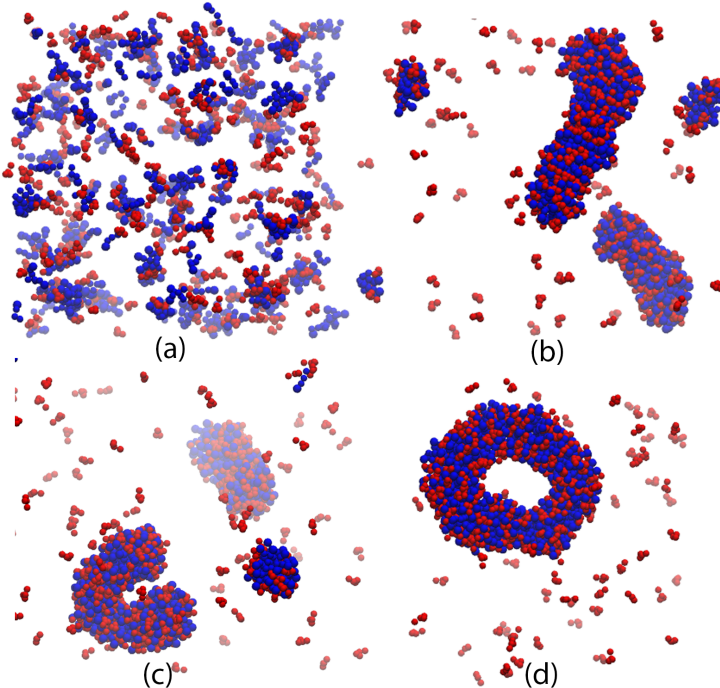


Figure S6: Different stages of the self-assembly of the SDS/TMPAC system for  $R = 1.0$  at (a) the beginning of the simulation (b) 160 ns (c) 170 ns and (d) 600 ns. Blue and red color represent SDS and TMPAC respectively.  $\text{NA}^+$ ,  $\text{CL}^-$  ions and water beads are removed for clarity.

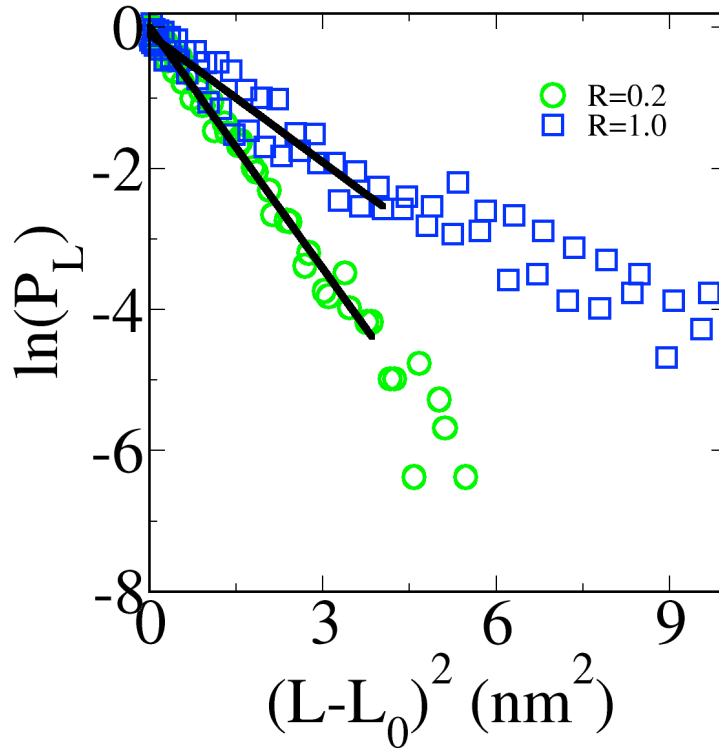


Figure S7:  $\ln(P_L)$  as a function of  $(L - L_0)^2$  for  $R = 0.2$  and  $R = 1.0$ . See text below for details.

SDS/TMPAC micelle thickness decreases with TMPAC hydrotrope concentration which should increase the micelle flexibility and hence should decrease the bending rigidity. We estimate the micelle flexibility of a periodic worm-like micelle from the box length fluctuations along the micelle axis. The energy cost associated with a small deviation in micelle length,  $(L - L_0)$ , from its equilibrium value  $L_0$  is given by  $E \sim K(L - L_0)^2$ , where  $L$  is the instantaneous length of the micelle and  $K$  is constant. The probability distribution of end-to-end distance  $P_L$  can be expressed as  $\ln(P_L) = -C(L - L_0)^2$ , where  $C$  is a positive constant related to micelle flexibility, whose value decreases with increasing flexibility. In **figure S5**, we plot  $\ln(P_L)$  vs  $(L - L_0)^2$  for  $R = 0.2$  and  $1.0$  and the corresponding  $C$  values are  $1.14 \text{ nm}^{-2}$  and  $0.60 \text{ nm}^{-2}$ , respectively. Clearly, the micelle is more flexible at  $R = 1.0$  than at  $R = 0.2$ .

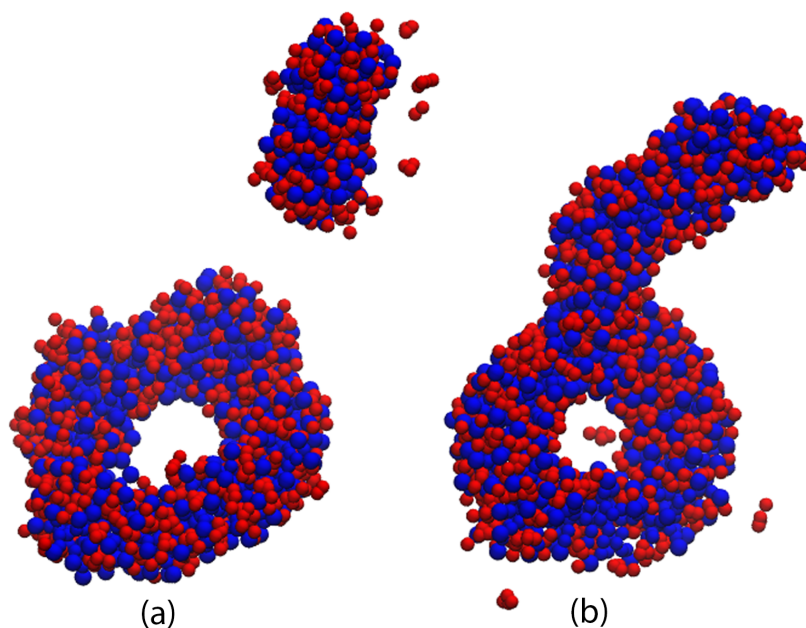


Figure S8: Formation of a ring-like structure attached to cylindrical micelle at  $R = 1.5$  in the SDS/TMPAC system. (a) SDS surfactants (blue) and TMPAC hydrotropes (red) first self-assemble to form ring-like and cylindrical micelles. (b) one end of the cylinder is then fused with the ring surface. Similar structure was synthesized from block copolymers as shown in **figure S9(b)**.

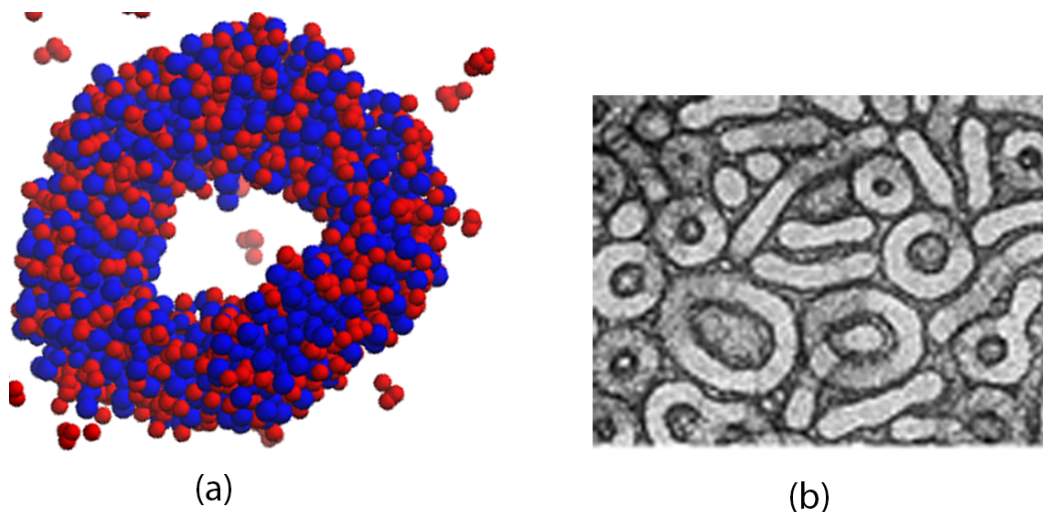


Figure S9: (a) Ring-like or toroidal shaped micelle sampled from an independent simulation other than shown in **figure S6**. (b) TEM images of worm-like, ring-like, and ring-like structure attached to cylindrical micelles synthesized experimentally from block copolymers. The figure is adapted from the **reference [72]** in the main text.

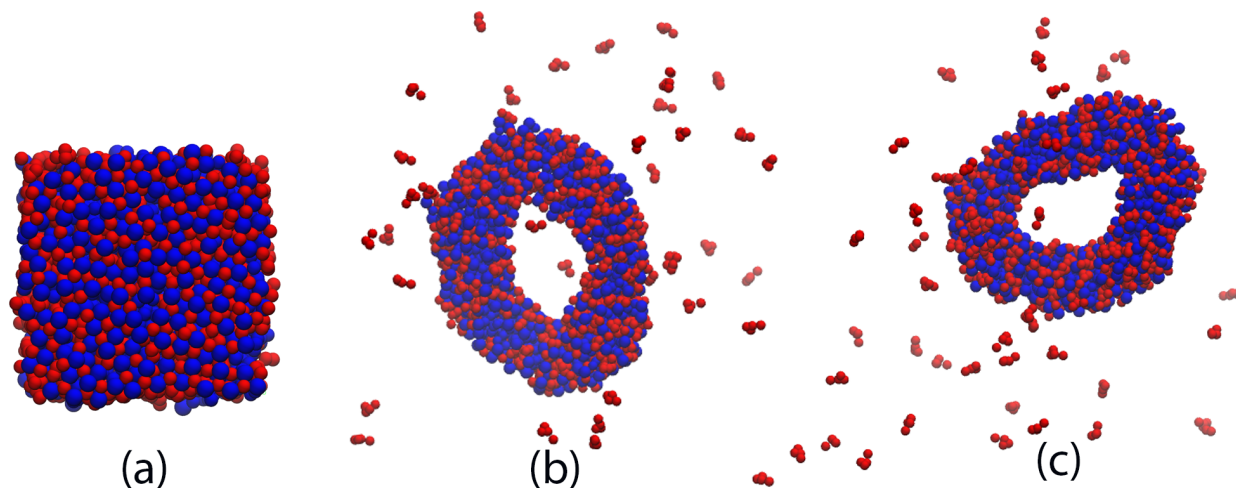


Figure S10: Snapshots at different stages (a) 0 ns (b) 100 ns, and (c) 2000 ns during lamella-to-toroid structure transformation at  $R = 1.0$ . Water,  $\text{Na}^+$  and  $\text{Cl}^-$  beads are removed for better visibility.

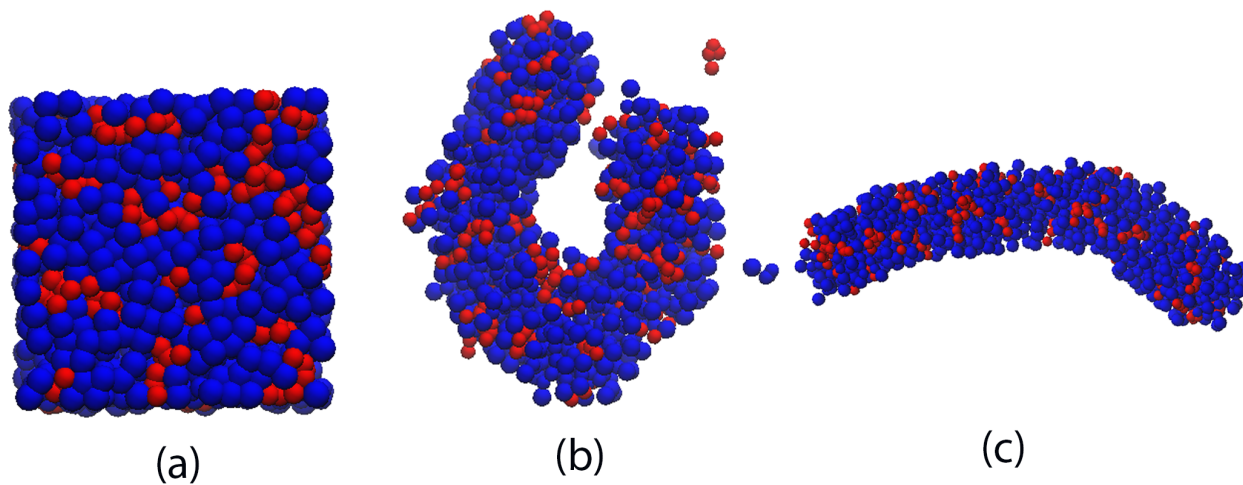


Figure S11: Snapshots at different stages (a) 0 ns (b) 10 ns, and (c) 1500 ns during lamella-to-linear micelle structure transformation at  $R = 0.2$ . Water,  $\text{Na}^+$  and  $\text{Cl}^-$  beads are removed for better visibility. All of the  $\text{TMPA}^+$  ions remain adsorbed on the micelle surface at  $R = 0.2$ .

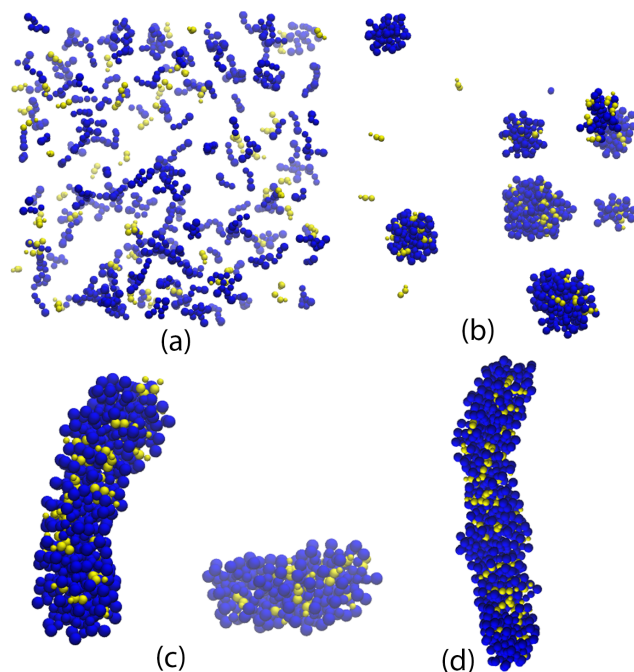


Figure S12: Different stages of the self-assembly of the SDS/OTAB system for  $R = 0.2$  at (a) the beginning of the simulation (b) 100 ns (c) 500 ns and (d) 1200 ns. Blue and yellow color represent SDS and OTAB respectively.  $\text{NA}^+$ ,  $\text{CL}^-$  ions and water beads are removed for clarity.

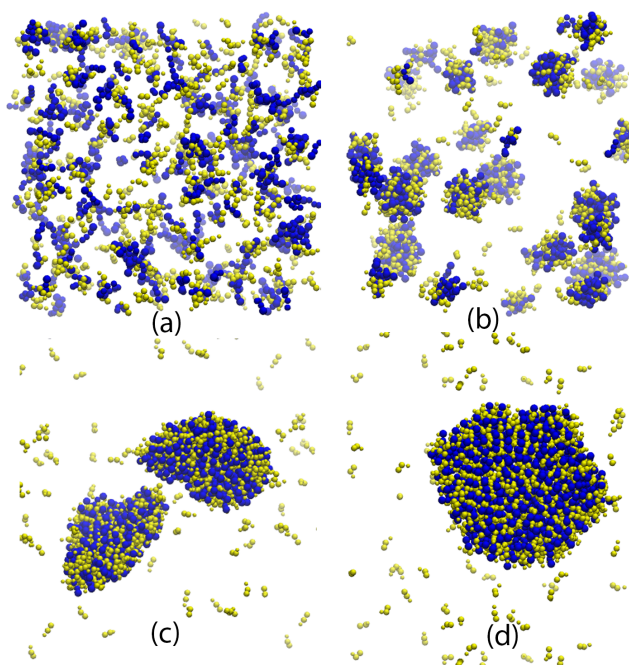


Figure S13: Different stages of the self-assembly of the SDS/TMPAC system for  $R = 1.5$  at (a) the beginning of the simulation (b) 20 ns (c) 200 ns and (d) 400 ns. Blue and red color represent SDS and TMPAC respectively.  $\text{NA}^+$ ,  $\text{CL}^-$  ions and water beads are removed for clarity.



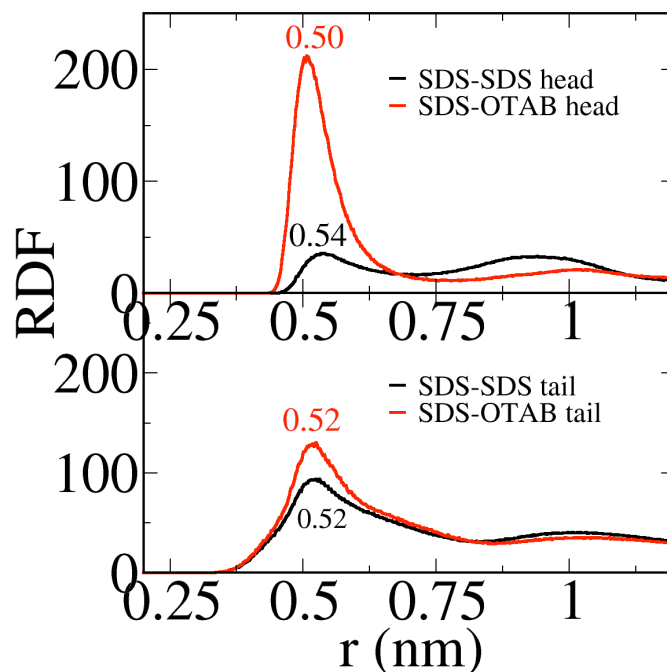


Figure S14: Radial distribution functions (RDF) between different parts of the SDS and OTAB molecules. Different numbers on the plots indicate the location of the first peaks. In a pure SDS micelle, the distance between two neighbor heads is 0.54 nm, and the distance between centers of two neighbor tails is 0.52 nm. In the SDS/OTAB micelle, the distance between neighbor SDS and OTAB heads is 0.50 nm, and the distance between neighbor SDS and OTAB tails is 0.52 nm.

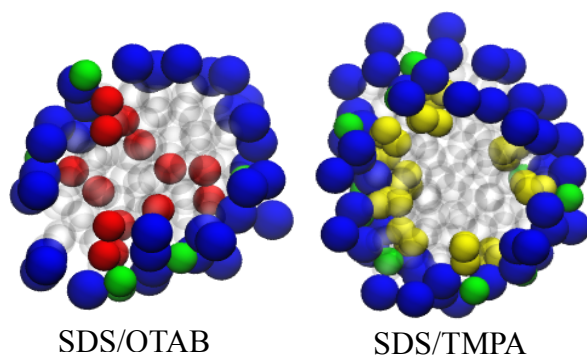


Figure S15: Cross-sectional view of worm-like micelles formed by (left panel) OTAB and (right panel) TMPAC additives. Red and yellow spheres represent the OTAB tail and TMPAC tail, respectively. SDS head and tails are shown by blue and transparent white spheres, respectively. Heads of the OTAB and TMPAC are shown by green spheres. OTAB tails (red) penetrate deep inside the micelle core and pack well with the SDS tails.