Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

The Self-assemble Structure and the CO_2-philicity of Hybrid Surfactant in Supercritical CO_2: Effects of Hydrocarbon Chain Length

*Muhan Wang [a], Timing Fang [a], Pan Wang [a], Xinpeng Tang [a], Baojiang Sun [c], Jun Zhang [a, b, *], Bing Liu [a]*

[a] College of Science, China University of Petroleum, 266580 Qingdao, Shandong, China

[b] Key Laboratory of New Energy Physics & Materials Science in Universities of Shandong, China University of Petroleum, 266580 Qingdao, Shandong, China

[c] School of Petroleum Engineering, China University of Petroleum, 266580 Qingdao, Shandong, China

* Corresponding author at: College of Science, China University of Petroleum, 266580 Qingdao, Shandong, China. Tel.: +86 0532-86983366.

E-mail address: zhangjun.upc@gmail.com (Jun Zhang).

S1 - The Folding of Dihedral Angle Distributions

The OPLS force field is expressed as:

$$E_{total} = E_{bonds} + E_{angles} + E_{dihedrals} + E_{nonbonded} \quad (1)$$

$$E_{bonds} = \sum_{bonds} K_r(r - r_0)^2 \quad (2)$$

$$E_{angles} = \sum_{angles} K_\theta(\theta - \theta_0)^2 \quad (3)$$

$$E_{dihedrals} = \sum_{dihedrals} \left(\frac{V_1}{2}[1 + cos(\varphi - \varphi_1)] + \frac{V_2}{2}[1 - cos(2\varphi - \varphi_2)] + \frac{V_3}{2}[1 + cos(3\varphi - \varphi_3)] + \frac{V_4}{2}[1 - cos(4\varphi \right. \quad (4)$$

$$E_{nonbonded} = \sum_{i>j} \left[\varepsilon_{ij} \left(\frac{\sigma^{12}}{r_{ij}^{12}} - \frac{\sigma^6}{r_{ij}^6} \right) + \frac{q_i q_j e^2}{4\pi\varepsilon_0 r_{ij}} \right] \quad (5)$$

Where E_{total} is the total energy in the system which is equal to the energy of bond stretching (E_{bonds}) plus angles shake (E_{angles}) plus dihedrals shake ($E_{dihedrals}$) plus pairwise ($E_{nonbonded}$). The force field parameters of F7Hn surfactants are shown in the moltemplate files which are named as moltemplate.txt.

S2 - Self-assemble process of F7H1, F7H4 and F7H10

The parallel simulations of self-assembly of FmHn surfactants with different hydrocarbon (HC) chain length (F7H10, F7H4 and F7H1) were shown in Figure S2-1 S2-2 and S2-3. The similar self-assemble process of F7Hn with F7H7 have been shown in others self-assembly.

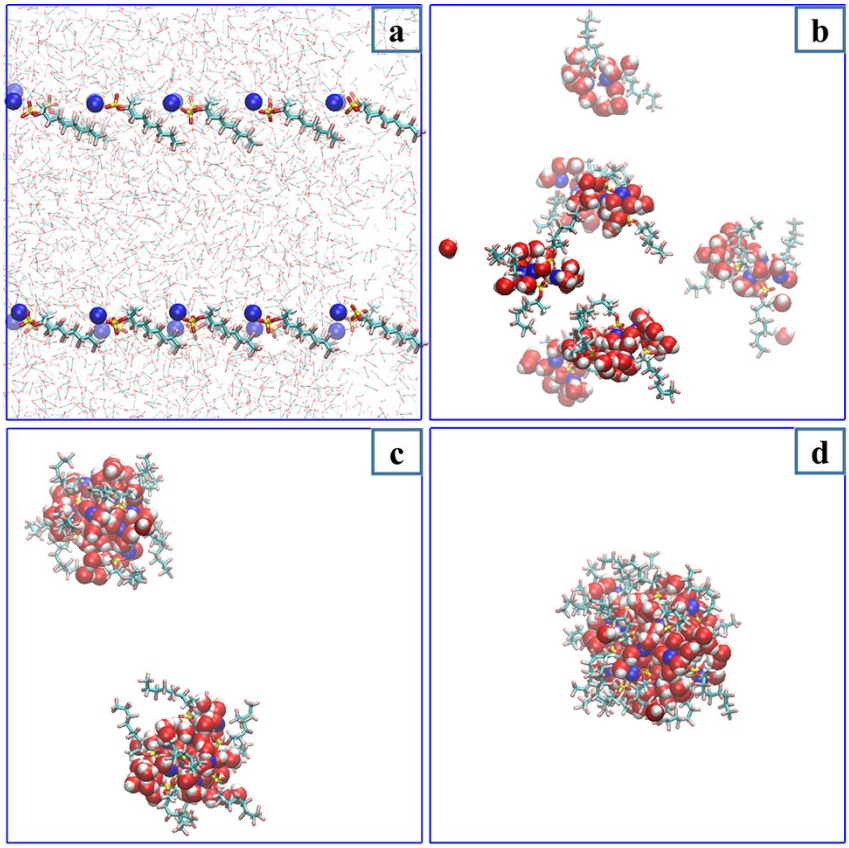


Figure S2-1. Time evolution of the ternary mixture of water/F7H1/CO_2 at W_0 = 6.25. Snapshots are taken at (a) 0 ns (b) 0.4 ns (c) 2 ns (d) 2.6 ns. Color scheme: red = oxygen; gray = carbon; brown = fluorine; white = hydrogen; yellow = sulfur; blue balls = sodium. In (b-d), CO_2 is omitted for clarity.

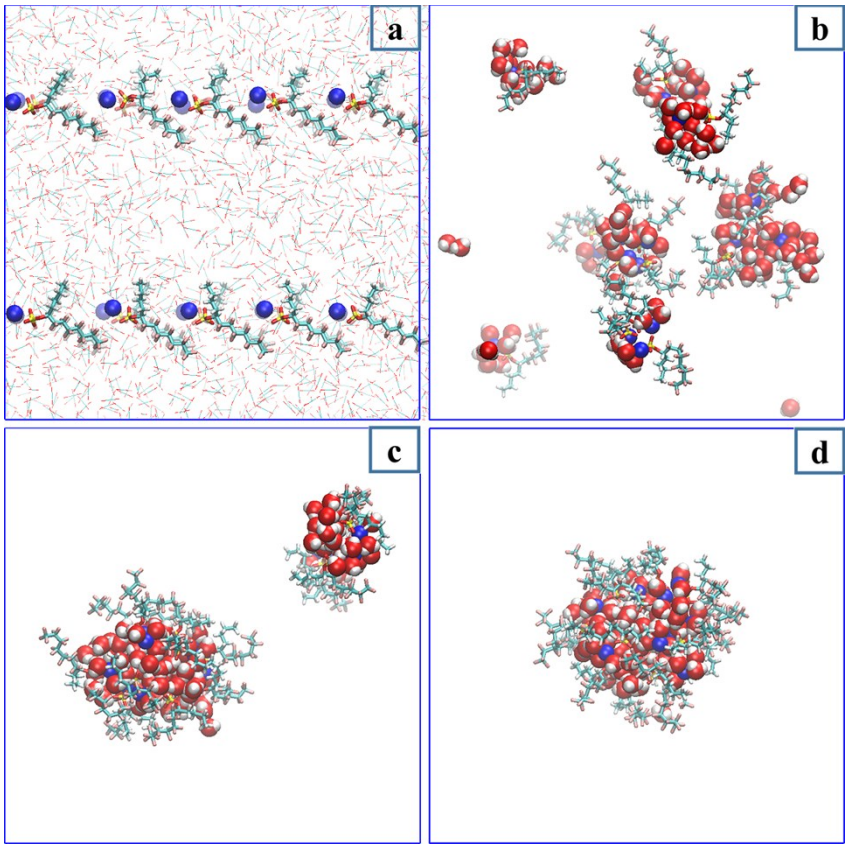


Figure S2-2. Time evolution of the ternary mixture of water/F7H4/CO_2 at W_0 = 6.25. Snapshots are taken at (a) 0 ns (b) 0.4 ns (c) 2 ns (d) 5.5 ns.

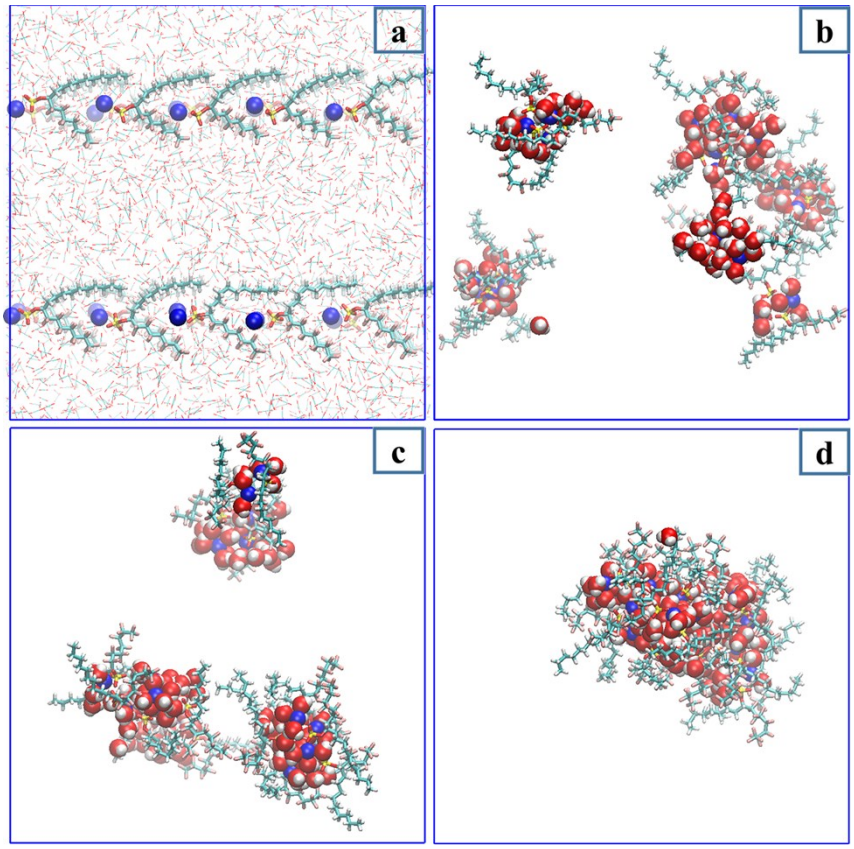
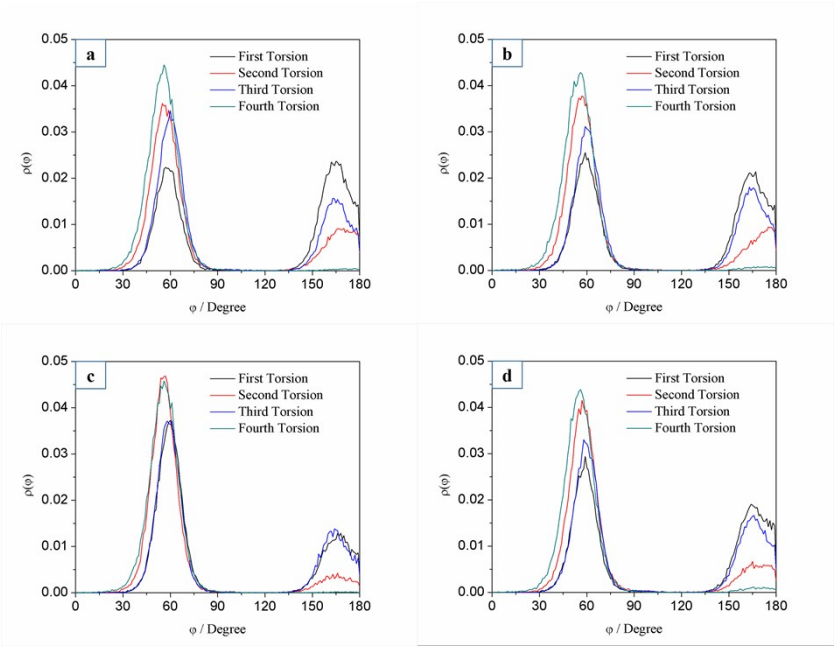


Figure S2-3. Time evolution of the ternary mixture of water/F7H10/CO_2 at W_0 = 6.25. Snapshots are taken at (a) 0 ns (b) 0.4 ns (c) 2 ns (d) 6.4 ns.

S3 - The distributions of dihedral angle on fluorocarbon chain

The distributions of dihedral angle are well matching the chain length distributions. Figure S3 shows that all of dihedral angle on the fluorocarbon (FC) chains prefer to curve at a similar range around 60° and 180°. But in the F7H10 and F7H7, the dihedral angle exhibit a similar high peak between the 180° and the 60°. Then F7H1 dihedral distribution shows slight lower peak on the 180°. In F7H4, almost all the dihedral angles are distributed near 60°. The dihedral angle shifting from 180° to 60° indicates the FC chain conformation become shorter. Such shifting of dihedral angle point out why F7H4 FC chain length only distribute in one peak. According to the knowledge of conformation, the 60° dihedral angle exhibit a metastable characteristic referred to synclinal conformation. It require interaction to cross the energy barrier from anti-periplanar conformation (180° dihedral angle). And the interaction will be most significant on the F7H4 system.



S3. The dihedral angles distributions of fluorocarbon tail of (a) F7H10, (b) F7H7, (c) F7H4 and (d) F7H1. Numbered beginning with the C (connecting headgroup carbon) –C (CF2)-C (CF2)–C (CF2) fragment.