Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Molecular Dynamics Study of di-CF4 Based Reverse Micelle in Supercritical CO_2

Bing Liu [a,b,*], Xinpeng Tang [a], Wenjing Fang [a], Xiaoqi Li [a], Jun Zhang [a], Zhiliang Zhang [b], Yue Shen [a], Youguo Yan [a], Xiaoli Sun [a], Jianying He [b,*]

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

[b] NTNU Nanomechanical Lab, Department of Structural Engineering, Norwegian University of Science and Technology (NTNU), Trondheim, 7491, Norway

* Corresponding authors:

Email：liubing19720115@gmail.com

Email：jianying.he@ntnu.no

The surfactant [Na][di-CF4]

The surfactant [Na][di-CF4] used in this work is shown in Fig. S1.

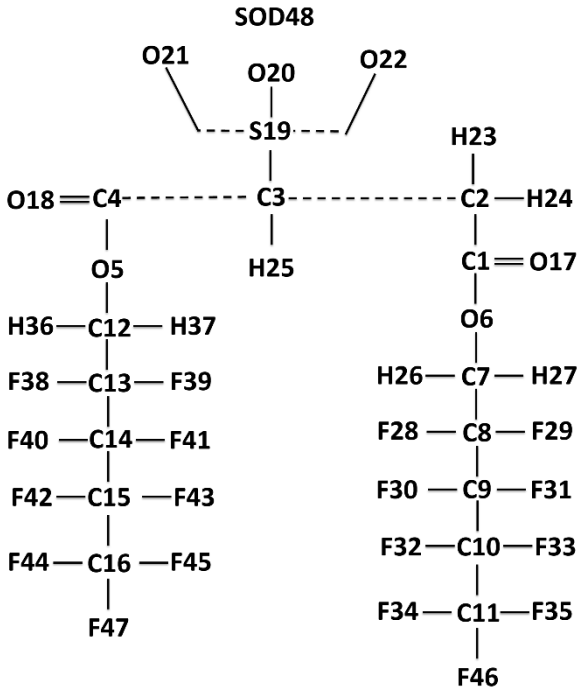

Fig. S1. Molecular structure and the atom number of the surfactant [Na][di-CF4].

The CHARMM 27 forcefield used in GROMACS is expressed as [1, 2]

$$\mathrm{E} = \sum_{bonds} \frac{1}{2} K_r (r - r_0)^2 + \sum_{angles} \frac{1}{2} K_\theta (\theta - \theta_0)^2 + \sum_{dihedrals} K_\Phi [1 + \cos(n\varphi - \gamma)] + \sum_{impropers} \frac{1}{2} K_\omega (\omega - \omega_0)^2 + \sum_{Uray-Bradley} \frac{1}{2} K_u (u - u_0)^2 + \sum_{i<j} \varepsilon \left[\left(\frac{R_{min}}{r_{ij}} \right)^{12} - 2 \left(\frac{R_{min}}{r_{ij}} \right)^{6} \right] + \sum_{i<j} \frac{q_i q_j}{r_{ij}} \quad (1)$$

The first term in the energy function accounts for the bond stretches where K_r is the bond force constant and $r - r_0$ is the distance from equilibrium that the atom has moved. The second term in the equation accounts for the bond angles where K_θ is the angle force constant and $\theta - \theta_0$ is the angle from equilibrium between 3 bonded atoms. The third term is for the dihedrals where K_ϕ is the dihedral force constant, n is the multiplicity of the function, φ is the dihedral angle and γ is the phase shift. The fourth term accounts for the impropers that is out of plane bending where K_ω is the force constant and $\omega - \omega_0$ is the out of plane angle. The Urey-Bradley component (cross-term accounting for angle bending using 1,3 nonbonded interactions) comprises the fifth term, where K_u is the respective force constant and u is the distance between the 1,3 atoms in the harmonic potential. Nonbonded interactions between pairs

of atoms (i,j) are represented by the last two terms. By definition, the nonbonded forces are only applied to atom pairs separated by at least three bonds. The van Der Waals (VDW) energy is calculated with a standard 12-6 Lennard-Jones potential and the electrostatic energy with a Coulombic potential.

The CHARMM 27 forcefield parameters of the surfactant di-CF4 are given in Table S1.

Table. S1. Nonbonded Parameters (the VDW and Coulombic Interaction Parameters)

atom	ε_{ii} (kJ/mol)	R_{min} (nm)	q_i(e)
C1	0.46024	0.356359	0.659
C2	0.23012	0.387541	0.061
C3	0.23012	0.387541	0.1662
C4	0.46024	0.356359	0.659
O5	0.63639	0.315378	-0.43
O6	0.63639	0.315378	-0.43
C7	0.23012	0.387541	0.28
C8	0.23012	0.387541	0.68
C9	0.23012	0.387541	0.68
C10	0.23012	0.387541	0.68
C11	0.23012	0.387541	1.02
C12	0.23012	0.387541	0.28
C13	0.23012	0.387541	0.68
C14	0.23012	0.387541	0.68
C15	0.23012	0.387541	0.68
C16	0.23012	0.387541	1.02
O17	0.50208	0.302905	-0.57
O18	0.50208	0.302905	-0.57
S19	1.96648	0.374177	1.3448
O20	0.50208	0.302905	-0.8167
O21	0.50208	0.302905	-0.8167
O22	0.50208	0.302905	-0.8167
H23	0.09205	0.235197	0.00
H24	0.09205	0.235197	0.00
H25	0.09205	0.235197	0.00
H26	0.09205	0.235197	0.00
H27	0.09205	0.235197	0.00
F28	0.56484	0.290433	-0.34
F29	0.56484	0.290433	-0.34
F30	0.56484	0.290433	-0.34
F31	0.56484	0.290433	-0.34
F32	0.56484	0.290433	-0.34
F33	0.56484	0.290433	-0.34
F34	0.56484	0.290433	-0.34
F35	0.56484	0.290433	-0.34

H36	0.09205	0.235197	0.00
H37	0.09205	0.235197	0.00
F38	0.56484	0.290433	-0.34
F39	0.56484	0.290433	-0.34
F40	0.56484	0.290433	-0.34
F41	0.56484	0.290433	-0.34
F42	0.56484	0.290433	-0.34
F43	0.56484	0.290433	-0.34
F44	0.56484	0.290433	-0.34
F45	0.56484	0.290433	-0.34
F46	0.56484	0.290433	-0.34
F47	0.56484	0.290433	-0.34
SOD48	0.19623	0.242993	1.00

The parameters of SPC/E water model [3] and EPM2 CO_2 model [4] are shown in Table. S2 and Table. S3.

Table. S2. Nonbonded Parameters for SPC/E water model.

atom	ε_{ii} (kJ/mol)	R_{min} (nm)	q_i(e)
O	0.64962	0.3553	-0.8476
H	0	0	0.4238

Table. S2. Nonbonded Parameters for EPM2 CO_2 model.

atom	ε_{ii} (kJ/mol)	R_{min} (nm)	q_i(e)
O	0.66944	0.3033	-0.3256
C	0.27579	0.2343	0.6512

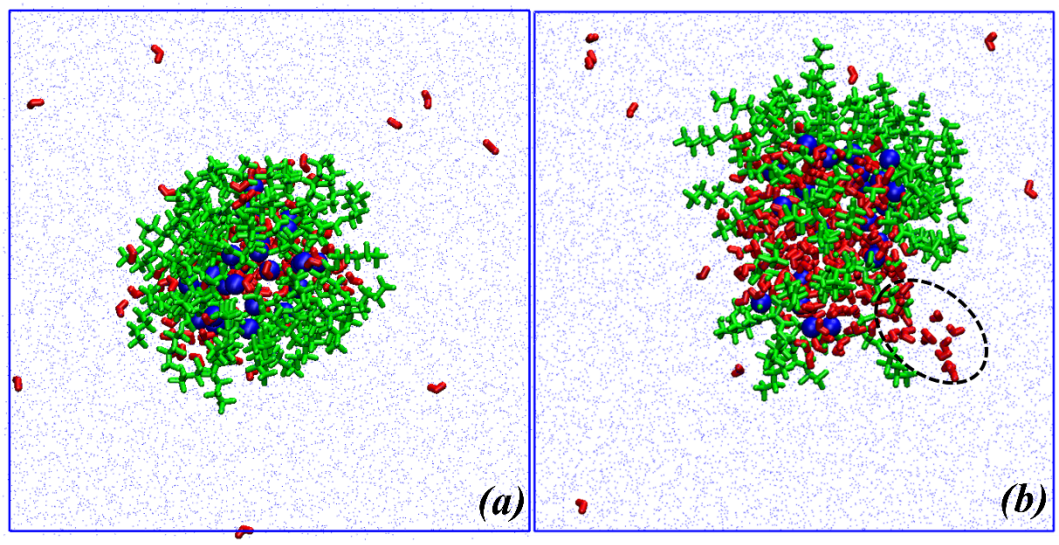

Fig. S2. The RMs with (a) W_0 = 5 and (b) W_0 = 10. Color code: green: di-CF4 surfactants; red: water; blue: Na^+; gray: CO_2. Temperature: 313K; Pressure: 400bar.

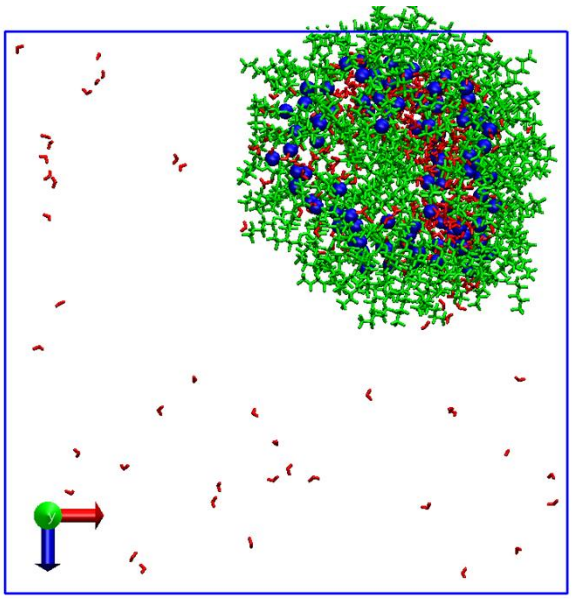

Fig. S3. The structure of reverse micelle formed by 100 di-CF4 molecules and 500 water molecules.

The relative surfactant coverage calculating method.

The method in calculating the surfactant coverage in this work was introduced below. The average surfactant coverage Φ_{surf} was calculated by [5]

$$\Phi_{surf} = \frac{V_{cal}}{V_{meas}} \tag{2}$$

Where the V_{cal} is the total physical volume of surfactant molecular fragment and Vmeas is 0.720 nm^3. The values of the various fragments in di-CF4 molecule were presented in Table S2.

Table S2: The volume of fragment in di-CF4 surfactant.

fragment	vol (nm^3)
COO^-	0.0370[a]
CF2	0.0380[b]
CF3	0.0920[b]
CH2	0.0270[b]

[a] Data was collected by Berr [6].

[b] Data was collected by Li Zhang [7]

The totle number surfactant coverage is

$$V_{meas} = \frac{\left[\ \frac{4}{3}\pi\left(R_{gtail}^3 - R_{ghead}^3\right)\ \right]}{25} \tag{3}$$

$$V_{cal} = V_{CH2} + (V_{COO^-} + V_{CH2} + V_{CF2} * 3 + V_{CF3}) * 2 \tag{4}$$

Where $R_{gtail} = 1.6$ nm, $R_{ghead} = 0.85$ nm. So we obtain $V_{meas} = 0.720$ nm^3. The totle number of surfactant molecule is 25 and $V_{cal} = 0.567$ nm^3. Then we obtain $\Phi_{surf} = 0.788$.

The surfactant coveage of τ_1 was calculated by the following equations

$$V_{meas1} = \frac{\left[\ \frac{4}{3}\pi\left(R_{gtail1}^3 - R_{ghead}^3\right)\ \right]}{25} \tag{5}$$

$$V_{cal1} = V_{cal} - (V_{CF2} + V_{CF3}) \tag{6}$$

Where $R_{gtail1} = \ R_{ghead} + 0.713\ nm$. So the surfactant coverage Φ_{surf1} is:

$$\Phi_{surf1} = \frac{V_{cal1}}{V_{meas1}} = 0.346 \tag{7}$$

The surfactant coverage Φ_{surf2} of τ_2 was calculated by the following equations

$$V_{meas2} = \frac{\left[\ \frac{4}{3}\pi\left(R_{gtail2}^3 - R_{gtail1}^3\right)\ \right]}{25} \tag{8}$$

$$V_{cal2} = V_{CF2} + V_{CF3} \tag{9}$$

Where the $R_{gtail2} = \ R_{ghead} + 0.972\ nm$. So the surfactant coverage Φ_{surf1} is:

$$\Phi_{surf2} = \frac{V_{cal2}}{V_{meas2}} = 0.824 \tag{10}$$

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