Hydrate Particle – Water Droplet Coalescence in Oil: Anti-Agglomerants Effect

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Supplemental Material

Algorithms: Potential of mean force calculations

To construct the potential of mean force profile for one water molecule as it is moved from the water droplet to the hydrate particle (Figure 7 in main article) we implemented the umbrella sampling algorithm.^{1,2} The center of mass (COM) of the tagged water molecule was forced to remain at given distances from the COM of the hydrate particle using harmonic springs of elastic constant 30000 kJ/mol.nm². For one system, 80 - 148 independent simulations were conducted, imposing that the equilibrium molecule–surface distance changes by 0.025 nm from one simulation to another. Within each window (separation distance) the simulation was conducted for up to 8 ns, during which time the histogram representing the distances between the COM of the water molecule and that of the hydrate particle was populated.³ The WHAM algorithm was then used to reconstruct the potential of mean force from combining the histograms obtained at various molecule–surface separations.²

Results



Figure S1. *Top*: Individual force-distance curves plotted as a function of the distance between the COM of the hydrate particle and that of the water droplet coated with C16C1. Results are shown for different pulling rates: 0.2 (left), 0.1 (middle), and 0.05 (right) nm/ns. *Bottom*: Approximate potentials of mean force (PMF) obtained by numerically integrating the force profiles as shown in the top panels at various pulling rates: 0.2 (green circles), 0.1 (purple triangles), and 0.05 (blue

diamonds) nm/ns.

In Figure S1, we report the individual force-distance curves (top panels) recorded while pulling the water droplet coated with C16C1 surfactants towards the hydrate particle. Results are shown for various pulling rates: 0.2 (left), 0.1 (middle), and 0.05 (right) nm/ns. The approximate potentials of mean force profiles (PMF) are shown in the bottom panel. The PMFs are obtained by numerically integrating the force profiles. The PMF results show that as the pulling rate decreases the local minima in the PMF profile become more pronounced. The differences observed when the pulling rate was either 0.1 or 0.05 nm/ns were considered not very large, compared to the uncertainties in the individual force-distance profiles.



Figure S2. Simulated force-distance curves obtained while pulling the water droplet towards the hydrate particle. Results are obtained from three independent steered simulations for bare water droplets. The surfactants used are C16C1 (top panels), C16C4 (middle panels) and C12C4 (bottom panels). Instantaneous forces (blue lines) and averages (red lines) are both shown. The distance is that between the COM of the hydrate particle and that of the water droplet.

In Figures S2 and S3 we report the individual force-distance curves obtained from independent steered simulations for the bare and coated water droplets, respectively. Results are shown when C16C1 (top), C16C4 (middle), and C12C4 (bottom) were used as surfactants. The results in Figures S2 and S3 show that force-distance curves obtained for the same system are qualitatively consistent

with each other. We averaged the force data obtained at each COM-COM distance to obtain curves such as those shown in Figure 3, main article.



Figure S3. Same as Figure S2, but for systems in which both the hydrate particles and the water droplets are coated with surfactants: C16C1 (top), C16C4 (middle), and C12C4 (bottom).

In Figure S4, we present sequences of simulation snapshots obtained during the coalescence of the bare water droplet and the hydrate particle. Results are shown when C16C1 (top), C16C4 (middle), and C12C4 (bottom) used as surfactants (only on the hydrate particle). The distance D is measured between the COM of the bare droplet and that of the hydrate particle. In the initial conditions the water droplet is far from the hydrate particle (D > 5 - 6 nm, left); the system evolves until the droplet

begins to touch the hydrate particle (D ~ 4.1 - 4.5 nm, middle). The simulations are interrupted when coalescence occurs (*D* ~ 2.5 nm, right). In Figure S5 we report similar results obtained when both the water droplet and the hydrate particles are covered with surfactants.



Figure S4. Sequence of simulation snapshots representing typical hydrate particle – bare droplet coalescence processes. Results are shown for C16C1 (top), C16C4 (middle), and C12C4 (bottom) used as surfactants. Small red and white spheres represent oxygen and hydrogen atoms in water molecules of hydrate, respectively, while enlarged red and white spheres represent oxygen and hydrogen atoms in water molecules initially within the droplet. Yellow, green, and gray spheres represent chloride ions, nitrogen atoms and alkyl groups in surfactants, respectively. The hydrocarbon mixture is not shown for clarity.



Figure S5. Same as Figure S4, but for systems in which both the hydrate particles and the water droplets are coated with surfactants: C16C1 (top), C16C4 (middle), and C12C4 (bottom).



Figure S6. Density distributions of chloride counterions when C16C1 (red), C16C4 (blue), and C12C4 (green) surfactants are adsorbed on the hydrate surface. The distance r is measured radially from the COM of the hydrate particle.

In Figure S6 we show the radial density distribution of chloride counterions when C16C1 (red), C16C4 (blue), and C12C4 (green) surfactants are adsorbed on the hydrate surface. The distance r is measured radially from the COM of the hydrate. We observe that the chloride counterions extend further away from the hydrate when either C16C4 or C12C4 are used rather than C16C1.



Figure S7. Sequence of simulation snapshots for the system in which initially the surfactants were adsorbed densely on one region of the hydrate particle covered by a thin water film. The color code is the same as that of Figure S1, except that reduced red and white spheres represent oxygen and hydrogen atoms in water molecules initially within the droplet. The hydrocarbon mixture is not shown for clarity.

In Figure S7 we show sequences of simulation snapshots obtained for one system in which the surfactants were initially densely adsorbed on one region of the hydrate particle. A thin water film covered the hydrate. The simulations, which were conducted at 277 K, show that after 20 ns, the surfactants distributed uniformly on the hydrate – water surface.



Figure S8. Sequence of simulation snapshots illustrating the coalescence between one hydrate particle and one bare water droplet. The simulations were conducted without steering forces. Results are shown in the presence of C16C4 (top) and C12C4 (bottom) surfactants. The color code is the same as that of Figure S4. The hydrocarbon mixture is not shown for clarity.

In Figure S8, we report sequences of simulation snapshots obtained for systems containing the hydrate particle coated with C16C4 (top) or C12C4 (bottom) surfactants and one bare droplet. The simulations were conducted without steering forces. From initial conditions (t = 0 ns, left), the system evolves until coalescence is well underway (t = 29 or 39.7 ns, right). Similar results were obtained when using C16C1. Note that in a few ns after coalescence has started, the surfactants cover the water-oil interface.



Figure S9. Same as Figure S8, but for the water droplet coated with C16C4 surfactants. Top and bottom panels represent two sequences of simulations started from slightly different initial configurations. *Top*: $D \sim 4.94$ nm. *Bottom*: $D \sim 4.92$ nm. In the bottom middle panel, at t = 7 ns, one water molecule establishes a molecular bridge (see main text for details).

When we repeat a simulation similar to the one discussed in Figure S8 for a droplet coated with C16C4 or C12C4, we do not observe coalescence even after hundreds of nanoseconds, instead the water droplet moves further apart from the hydrate particle. Using information from PMF shown in Figure 4, main text, we test the probability of occurrence of coalescence when the coated droplets are brought close to the hydrate particle. The results are shown in Figure S9 and S10. Starting from $D \sim 4.9$ or 4.6 nm when using C16C4 or C12C4, respectively, coalescence can be observed.



Figure S10. Same as Figures S8 and S9, but for the water droplet coated with C12C4 surfactants. *Top*: $D \sim 4.7$ nm. *Bottom*: $D \sim 4.6$ nm. In the bottom middle panel, at t = 13.95 ns, one water molecule establishes a molecular bridge between the hydrate particle and the droplet.



Figure S11. Top views of sequence of simulation snapshots illustrating the displacement of C16C1 (top) and C12C4 (bottom) surfactants adsorbed on the hydrate surface during the coated droplet – hydrate particle coalescence processes. The images represent the evolution of the system from initial conditions that the water droplet is not at contact with the hydrate particle (D > 6 nm, left), until they merge ($D \sim 3.51$ nm, right). Only a portion of hydrate particle and some representative surfactants adsorbed on the hydrate surface are shown for clarity. A yellow cross represents the position where the droplet first touches the hydrate surface.

In Figure S11, we show a sequence of representative simulation snapshots illustrating the displacement of C16C1 (top) and C12C4 (bottom) surfactants adsorbed on the hydrate surface when the droplet approaches and adsorbs on the hydrate. Only a portion of hydrate particle and some representative surfactants adsorbed on the hydrate surface are shown for clarity. At the initial conditions the water droplet is not at contact with the hydrate particle (D > 6 nm, left). In the final configuration water droplet and hydrate particle merge ($D \sim 3.51$ nm, right). Visual inspection of the snapshots confirm that when the droplet and the hydrate particle merge the water molecules of the droplet are more likely to push away the C16C1 surfactants adsorbed on the hydrate surface than C12C4 or C16C4 (results not shown for brevity).



Figure S12. In-plane density distributions of n-decane molecules found in a slab with thickness 4 Å confined between the hydrate particle and the water droplet. Results are obtained for the systems containing the hydrate particle coated with C16C1 surfactants and the bare at D = 5.24 nm (left panel) or coated droplet at D = 6.01 nm (right panel).

In Figure S12 we present the in-plane density distributions of n-decane molecules found in a slab with thickness 4 Å in the region between the hydrate particle and the water droplet. Results are obtained for the hydrate particle coated with C16C1 surfactants and the bare droplet at D = 5.24 nm (left panel) or coated droplet at D = 6.01 nm (right panel). The results suggest that the alkyl tails of C16C1 surfactants on the droplet disrupt the hydrocarbon phase.

To quantify the effect of alkyl groups on the quaternary head groups of surfactants on the water – water hydrogen bond (HB) network, we analyze the pair density for the water oxygen – ammonium head group pairs in the coated droplet and we then calculate the average number of HBs per water molecule in the first shell around ammonium head groups. We report the results for pair density profiles and the average number of HBs in Figure S13. Results are obtained for C16C1 (red), C16C4 (blue), and C12C4 (green). The average number of HBs per water molecule in the first shell around ammonium for HBs per water molecule in the first shell around a number of HBs per water molecule in the first shell around



Figure S13. Pair density for the water oxygen – ammonium head group pairs in the droplet coated with C16C1 (red), C16C4 (blue), and C12C4 (green). The results of average number of the water – water hydrogen bonds per water molecule in the first shell around ammonium head groups (represented by the region between two dashed lines) for each surfactant used are shown.



Figure S14. Probability distribution for the angle of the vector connecting the ammonium head group and the end of the hydrocarbon tail with respect to the surface normal. Results are obtained for C16C4 (blue) and C12C4 (red) surfactants adsorbed on the top of hydrate surface only.

In Figure S14 we report the probability distribution for the angle of vector connecting the ammonium head group and the end of the hydrocarbon tail with respect to the surface normal. Results are obtained for C16C4 (blue) and C12C4 (red) surfactants adsorbed on the top of hydrate surface. The results suggest that C12C4 surfactants are slightly more likely to maintain their hydrophobic tails parallel to the hydrate surface than C16C4 (~85° obtained for C12C4 vs. ~55° obtained for C16C4). In Table S1 we present the results of the average radius of the water core of the coated droplet using different surfactants. The method for calculating the averaged radius of the water core is described elsewhere.^{4,5} We also report the radius of the hydrate particle covered by a layer of chloride ions. The results show that the sum of the averaged radius of the water core and the radius of hydrate particle covered by a layer of chloride ions approximately matches the hydrate-droplet separation at which coalescence occurs.

 Table S1. Averaged radius of the water core of the coated droplet and the hydrate particle covered by a layer of chloride ions. Results are shown for C16C1, C16C4 and C12C4 surfactants

Simulation	[A] Averaged radius of the water core (nm)	[B] Radius of the hydrate particle covered by a layer of chloride ions (nm)	[A] + [B] (nm)
C16C1	1.75	2.44	4.19
C16C4	1.87	2.95	4.82
C12C4	1.89	2.80	4.69

References

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