Supporting Information

Steric Effect Stabilize Reverse Micelles Domains in Supercritical CO_2 by Determined Conformation: Restrictions of Water and Cations

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TABLE S1. The parameters of SPC/E and EPM2 models

	H_2O, SPC/E type		CO_2, EPM2 type	
q (e)	H	0.4238	C	0.6512
	O	-0.8476	O	-0.3256
ε_{ij} (kcal/mole)	O-O	0.1553	C-C	0.0559
	H-H, H-O	0	O-O	0.1599
			C-O	0.0946
σ_{ij} (Å)	O-O	3.166	C-C	2.757
			O-O	3.033
			C-O	2.892
r_0 (Å)	H-O	1.0	C-O	1.149
θ_0 (deg)	H-O-H	109.47	O-C-O	180

The functional form of the COMPASS force field is:

$$
\begin{aligned}
E_{\text{total}} = & \sum_b \left[k_2(b-b_o)^2 + k_3(b-b_o)^3 + k_4(b-b_o)^4\right] + \sum_\theta \left[k_2(\theta-\theta_o)^2 \right. \\
& + \sum_\phi \left[k_1(1-\cos\phi) + k_2(1-\cos 2\phi) + k_3(1-\cos 3\phi)\right] + \sum_\chi k_2\chi^2 + \sum_{b,b'} k(b-b_o)\left(b \right. \\
& + \sum_{b,\theta} k(b-b_o)(\theta-\theta_o) + \sum_{b,\phi}(b-b_o)[k_1\cos\phi + k_2\cos 2\phi + \\
& + \sum_{\theta,\phi}(\theta-\theta_o)[k_1\cos\phi + k_2\cos 2\phi + k_3\cos 3\phi] + \sum_{b,\theta} k\left(\theta' \right. \\
& (\theta-\theta_o) + \sum_{\theta,\theta,\phi} k(\theta-\theta_o)\left(\theta'-\theta_o'\right)\cos\phi + \sum_{i,j}\frac{q_i q_j}{r_{ij}} + \sum_{i,j}\epsilon_{ij}\left[2\left(\frac{r_{ij}^{\circ}}{r_{ij}}\right)^9 - 3\left(\frac{r_{ij}^{\circ}}{r_{ij}}\right)^6\right]
\end{aligned}
$$

The force field parameters of the fluorine atom are shown in **Table S2.**

TABLE S2. COMPASS force field parameter values for fluorine and carbon atoms

Bond	b_0(Å)	$k_{b,2}(kcal/mol \cdot Å^2)$	$k_{b,3}(kcal/mol \cdot Å^3)$	$k_{b,4}(kcal/mol \cdot Å^4)$
CC	1.530	299.670	-501.77	679.81
CH	1.101	345.000	-691.89	844.60
CF	1.390	403.032	0	0
Angle	$\theta_0(deg)$	$k_{\theta,2}(kcal/mol \cdot rad^2)$	$k_{\theta,3}(kcal/mol \cdot rad^3)$	$k_{\theta,4}(kcal/mol \cdot rad^4)$
CCC	112.67	39.5160	-7.4430	-9.5583
CCH	110.77	41.4530	-10.6040	5.1290
HCH	107.66	39.6410	-12.9210	-2.4318
CCF	109.20	68.3715	0	0
FCF	109.10	71.9700	0	0
Torsion	$k_{\phi,1}(kcal/mol)$	$k_{\phi,2}(kcal/mol)$	$k_{\phi,3}(kcal/mol)$	
$CCCC$	0	0.0514	-0.1430	
$CCCH$	0	0.0316	-0.1681	
$CCCF$	0	0	0.1500	
$HCCF$	-0.1432	0.0617	-0.1530	
$FCCF$	0	0	-0.1	
bond/bond	$k_{bb'}(kcal/mol \cdot Å^2)$			
CC/CH (first neighboring)	3.3872			
CH/CH (first neighboring)	5.3316			
CC/CC (first neighboring)	0			
bond/angle	$k_{b\theta}(kcal/mol \cdot Å \cdot rad)$			
C-C/C-C-C	8.016			
C-C/C-C-H	20.754			
C-H/C-C-H	11.421			

C-H/H-C-H	18.103

angle/angle	$k_{\theta\theta'}(kcal/mol \cdot rad^2)$
C-C-C/C-C-C	-0.1729
C-C-C/C-C-H	-1.3199
H-C-C/C-C-H	-0.4825

angle/angle/torsional	$k_{\theta\theta'\phi}(kcal/mol \cdot rad^2)$
C-C-C/C-C-C/C-C-C-C	-22.045
C-C-C/C-C-H/C-C-C-H	-16.164
H-C-C/C-C-H/H-C-C-H	-12.564

Bond/torsion	$k_{b\phi,1}(kcal/mol \cdot$ Å$)$	$k_{b\phi,2}(kcal/mol \cdot$ Å$)$	$k_{b\phi,3}(kcal/mol \cdot$ Å$)$
C-C/C-C-C-C (central bond)	-17.787	-7.1877	0
C-C/C-C-C-H (central bond)	-14.879	-3.6581	-0.3138
C-C/H-C-C-H (central bond)	-14.261	-0.5322	-0.4864
C-C/C-C-C-C (terminal bond)	-0.0732	0	0
C-C/C-C-C-H (terminal bond)	0.2486	0.2422	-0.0925
C-H/C-C-C-H (terminal bond)	0.0814	0.0591	0.2219
C-H/H-C-C-H (terminal bond)	0.2130	0.3120	0.0777

angle/torsion	$k_{\theta\phi,1}(kcal/mol \cdot rad)$	$k_{\theta\phi,2}(kcal/mol \cdot rad)$	$k_{\theta\phi,3}(kcal/mol \cdot rad)$
C-C-C/C-C-C-C	0.3886	-0.3139	0.1389

C-C-C/C-C-C-H	-0.2454	0	-0.1136
C-C-H/C-C-C-H	0.3113	0.4516	-0.1988
H-C-C/H-C-C-H	-0.8085	0.5569	-0.2466

atom atom	$\epsilon(kcal/mol)$	r_0(Å)
CC	0.0400	3.854
HH	0.0230	2.878
FF	0.0598	3.200
CH	0.0215	3.526
CF	0.0422	3.600

atom atom	$q_1(e)$	$q_2(e)$
CC	0	0
CH	-0.053	+0.053
CF	+0.25	-0.25

More public version parameters of the COMPASS force field can be obtained from the web page(
https://github.com/lammps/lammps/blob/develop/tools/msi2lmp/frc_files/compass_published.frc
)

TABLE S3. The density of $scCO_2$ after the end of the NPT ensemble in four surfactant system

system	F7H7	PFPE	di-HCF4	AOK	Experimental value
density (g/cm^3)	0.7997	0.7258	0.8227	0.7258	0.8314

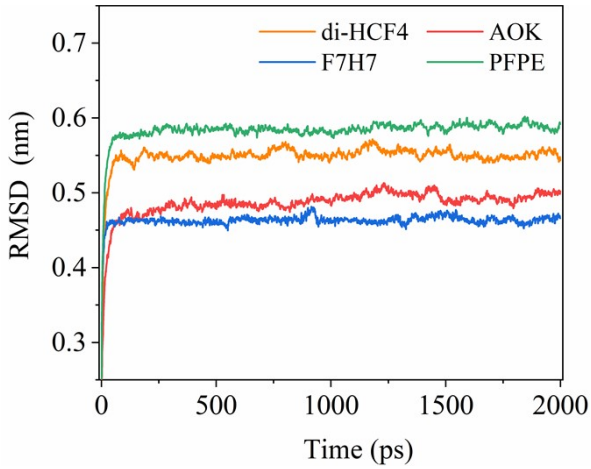

Figure S1. Root Mean Square Deviation (RMSD) of four surfactants reverse micellar systems.

The root mean square deviation (RMSD) of the reverse micelles was calculated over the final 2 ns of simulation time. The smooth RMSD curves observed during this period indicate that the system had reached equilibrium, with no significant changes in the micellar configuration. This provides evidence that our pre-assembled system achieved equilibrium and ensures the reliability and accuracy of the subsequent data analysis in our study.

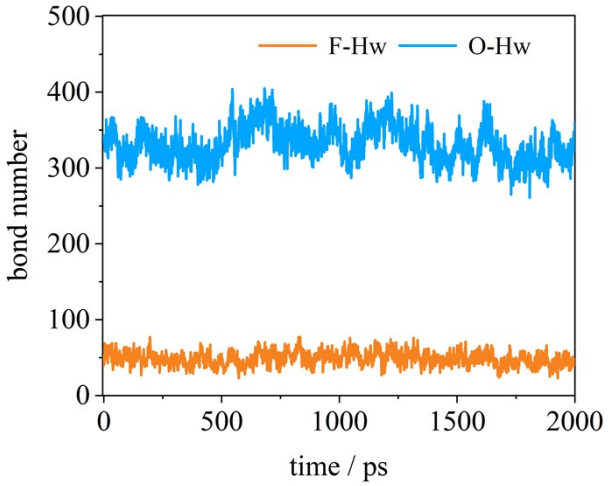

Figure S2. Time evolution of the number of bonds in the F7H7 surfactant molecule.

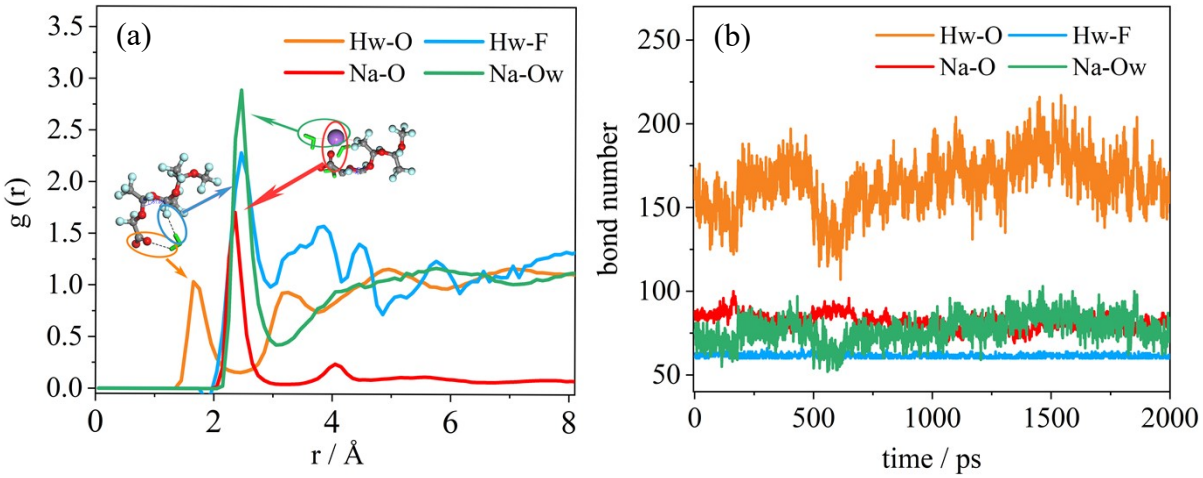

Figure S3. (a) Radial Distribution Function (RDF) of Hw–O (oxygen from PFPE surfactant），Hw（hydrogen from water molecular）-F, Na-O, and Na-Ow（oxygen from water molecular）. (b) Time evolution of the number of bonds in the PFPE surfactant molecule.

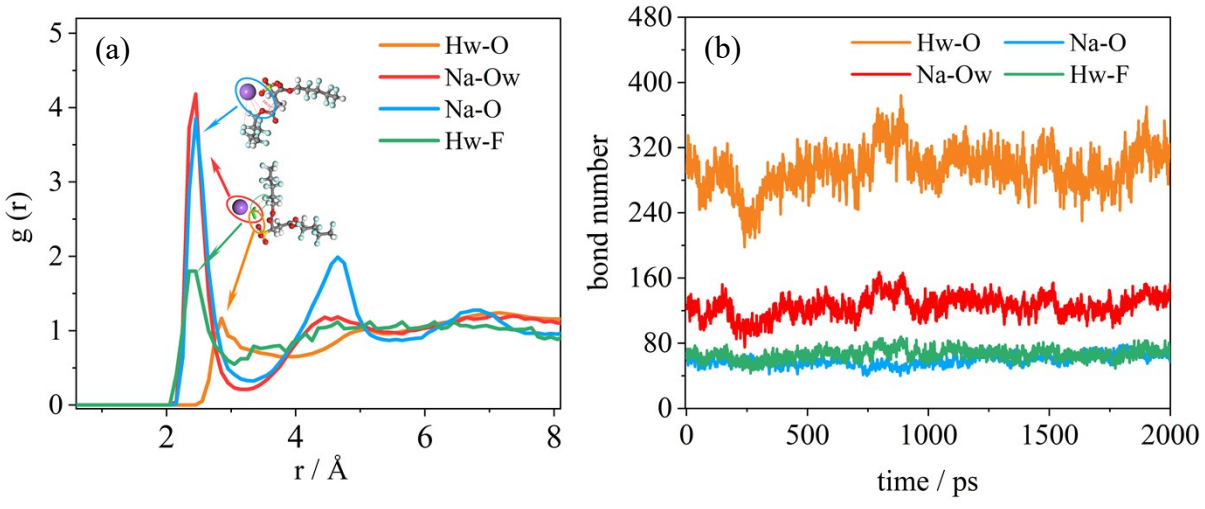

Figure S4. (a) Radial Distribution Function (RDF) of Hw–O (oxygen from di-HCF4 surfactant), Na-Ow and Na-O. (b) Time evolution of the number of bonds in the PFPE surfactant molecule.

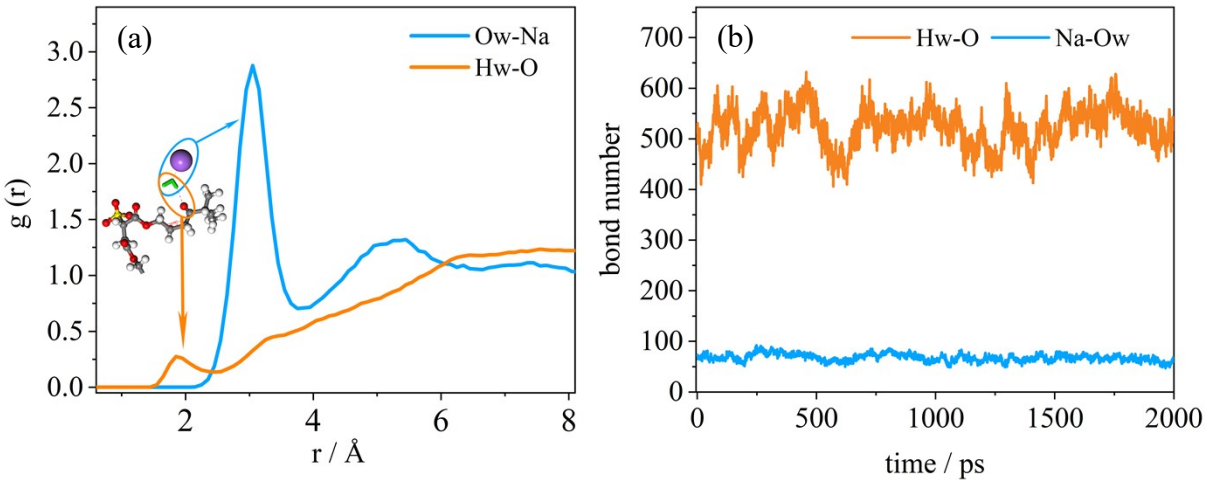

Figure S5. Radial Distribution Function (RDF) of Ow–Na (oxygen from water molecular) and Na-O (oxygen from AOK surfactant). (b) Time evolution of the number of bonds in the AOK surfactant molecule.

By analyzing the results presented in **Figure S2** to **Figure S5**, it is evident that hydrogen bonds are formed between water molecules and sodium ions with the surfactant molecules. This conclusion is supported by the calculations of the specific atom interactions between water molecules, sodium ions, and surfactant molecules. The findings highlight the presence of these hydrogen bonds and their role in the molecular interactions within the system, further contributing to our understanding of the surfactant behavior in the studied environment.

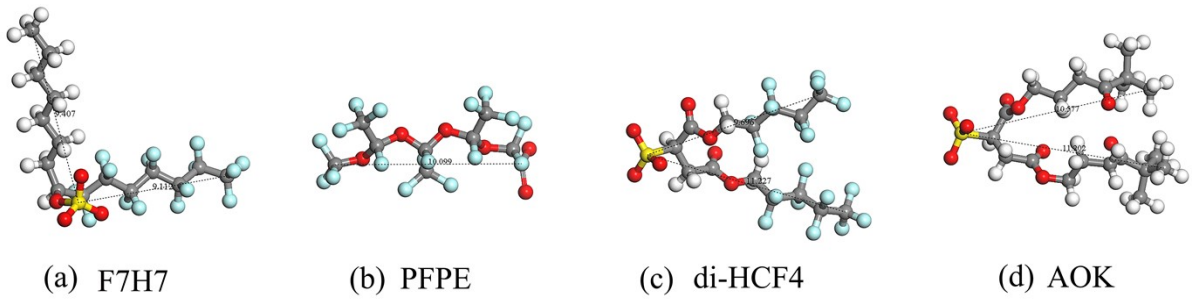

Figure S6. The optimized structures and chain lengths of four surfactant single molecules.

(1) Berendsen, H. J. C.; Grigera, J. R.; Straatsma, T. P. The Missing Term in Effective Pair Potentials. *J. Phys. Chem.* **1987**, *91* (24), 6269–6271.

(2) J. G. Harris and K. H. Yung, Carbon dioxide's liquid-vapor coexistence curve and critical properties as predicted by a simple molecular model, *J. Phys. Chem.,* **1995***, 99,* 12021–12024.

(3) Savin, A. V; Mazo, M. A. The COMPASS Force Field: Validation for Carbon Nanoribbons. *Phys. E Low-dimensional Syst. Nanostructures* **2020**, *118*, 113937.