Electronic Supplementary Information

Optimal Aggregation Number of Reverse Micelles in Supercritical Carbon Dioxide: A Theoretical Perspective

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S1 - The Details of MD Simulations and Calculation Methods

The OPLS includes the pairwise and the bonding interaction. The pairwise interaction is composed two part of the short range van der Waals (vdW) and the long range electrostatic interaction. The vdW interaction is represented by 12-6 Lennard-Jones potential and the electrostatic interaction is represented by Coulombic potential. For the bonding interaction, it includes three components of bond stretching, angle bending and dihedral torsion. The OPLS force field is expressed as:

$$E_{total} = E_{bonds} + E_{angles} + E_{dihedrals} + E_{nonbonded} \tag{1}$$

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

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

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

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

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 TC14 are modelled using the all-atom OPLS parameters[1-2] and the work of Canongia Lopes J N et al.[3]

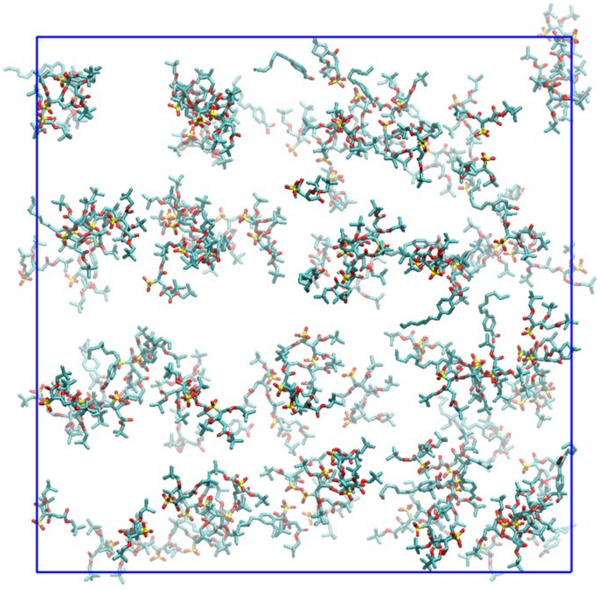

Fig. S1. The initial conformation of MD simulation. Color scheme: red = oxygen; green = carbon; white = hydrogen; yellow = sulfur. For clarity, all the CO_2 and water molecules is omitted.

S2 - 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
}
```

S3 – Calculation of the Free Energy of the RMs System

We assume that there are M surfactant in the system and all RMs in this system contain N surfactant. The free energy of RMs with N surfactants is the G_N. According the pulling process, the G_N. can be calculated by formula (6):

$$G_N = \Delta E_2 + \Delta E_3 + \cdots\cdots + \Delta E_N \tag{6}$$

In the system, there are $\frac{M}{N}$ surfactants. Therefore, the total free energy of the RMs system is:

$$G = \frac{M \times (\Delta E_2 + \Delta E_3 + \cdots\cdots + \Delta E_N)}{N} \tag{7}$$

We discuss that if the total number of surfactants M is constant. The the free energy (G(N)) of the RMs system that formed by N surfactants can be calculated by formula (8).

$$G(N) = \frac{\Delta E_2 + \Delta E_3 + \cdots\cdots + \Delta E_N}{N} \tag{8}$$

S4 – Radial Density Profiles of Different Number of Surfactants

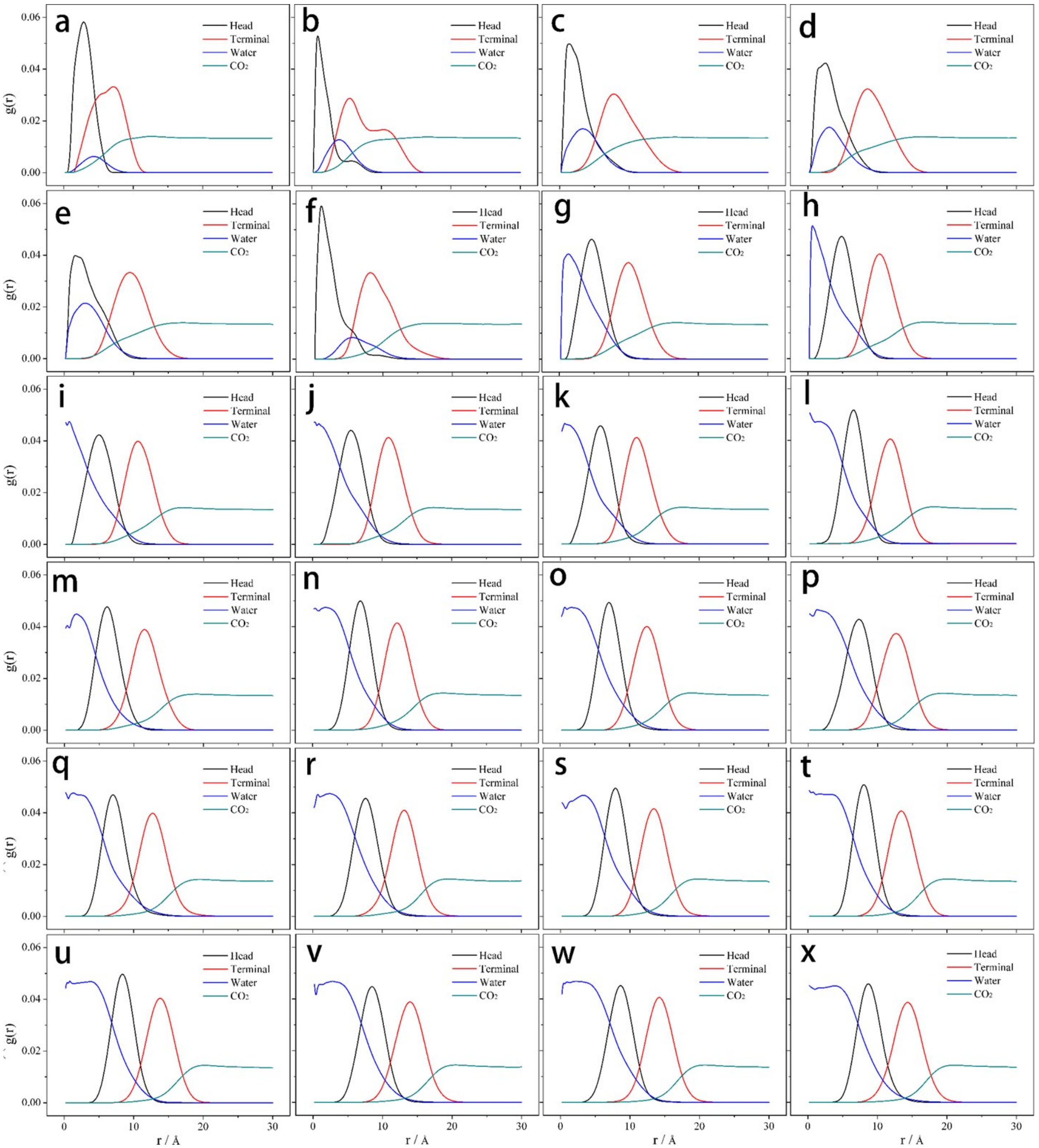

Fig. S2. The radial density profiles of number of surfactants (a) N = 2, (b) N = 3, (c) N = 4, (d) N = 5, (e) N = 6, (f) N = 7, (g) N = 8, (h) N = 9, (i) N = 10, (j) N = 11, (k) N = 12, (l) N = 13, (m) N

= 14, (n) N = 15, (o) N = 16, (p) N = 17, (q) N = 18, (r) N = 19, (s) N = 20, (t) N = 21, (u) N = 22, (v) N = 23, (w) N = 24, (x) N = 25.

In the optimal area, there is a clear core-shell structure. In the lower area, the water phase overflows the surfactant head-group shell. On this condition, we can infer that the RMs is unstable. In the higher area, the structure of radial density profiles is similar to the density profiles of optimal area.

S5 – The Radial Distribution Function

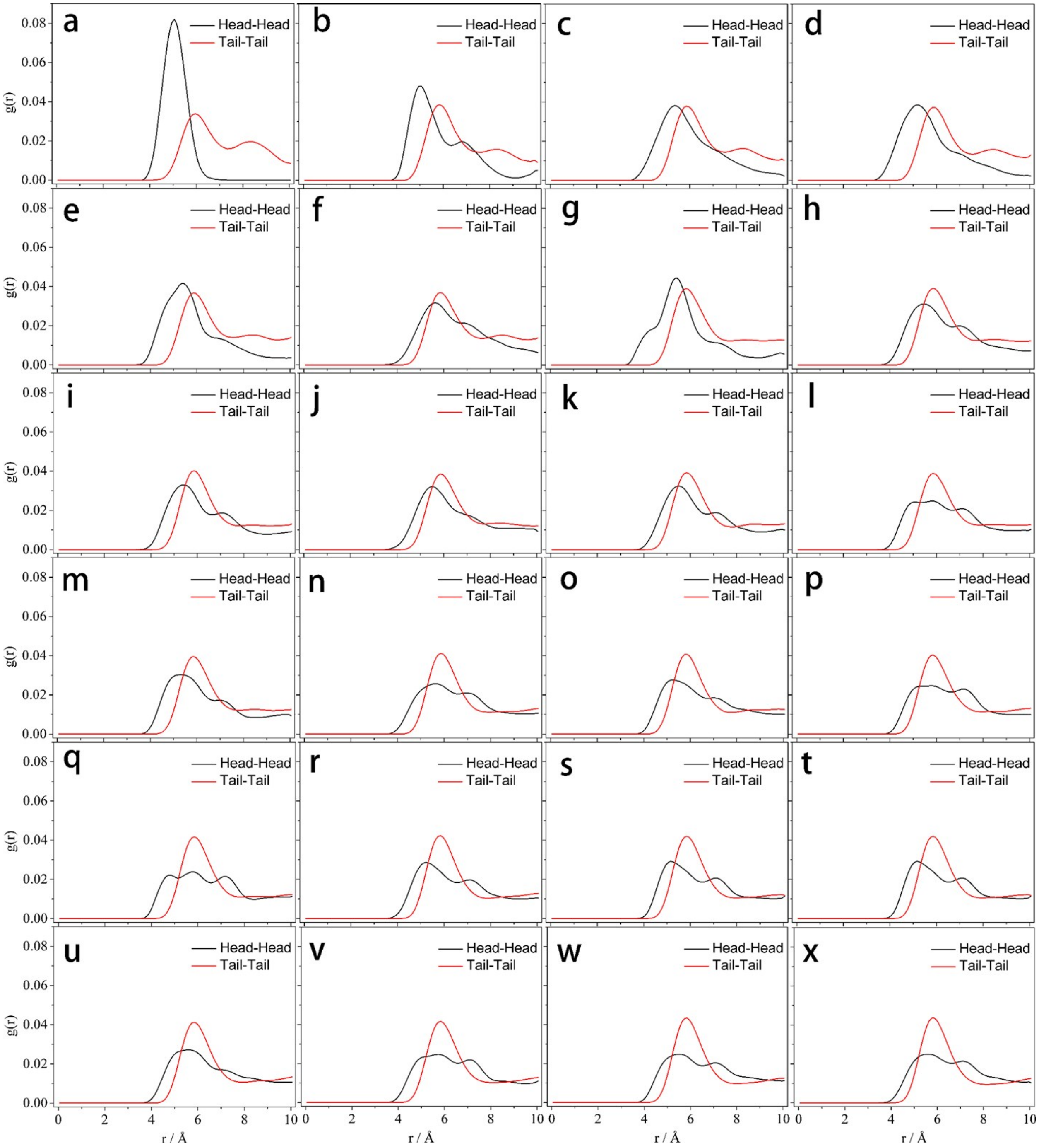

Fig. S3. The radial distribution function (RDF) between head-group and head-group and the RDF between tail-terminal and tail-terminal with the number of surfactants (a) N = 2, (b) N = 3, (c) N = 4, (d) N = 5, (e) N = 6, (f) N = 7, (g) N = 8, (h) N = 9, (i) N = 10, (j) N = 11, (k) N = 12, (l) N =

13, (m) N = 14, (n) N = 15, (o) N = 16, (p) N = 17, (q) N = 18, (r) N = 19, (s) N = 20, (t) N = 21, (u) N = 22, (v) N = 23, (w) N = 24, (x) N = 25.

In the optimal area, the RDFs show clear peak both head-head and tail-tail. In the lower area, the peak head-head RDFs is very high. In the higher area, the peak head-head RDFs is fussy.

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