Shape Transition of Water-in-CO_2 Reverse Micelles: Controlled by Surfactant Midpiece

*Muhan Wang,[a] Junfeng Wang,[a] Timing Fang,[a] Youguo Yan,[a] Zhiyuan Wang,[*b] and Jun Zhang,[*a]*

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

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

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* 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).

E-mail address: wangzy1209@126.com. (Zhiyuan Wang).

S1 - The Details of OPLS Force Field

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 ($E_{nonbonded}$).

S2 – The Interfacial Tension Calculation

The interfacial tension was calculated using the formulation of the Gibbs interfacial tension.[1] Two interfaces are both perpendicular to the z axis and parallel to the xy plane, hence the interfacial tension is evaluated from the expression of pressure tensor[2]:

$$IFT = -\frac{1}{2}\left(\frac{P_x + P_y}{2} - P_z\right)L_z \tag{6}$$

Where P_i (i = x, y, z) is the diagonal elements of the pressure tensor, and L_z is the length of the simulation box in z direction.

S3 – The Repeat MD Trajectory

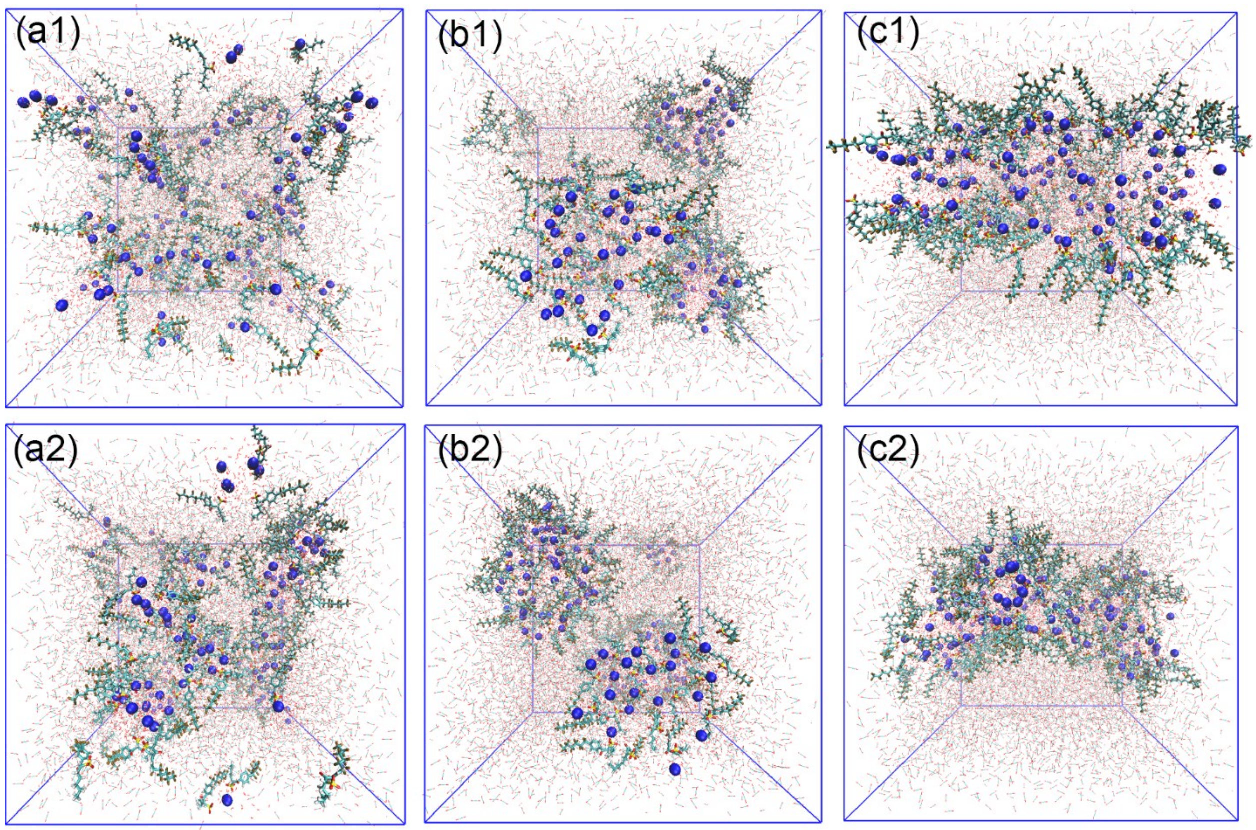

Figure S1. The repeated time evolutions of phenyl FC6-HC5 surfactant self-assembly. (a1) or (a2) 0 ns, (b1) or (b2) 2 ns, (c1) or (c2) 20 ns

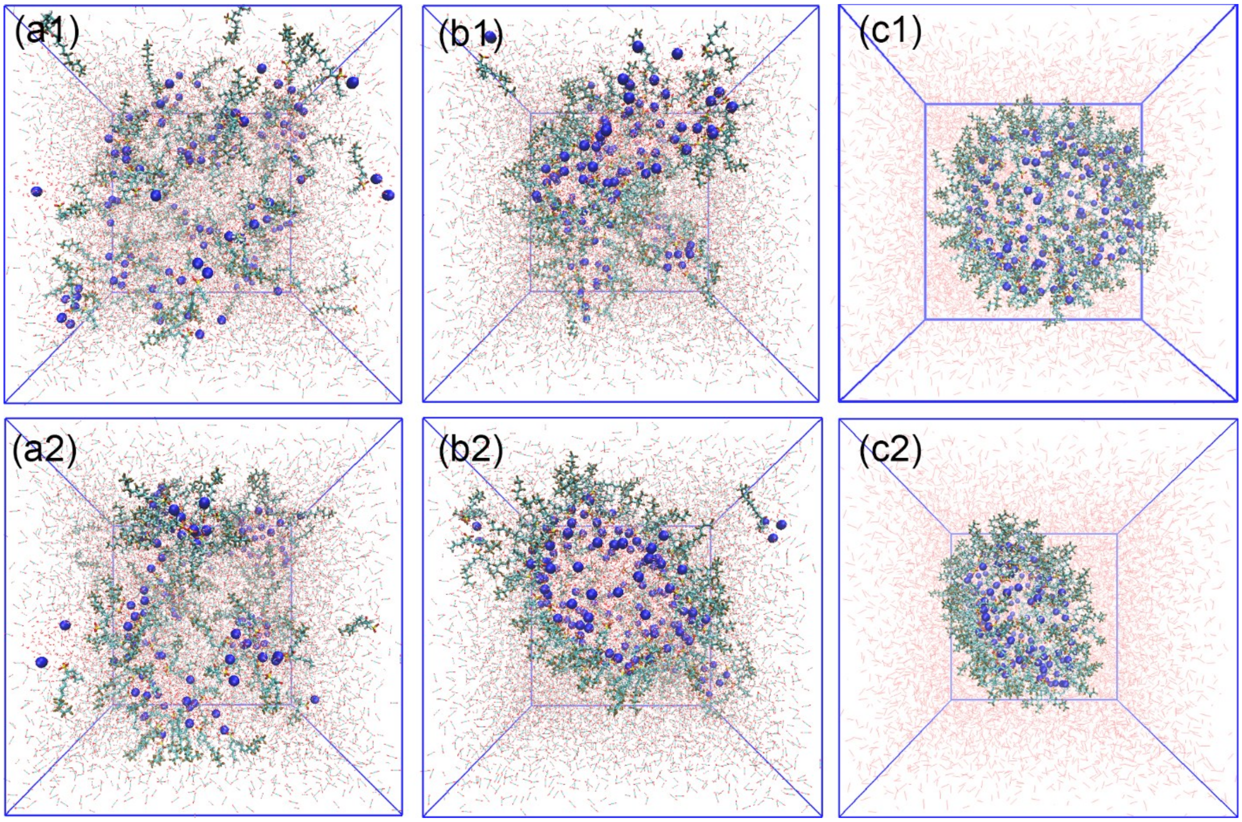

Figure S2. The repeated time evolutions of alkyl FC6-HC5 surfactant self-assembly. (a1) or (a2) 0 ns, (b1) or (b2) 10 ns, (c1) or (c2) 20 ns

S4 – Aspect Ratio of Rod-like Reverse Micelles

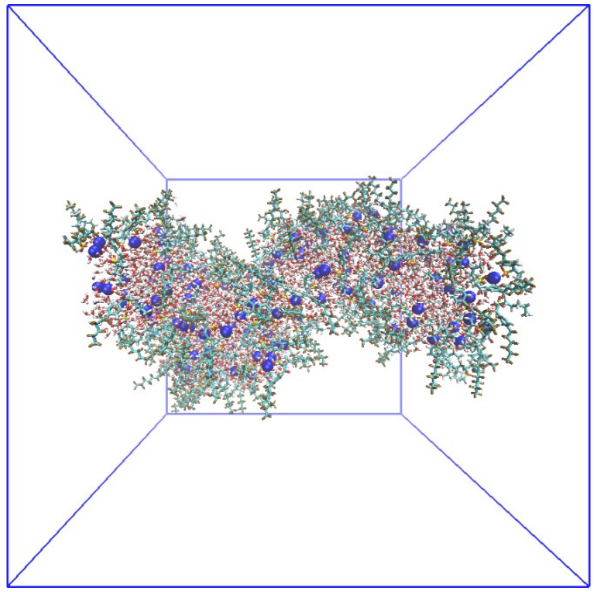

Figure S3. The periodic boundary condition of simulation box.

Due to the periodic boundary condition of simulation the length of rod-like RM is 99.7 Å. And the radius of rod-like RM is 24.16. Therefore, the Aspect Ratio of Rod-like Reverse Micelles is 0.24.

S5 – The Free Volume Calculation

The free volume of phenyl FC6-HC5 and alkyl FC6-HC5 have been calculated in Figure S1. We used radius of 1.5 Å, due to the van der Waals radius of CO_2. According to previously studies,[3] surfactant CO_2-philicity were high related with their free volumes. The higher free volumes is, the higher CO_2-philicity will be.

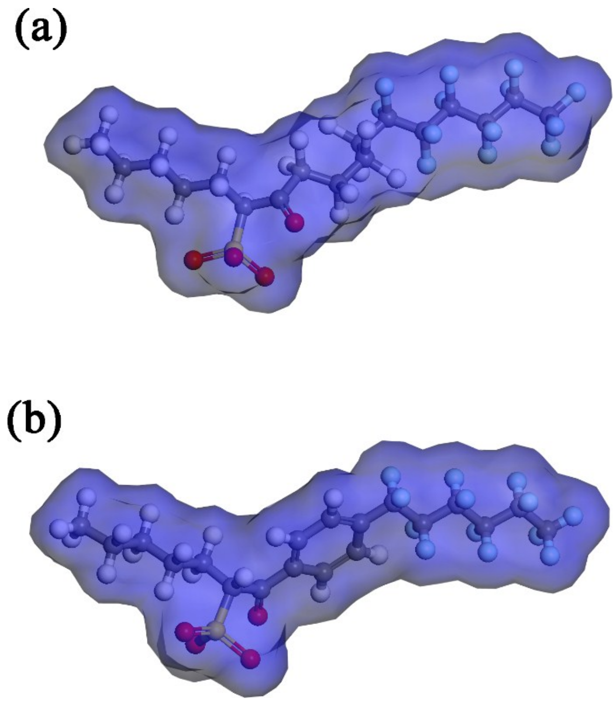

Figure S4. The free volume of (a) alkyl FC6-HC5 and (b) phenyl FC6-HC5

The free volume of alkyl FC6-HC5 is 2561 Å3 and the free volume of phenyl FC6-HC5 is 2507. There are only 2% difference, which indicates that they have similar CO_2-philicity.

S6 –The Detail of Umbrella Sampling Method

In this paper, all the PMF profiles were calculated by the Umbrella Sampling (US) method[4] using the *Colvars* software[5]. Us is already used for calculating the PMF profiles in MD simulations.[6-7] The example of detail configuration as follow:

```
colvarsTrajFrequency    100
colvarsRestartFrequency  5000
colvar {
  name US
  width 0.1
  lowerboundary 0.0
  upperboundary 50.0
  lowerwallconstant 10.0
  upperwallconstant 10.0
   distance {
    #forceNoPBC    yes
     group1 {
        atomNumbersRange { #Group 1# }
     }
     group2 {
        atomnumbersRange { #Group 2# }
    }
   }
  }
harmonic {
colvars US
forceConstant 0.01
centers 50
targetCenters 10
targetNumStages 40
targetNumSteps 200000
outputCenters on
}
```

S7 – Calculation of the Order Parameter

The order parameter can evaluate whether the molecules are ordered, which is mostly used in nematic liquid-crystal.[8]

Moreover, the order parameter is relevant parameter to evaluate the molecular arrangement and the aggregation structures which is expressed as follow:

$$S_m = \frac{1}{2}\langle 3cos^2\beta - 1\rangle \tag{7}$$

In the equation, β is the angle between two orientations of the vector along the head to carbon on the surfactant backbone. A value of 1 means that the vectors are parallel, a value of -0.5 means that the vectors are perpendicular, and 0 suggests random orientation.

S8 – Definition of Included Angle Calculation

The definition of included angle (θ) is the angle of two surfactant fluorocarbon tail which is shown in Figure S2.

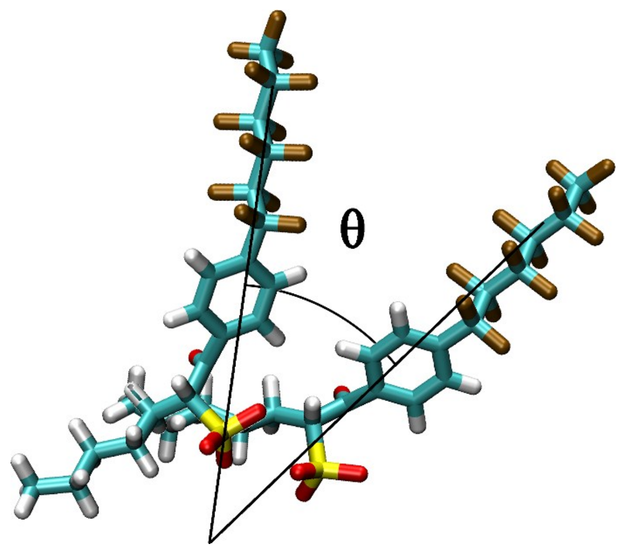

Figure S5. Definition of included angle calculation.

The included angle could be used to analyze the arrangement of surfactant on the interface of RMs.

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