Stability of Colloidal Gas Aphrons Based on Polymer-Surfactant Formulations and Molecular Dynamics Insights

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1. Supplementary material

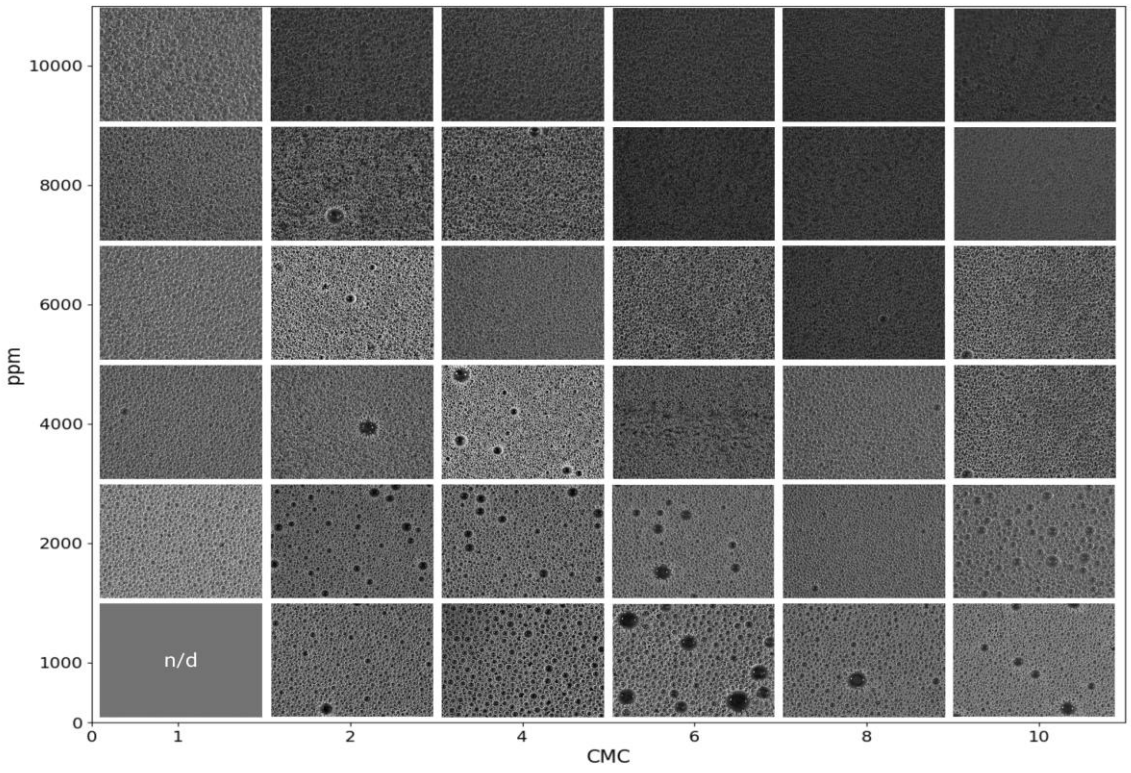
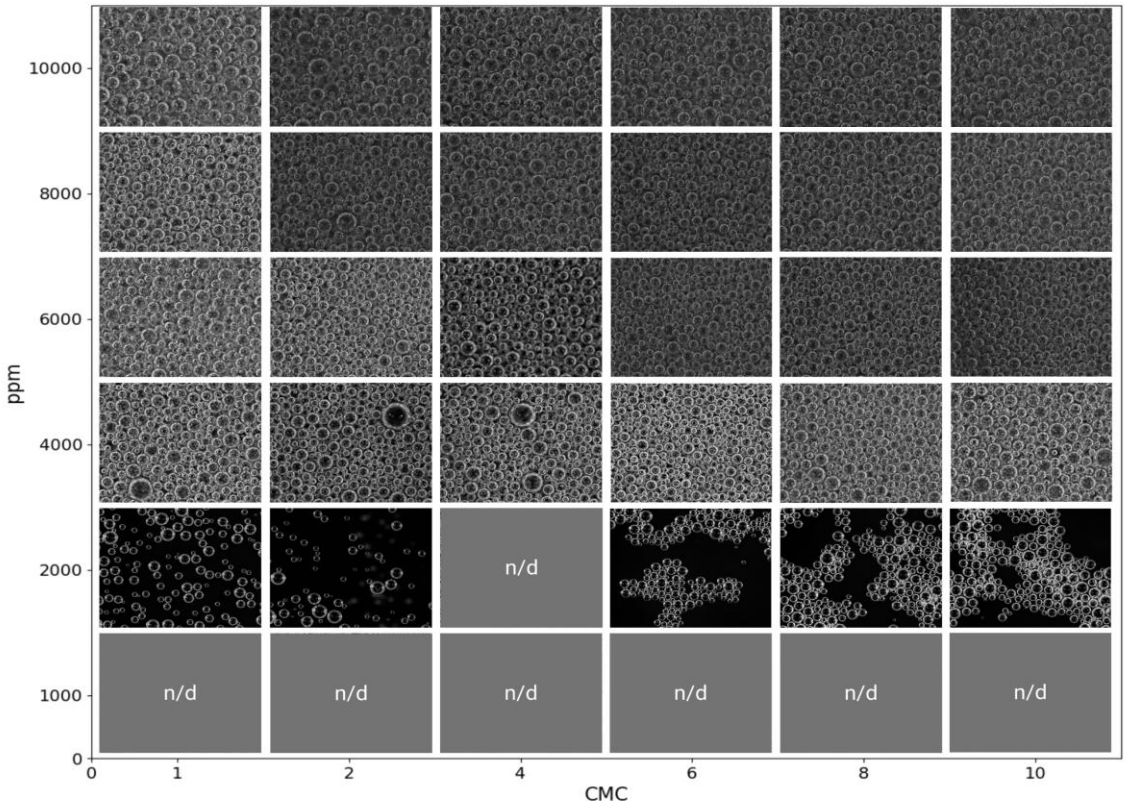


Figure S1. Images of 36 concentrations of CGA at t = 0 min



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18 **Figure S2**. Images of 36 concentrations of CGA at t = 60 min

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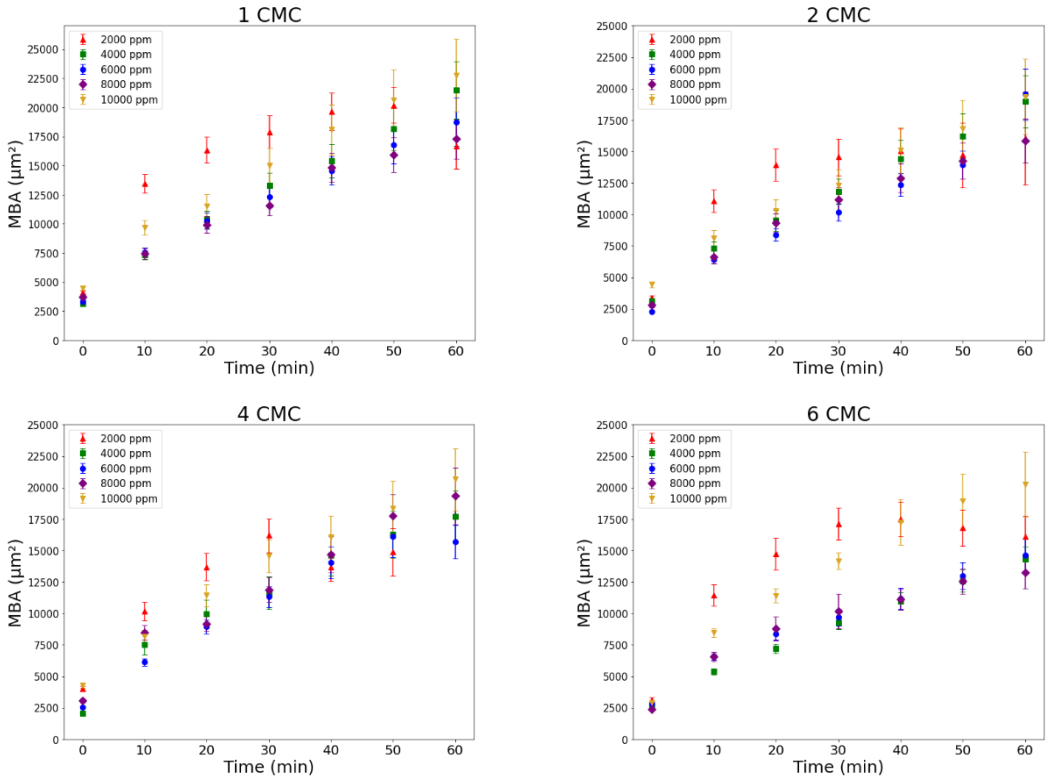

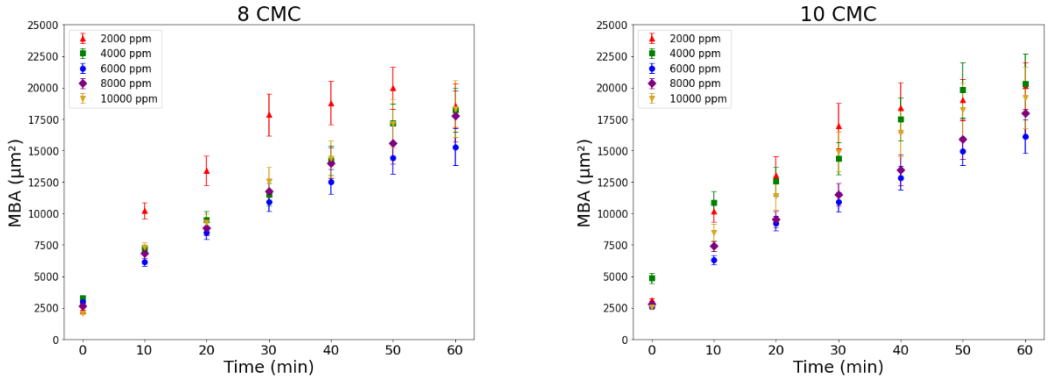

Figure S3. MBA change versus time for with error bars represented 95% of confidence interval

S2. Movement of N_2 molecules in the CGA model

The movement of N_2 molecules was studied in the aqueous bulk phase, in the absence of the vacuum. SDS and XG monomer molecules were randomly inserted into the simulation boxes with the size of 10*10*10 nm^3. The SPC water model was used for the solvation of the simulation box. To investigate the effect of XG concentration on the movement of gas molecules, the number of the XG monomers varied from 0 to 8, 16, and 24 molecules, in the presence of 128 SDS molecules. The representative snapshots of the simulation boxes at the beginning of the simulations are shown in Figure S3A-D, respectively. The required number of ions and molecules was inserted into the simulation box, according to Table S1. After filling the box with a required number of molecules, energy minimization was performed, with a constraint of maximum force to be less than 100 kJ/mol/nm on any atom, to optimize the starting configuration of the simulation box. Following energy minimization, the NVT step was conducted with a V-rescale thermostat for 0.25 ns at 323 K. Next, the NPT equilibration was performed at constant pressure of 1 bar with a V-rescale thermostat and a C-rescale barostat for 0.25 ns at 323 K. Finally, the production runs for each of the systems were performed for 25 ns at 323 K with the time step of 1 fs. During the simulations, all bonds were constrained with the LINCS algorithm. The MD simulations were performed for 25 ns at a constant temperature of 323 K and pressure of 1 bar with a V-rescale thermostat and a C-rescale barostat. PBC were applied in XYZ-directions for all simulations. The output parameters were saved each 1 ps. The movement of gas molecules was characterized by MSD of N_2 molecules within the first 10 ns of the MD simulation runs. The results were averaged among three runs for each system under the study.

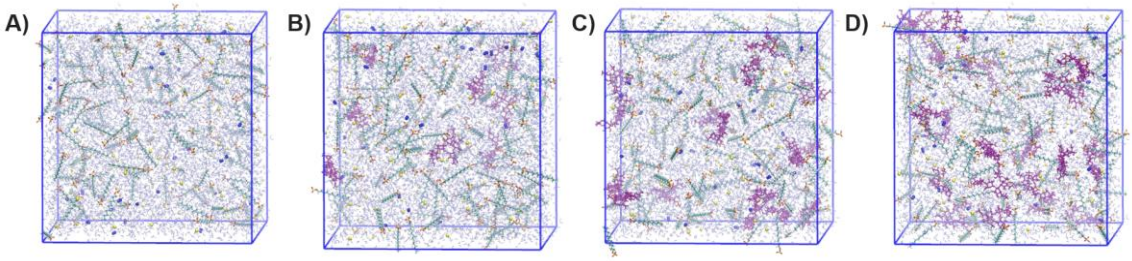

Figure S4. Representative snapshots of the simulated systems with gas movement in bulk water at the beginning of the simulations: A) N_2 in 128 SDS : 0 XG, B) N_2 in 128 SDS : 8 XG, C) N_2 in 128 SDS :

16 XG, D) N_2 in 128 SDS : 24 XG. Representation style: N_2: dark blue, XG monomer: purple, Na^+: yellow, H_2O: light blue, SDS atoms: C: cyano, H: white, O: red.

Table S1. The number of molecules and ions used in the simulations with gas movement in bulk water

Simulated system	N_2	SDS	Na^+	Water	XG
N_2 in 128 SDS : 0 XG	30	128	128	10263	0
N_2 in 128 SDS : 8 XG	30	128	128	9919	8
N_2 in 128 SDS : 16 XG	30	128	128	9429	16
N_2 in 128 SDS : 24 XG	30	128	128	7946	24

S3. RDF analysis

The effect of XG concentration on the interfacial intermolecular interactions was further studied via RDF analysis, performed for the last 5 ns of the production run (Figure S4-5). According to the RDF analyses, the presence of XG molecules at various concentrations did not significantly affect the interfacial interactions between SDS and Na^+ ions (Figure S4), and interactions between surfactants (Figure S5). The observation indicated that although the movement of molecules was suppressed at high XG concentrations, the interfacial interactions were not influenced by XG molecules.

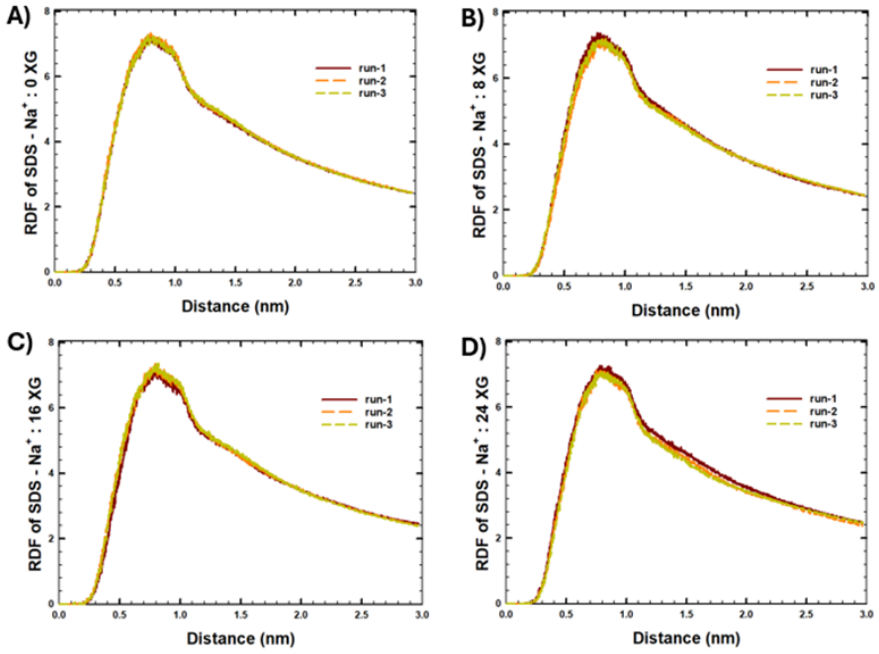

Figure S5. RDF interactions between Na^+ ions and SDS molecules were observed in the last 5 ns of the production run in the simulated systems with A) 0 XG, B) 8 XG, C) 16 XG, D) 24 XG molecules

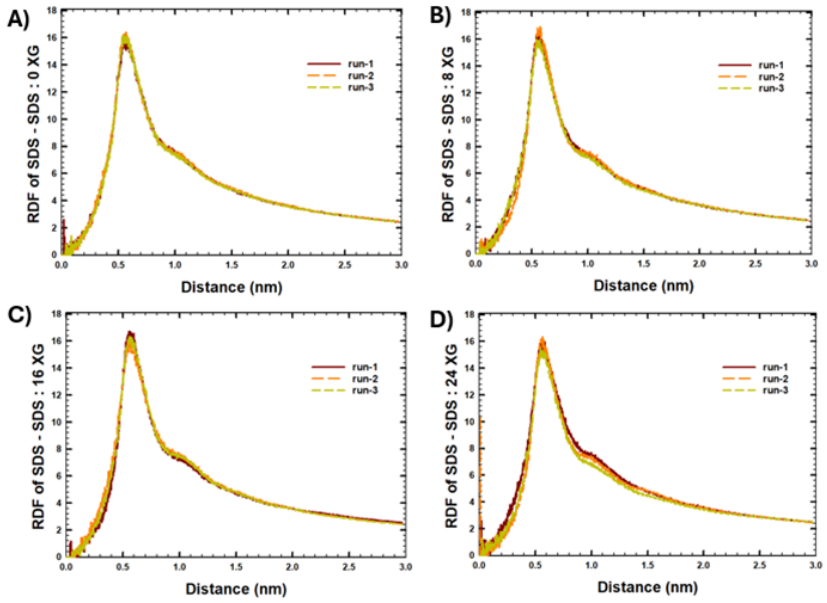

Figure S6. RDF interactions between XG and SDS molecules observed in the last 5 ns of the production run in the simulated systems with A) 0 XG, B) 8 XG, C) 16 XG, D) 24 XG molecules

S4. Density analysis

The XY-density maps of SDS and XG molecules were generated for two distinct interfaces, depicted at 9-12 nm and 18-21 nm distances along the z-direction of the simulation boxes, as shown in Figure S6 and Figure S7, respectively. According to Figure S7, the XY-density maps did not show a significant effect of XG concentration on the distribution of SDS molecules on the interfaces. In the system with low XG concentration, 8 XG molecules were distributed on both interfaces in run #2 (Figure S8A, S8D). In contrast, at higher XG concentrations, XG molecules were observed only on one interface due to the aggregation of XG molecules, particularly, in run #3 of the system with 16 XG molecules and run #2 of the system with 24 XG molecules (Figure S8B, S8C, S8E, S8F).

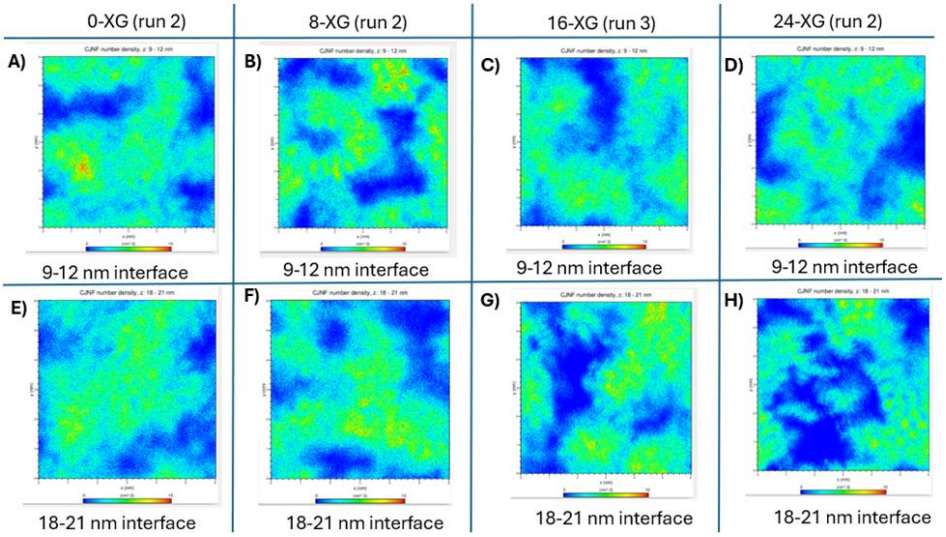

Figure S7. XY-density map of SDS molecules at two distinct interfaces (at 9-12 nm distance, and 18-21 nm distance along the z-direction of the simulation box) in the systems with: A, E) 0 XG; B, F) 8 XG; C, G) 16 XG; D, H) 24 XG molecules.

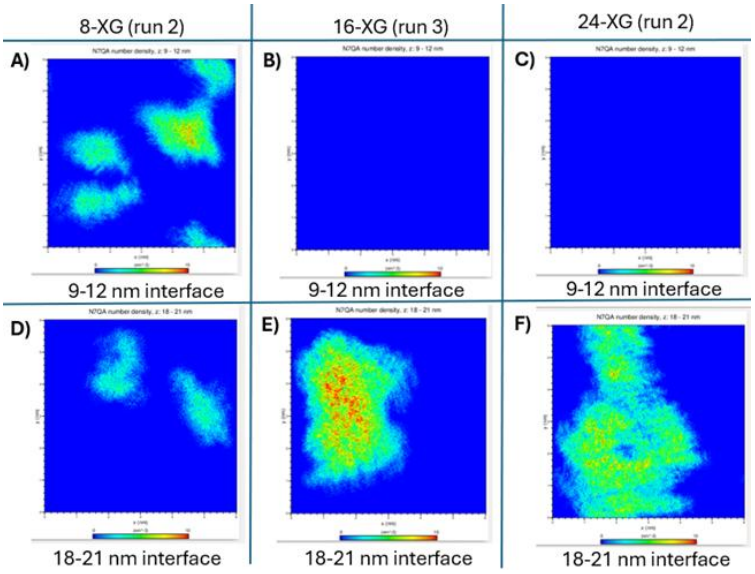

Figure S8. XY-density map of XG molecules at two distinct interfaces (at 9-12 nm distance, and 18-21 nm distance along the z-direction of the simulation box) in the systems with: A, D) 8 XG; B, E) 16 XG; C, F) 24 XG molecules.

In addition, we calculated mass densities along the Z-axis, which were observed at the end of the NVT runs in the CGA models with vacuum layers and SDS monolayers (Figure S8). According to Figure 1, mass densities in the water slab in the simulated systems with 0 XG are around 1000 kg/m^3, and densities increase at the vacuum-water (SDS) interfaces, where we have SDS molecules. The density values are also higher in the simulated systems with XG molecules in the boxes. The results were consistent with the MD study of the surfactant-water-vacuum systems reported in the MD study by Jiao et al. (2024)[1]:

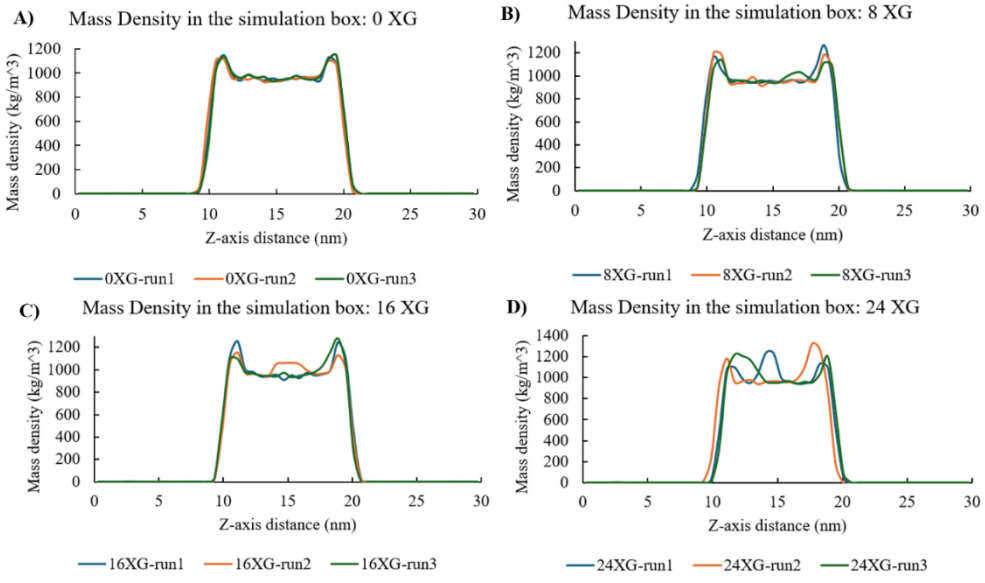

Figure S9. Mass densities along the Z-axis, which were observed at the end of the NVT runs in the CGA models with vacuum layers and SDS monolayers: A) 0 XG, B) 8 XG, C) 16 XG, D) 24 XG.

References

1. Jiao, J. *et al.* Molecular Dynamics Simulations of the Short-Chain Fluorocarbon Surfactant PFHXA and the Anionic Surfactant SDS at the Air/Water Interface. *Molecules* 29, (2024).