Supporting Information

Coarse-grain molecular dynamics Simulation framework
to unravel the interactions of surfactants on silica surfaces
for oil recovery

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Table of contents

Table S1. Details of the simulation boxes; number of water molecules for 8 %wt., 13 %wt., 30 %wt. and 60 %wt. C16E6 concentrations besides 8 %wt., 13 %wt., 30 %wt. for C16TAB solutions and dimension in Z (normal direction to the silica surface).

Figure S1. CG-MD simulation snapshots for 8 %wt., 13 %wt., 30 %wt. and 60 %wt. C16E6 concentrations in aqueous solution with eicosane over the silica surface.

Figure S2. Simulation snapshots for 8 %wt. and 13 %wt. of C8E6 concentrations denoting the absorption of the eicosane by C8E6 micelles.

Figure S3. CG-MD simulation snapshots for 8 %wt., 13 %wt., 30 %wt. and 60 %wt. C16E6 concentrations besides 13 %wt., 30 %wt. and 60 %wt. C16TAB concentrations with the dodecane.

Figure S4. CG-MD simulation snapshots for 8 %wt., 13 %wt., 30 %wt. and 60 %wt. C16E6 concentrations besides 13 %wt., 30 %wt. and 60 %wt. C16TAB concentrations in aqueous solution with eicosane.

Figure S5. Solvent accessible surface area (SASA) profiles of dodecane and eicosane overall C12E6 concentrations.

Figure S6. Solvent accessible surface area (SASA) profiles of dodecane and eicosane overall C8E6 concentrations.

Figure S7. Solvent accessible surface area (SASA) profiles of dodecane and eicosane overall C16E12 concentrations.

Figure S8. Solvent accessible surface area (SASA) profiles of dodecane and eicosane overall C8E12 concentrations.

Figure S9. Structures obtained in the 60 %wt. C16E12 and C8E12 solutions exhibiting parallel rods and a singular structure of parallel rods with intercalated spherical micelles.

Figure S10. Density profile along the Z-axis normal to the reference silica surface overall C12E6 concentrations.

Figure S11. Density profile along the Z-axis normal to the reference silica surface overall C8E6 concentrations.

Figure S12. Density profiles along the Z-axis normal to the reference silica surface overall C16E12 concentrations.

Figure S13. Density profiles along the Z-axis normal to the reference silica overall C8E12 concentrations.

Figure S14. Density profiles along the Z-axis normal to the reference silica overall C16TAB concentrations for dodecane and eicosane systems.

Figure A1. MARTINI 2.2 CG mapping for C12E6, C16TAB, water molecules, the silica model, dodecane and eicosane.

Figure A2.1. Number density of the dodecane as a function of the z-coordinate of the simulation box.

Figure A2.2. CG-MD simulation snapshots for the silica surface and dodecane in contact with water at 100 and 1000 ns of simulation time. b) CG-MD simulation tests for silica-water, graphene-water and silica-polarisable water performed to evaluate the silica or graphene interaction with water.

Figure A2.3. Comparison of the number density of the dodecane in the normal direction to the silica surface between MARTINI 2.2 and MARTINI 3.0 besides a CG-MD simulation snapshot after 1000 ns for the silica-dodecane-water systems.

Figure A3.1. CG-MD simulation snapshots after 2000 ns using the 8 %wt., 13 %wt. and 30 %wt. surfactant concentration runs but without surfactants for a) dodecane and b) eicosane.
**Table S1.** Number of water molecules for 8 %wt., 13 %wt., 30 %wt. and 60 %wt. C\textsubscript{16}E\textsubscript{j} concentrations besides 8 %wt., 13 %wt., 30 %wt. for C\textsubscript{16}TAB solutions used in the CG-MD simulation runs. The number of surfactants, dodecane and eicosane molecules was 2000, 1664 and 1000, respectively. The same number of water molecules (CG beads entailing 4 water molecules each) were used in dodecane and eicosane systems to maintain the surfactant/water ratio overall systems. The X-Y dimensions of the simulation boxes (silica surface plane) were fixed to 23x17.25 nm.

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Figure S1. CG-MD simulation snapshots obtained after 2000 ns of simulation time for 8 \%wt., 13 \%wt., 30 \%wt. and 60 \%wt. C$_i$E$_j$ concentrations in aqueous solution with eicosane over the silica surface. Green and purple colours represent the alkyl tail beads and EO units of C$_i$E$_j$, respectively. Eicosane is coloured grey and the silica surface in yellow. The size of some simulation boxes was scaled for a clearer comparison and water molecules were removed for clarity.
Figure S2. Simulation snapshot of 8 %wt. (left) and 13 %wt. (right) of C₈E₆ concentrations with eicosane. After 2000 ns of simulation time, most of the eicosane remained partially attached to the surface involved by the of C₈E₆ surfactant. Though, some micelles in the water phase confirmed some degree of eicosane detachment marked with red circles. The colour code is the same as in Figure S1 where water molecules were removed for clarity. The size of green and purple beads of C₈E₆ were reduced to highlight the absorbed eicosane.
Figure S3. CG-MD simulation snapshots for 8 %wt., 13 %wt., 30 %wt. and 60 %wt. C_{12}E_6 concentrations besides 13 %wt., 30 %wt. and 60 %wt. C_{16}TAB concentrations in aqueous solution with dodecane. Only the alkyl tails of the surfactant were shown (green) to enhance the view and dodecane was coloured in grey. Water molecules were removed for clarity.
**Figure S4.** CG-MD simulation snapshots for 8 %wt., 13 %wt., 30 %wt. and 60 %wt. C_{12}E_6 concentrations besides 13 %wt., 30 %wt. and 60 %wt. C_{16}TAB concentrations in aqueous solution with eicosane. Only the alkyl tails of the surfactant were shown (green) to enhance the view and eicosane was coloured in grey. Water molecules were removed for clarity.
1. Detailed analysis of SASA

Figure S5. Solvent accessible surface area (SASA) profiles of dodecane a) and b) eicosane overall C_{12}E_{6} concentrations after 2000 ns simulation time. The colour code for each concentration is as follows: black for 8 %wt., green for 13 %wt., purple for 30 %wt., and red for 60 %wt. C_{12}E_{6} concentrations. The simulation snapshots, before and after the noticeable variations are also shown as insets with coloured arrows.
Figure S6. Solvent accessible surface area (SASA) profiles of dodecane a) and b) eicosane overall $C_8E_6$ concentrations after 2000 ns simulation time. The colour code for each concentration is as follows: black for 8 %wt., green for 13 %wt., purple for 30 %wt., and red for 60 %wt. $C_8E_6$ concentrations. The simulation snapshots, before and after the noticeable variations are also shown as insets with coloured arrows.
Figure S7. Solvent accessible surface area (SASA) profiles of dodecane a) and b) eicosane overall C₁₆E₁₂ concentrations after 2000 ns simulation time. The colour code for each concentration is as follows: black for 8 %wt., green for 13 %wt., purple for 30 %wt., and red for 60 %wt. C₁₆E₁₂ concentrations. The simulation snapshots, before and after the noticeable variations are also shown as insets with coloured arrows.
Figure S8. Solvent accessible surface area (SASA) profiles of dodecane a) and b) eicosane overall $C_{8}E_{12}$ concentrations after 2000 ns simulation time. The colour code for each concentration is as follows: black for 8 %wt., green for 13 %wt., purple for 30 %wt., and red for 60 %wt. $C_{8}E_{12}$ concentrations. The simulation snapshots, before and after the noticeable variations are also shown as insets with coloured arrows.
Figure S9. Structures obtained in the 60 %wt. C_{16}E_{12} and C_{8}E_{12} solutions exhibiting parallel rods and a singular structure of parallel rods with intercalated spherical micelles, respectively. The colour code is the same as in Figure S1. The EO groups, dodecane and water molecules were removed for clarity.
2. Structural analysis throughout density profiles

2.1. C₁₂E₆

The density profile of the 8 %wt. system with dodecane is shown in Figure S10a where some dodecane molecules remained close to the silica surface (< 2nm) in a layered structure but most was wrapped by C₁₂E₆ assemblies. At higher distances, the density profile of C₁₂E₆ abruptly decayed since the C₁₂E₆ surfactant could only form some rods close to the surface rather homogeneously distributed in the water rich phase as observed in the C₈E₆ and C₈E₁₂ solutions. From the density profile of the dodecane (grey), one can roughly establish a size of ~ 12 nm for the cluster visualised in Figure 2. Only a few dodecane molecules were detached from the surface in the 13 %wt. solution (not captured in the density profile) while most of the dodecane remained as layered structures close to the silica as it can be seen in Figure S10b. The alkyl tails of C₁₂E₆ (green) also penetrated the dodecane coat with the EO groups pointing towards the water rich phase (purple). Different scenario was displayed in the 30 %wt. and 60 %wt. solutions (Figures S10c-d) where the dodecane was partially detached, resembling the 8 %wt. density profile but the C₁₂E₆ cluster surrounding the dodecane was less obvious. Figures S10e-g display the profiles for the 8 %wt., 13 %wt. and 30 %wt. solutions with eicosane, totally attached to the silica surface and presenting layered structures for the eicosane and the C₁₂E₆ surfactant acting as a coat to the water rich phase. Figure S10h denoted the partial detachment of eicosane whose density could be measured up to ~ 4 nm away from the silica surface. Some C₁₂E₆ aggregates can be found along the simulation box suggesting a C₁₂E₆ gyroid-like structure with some eicosane molecules immersed in the branches as also noticed in Figure S1. 
Figure S10. Density profiles along the Z-axis normal to the reference silica surface in yellow whereas the oil besides the hydrophobic segment and the hydrophilic EO groups of C_{12}E_6 are shown in grey, green and purple, respectively. a), b), c) and d) correspond to the 8 %wt., 13 %wt., 30 %wt. and 60 %wt. C_{12}E_6 concentration for the systems with dodecane whilst e), f) g) and h) for the systems with eicosane. The density profiles were obtained with the last 500 ns of simulation time.

2.2. C_{8}E_6

Figures S11a-b show the density profiles for the 8 %wt. and 13 %wt. solutions where dodecane was totally removed from the silica surface. The density profile of C_{8}E_6 EO hydrophilic groups (purple) and alkyl hydrophobic groups (green) can be found well immersed in the water
phase, highlighting the fact that all C$_8$E$_6$ micelles with absorbed dodecane (denoted by the maximum in grey) were detached from the silica surface (yellow). Figures S11c-d show the density profiles of 30 %wt. and 60 % wt. stressing out how the dodecane cannot be totally detached from silica. In fact, a layered structure of water, dodecane and C$_8$E$_6$ (purple and green) was formed over the silica surface, resembling the arrangement observed in the simulation snapshots (Figure 2). Figure 11e shows the 8 %wt. solution denoting the formation of a water and eicosane layered structure relatively close to the silica surface with C$_8$E$_6$ partially wrapping the eicosane as denoted in the simulation snapshot shown in Figure S1 whereas the C$_8$E$_6$ was found in the water phase. Figure S11f shows the 13 %wt. system denoting bulky C$_8$E$_6$ micelles as the constant green and purple lines along Z stress. The majority of the eicosane can be found close to the silica surface, denoted by the first intense maximum (grey curve). However, some eicosane was absorbed by C$_8$E$_6$ micelles (2$^\text{nd}$, 3$^\text{rd}$ and 4$^\text{th}$ peaks in grey), mainly found in the water phase. Figure S11g displays the 30 %wt. solution somehow resembling the 8 %wt. density profile with a relatively constant C$_8$E$_6$ density along the Z-axis but without bulky micelles as can be also noticed in Figure S1. Conversely, the 60 %wt. solution shown in Figure S11h, shows how the eicosane remained attached to the surface as a layer, with a constant C$_8$E$_6$ density along the simulation box while most of the water was displaced from the silica surface (Figure S1) as in the solution with dodecane (Figure 2).
Figure S11. Density profiles along the Z-axis normal to the reference silica surface in yellow whereas the oil besides the hydrophobic segment and the hydrophilic EO groups of C₆E₆ are shown in grey, green and purple, respectively. a), b), c) and d) correspond to the 8 %wt., 13 %wt., 30 %wt. and 60 %wt. C₆E₆ concentration for the systems with dodecane whilst e), f) g) and h) for the systems with eicosane. The density profiles were obtained with the last 500 ns of simulation time.

2.3. C₁₆E₁₂

Figure S12a denotes the 8 %wt. C₁₆E₁₂ solution with the water and dodecane arranged in a layered structure close to the silica surface with C₁₆E₁₂ clusters partially wrapping some of dodecane (grey line) up to 10 nm away from the silica surface. Green and purple lines a above 10 nm correspond to the C₁₆E₁₂ spherical and rod-like structures shown in Figure 2. The density profiles of C₁₆E₁₂ alkyl tails in 8 %wt., 13 %wt. and 30 %wt. demonstrate that C₁₆E₁₂ clusters were formed and linked to the silica surface (insets < 5 nm). Figures S12b-c display a similar picture for 13 %wt. and 30 %wt. concentrations with the dodecane close to the silica surface, partially absorbed by C₁₆E₁₂ clusters with similar size (~ 10 nm). The sinusoidal shape of the C₁₆E₁₂ green and purple lines resembles the micellar structures in the water rich phase found in the 8 %wt. solution. Conversely, for the 60 %wt. solution, Figure S12d clearly shows a dodecane layer structure arranged over the silica followed by a thin layer of C₁₆E₁₂ with the alkyl tails (green) pointing towards the dodecane (inset between 0.5 and 2 nm). Above 2 nm, the C₁₆E₁₂ assembled into spherical and rod-like structures that fill the entire simulation box (Figure 2). Remarkably, the density profiles for 8 %wt., 13 %wt. and 30 %wt. solutions with eicosane shown in Figures S12e-g are almost identical. Thus, despite the difference in concentration, the water and eicosane
molecules were arranged as layered structures with water interpenetrating the eicosane and reaching the surface with no clear detachment, unlike the diluted systems with dodecane. The density profiles of $C_{16}E_{12}$ (green and purple lines in Figures S12e-g) denotes that no clear partial eicosane detachment occurred since the $C_{16}E_{12}$ alkyls tails were found further away from the silica surface compared with the dodecane solutions (Figures 12a-c). Green and purple lines demonstrate that spherical and rod-like $C_{16}E_{12}$ micellar structures are distributed along the simulation box. Finally, Figure S12h resembles the profile found with dodecane at 60 %wt., with a consecutively layered structure of eicosane and water followed by densely packed $C_{16}E_{12}$ micelles.
Figure S12. Density profiles along the Z-axis normal to the reference silica surface in yellow whereas the oil besides the hydrophobic segment and the hydrophilic EO groups of C_{16}E_{12} are shown in grey, green and purple, respectively. a), b), c) and d) correspond to the 8 %wt., 13 %wt., 30 %wt. and 60 %wt. C_{16}E_{12} concentration for the systems with dodecane whilst e), f) g) and h) for the systems with eicosane. The density profiles were obtained with the last 500 ns of simulation time.

2.4. C_{8}E_{12}

Figure S13a shows that the dodecane (grey) in the 8 %wt. C_{8}E_{12} solution remained close to the surface in a layered structure, enclosed by the hydrophobic alkyl tails (green) and hydrophilic EO groups (purple) of C_{8}E_{12}. No trace of dodecane was observed inside the C_{8}E_{12} bulky micelles shown by the green and purple curves above 10 nm. Figure S13b shows the formation of a water layered structure over the silica surface at the 13 %wt. concentration, with a similar arrangement of dodecane over it and surrounded by a C_{8}E_{12} cluster enclosing the partial detached dodecane. The irregular profile arises from the late partial separation of dodecane (Figure 2) as also denoted in the SASA profile (Figure 3 > 1700 ns). Thus, only the trajectory of the last 300 ns of simulation were taking to obtain the density profile. Figure S13c displays the density profile of the 30 %wt. C_{8}E_{12} solution where the water formed a layered structure with partial detached dodecane, similarly to the 13 %wt. solution. However, the sinusoidal shape of the C_{8}E_{12} and water density profiles along the Z-axis suggest the formation of a regular structure. An analysis of the simulation snapshot (Figure 2) points towards the formation of a gyroid-like phase where water occupies the inner channels. The extend of the partially detached dodecane corresponded with the 8 %wt. system as can be seen in the insets of Figures S13a and S13c. Figure S13d denotes the formation
of water and dodecane layered structures over the silica surface (between 0.5 and 1.5 nm) in the 60 %wt. solution. Above the dodecane layer, the regular pattern of the C₈E₁₂ curve indicates the formation of a long-range ordered hexagonal phase immersed in the water phase. Also, the density profile emphasizes how some water molecules reached the silica despite the dodecane completely covered the surface. The simulation snapshot inset included in Figure S13d emphasizes how the water molecules (blue) can be found at the bottom of the dodecane layer (silica is not shown for clarity). Figure S3e shows the partial eicosane removal from the surface in the 8 %wt. solution where C₈E₁₂ can be found along the simulation box denoting the formation of bulky micelles as observed in Figure S1. The C₈E₁₂ cluster size, with wrapped eicosane, was slightly smaller than the dodecane at 8 %wt. (Figure S13a). The 13 %wt. C₈E₁₂ concentration system shown in Figure S1 exhibited a gradual detachment process and almost identical to the system with dodecane. If one compares both SASA profiles (green curves in Figures S8a-b), the partial detachment occurred at ~ 1700 ns in both. In fact, the size of the structures found were comparable to the C₈E₁₂ cluster covering the partially detached oil, besides the formation of bulky micelles with no absorbed oil, as illustrated in the density profile of Figure S13f. Some water molecules were arranged into layers on the top of the surface, with a small amount of eicosane in close contact with the silica but mostly wrapped by the C₈E₁₂ cluster. Figures S13g-h display the 30 %wt. and 60 %wt. solutions with eicosane, whose density profiles resembled those found for dodecane. However, it must be noticing that the undulations of the C₈E₁₂ density profiles (green and purple curves) observed in the 30 %wt. system with dodecane were less clear in this system as can be seen in Figure S13g. This suggests that the gyroid-like phase is more diffused with eicosane. Finally, the density profile of the 60 %wt. solution with eicosane practically resembled the dodecane system if one compares Figures S13d and S13h. Thus, no eicosane was removed from the silica surface and the C₈E₁₂ formed a hexagonal phase over it as shown in Figure S1.
Figure S13. Density profiles along the Z-axis normal to the reference silica surface in yellow whereas the oil besides the hydrophobic segment and the hydrophilic EO groups of C₈E₁₂ are shown in grey, green and purple, respectively. a), b), c) and d) correspond to the 8 %wt., 13 %wt., 30 %wt. and 60 %wt. C₈E₁₂ concentration for the systems with dodecane whilst e), f) g) and h) for the systems with eicosane. The density profiles were obtained with the last 500 ns of simulation time.

2.5. C₁₆TAB

Figure S14a shows that water and dodecane molecules can be found in the C₁₆TAB gyroid-like phase shown for the 13 %wt. C₁₆TAB solutions, also denoted by the sinusoidal shape of the C₁₆TAB alkyl and ammonium centres (green and purple). The water reached the silica surface
overall concentrations (first peak in blue close to the silica surface revealed in the insets of Figures S14a-c) besides a noticeable amount of C\textsubscript{16}TAB ammonium centres close to the surface as denoted in the inset of Figure S14b. This was also reflected in the relatively high SASA values for the 30 \%wt. solution displayed in Figure 3 where the dodecane gained access to water. Figures S14d-f displays a similar behaviour found in the solutions with eicosane where the water molecules penetrated through the channels of the C\textsubscript{16}TAB gyroid-like phase, reaching the silica surface overall concentrations. However, the density profile of 13 \%wt. C\textsubscript{16}TAB solution with eicosane, displayed in Figure S14d, unveiled the poor population of water molecules and eicosane moieties over the silica surface. In fact, the alkyl chains of C\textsubscript{16}TAB mainly coated the entire silica surface pointing that the eicosane was partially detached from the surface, but still densely packed inside the gyroid-like C\textsubscript{16}TAB channels. In this regard, the density profiles provided a valuable picture that was not clearly comprehended in the simulation snapshot shown in Figure S1 but concords with the higher SASA of eicosane shown in the 13 \%wt. solution (Figure 5 solid green line). As observed in the 30 \%wt. solution with dodecane, in the 60 \%wt. system with eicosane the C\textsubscript{16}TAB ammonium centres were arranged closer to the silica surface as indicated in the inset of Figure S14f and denoted by the higher SASA of the ammonium centre displayed in Figure 5b (red dashed line) when compared with the 13 \%wt. and 30 \%wt. solutions. The C\textsubscript{16}TAB density help to understand the formation of water channels in cationic surfactants since from the CG-MD simulation snapshots displayed in Figure 3, the C\textsubscript{16}TAB and oil seem to be completely attached and covering the entire silica surface. Thus, the formation of C\textsubscript{16}TAB gyroid-like structures promoted water channels reaching the silica surface, as observed in previous atomistic simulations[1].
Figure S14. Density profiles along the Z-axis normal to the reference silica surface shown in yellow. The oil is coloured in grey, the hydrophilic charged ammonium head groups and the alkyl chains of C<sub>16</sub>TAB are shown in purple and green, respectively. a), b) and c) correspond to 13% wt., 30% wt. and 60% wt. C<sub>16</sub>TAB concentration with dodecane and d), e) and f) the 13% wt., 30% wt. and 60% wt. C<sub>16</sub>TAB concentrations with eicosane. The density profiles were obtained with the last 500 ns of simulation time.
Appendix

A.1. ClE\textsubscript{j}, C\textsubscript{16}TAB, silica surface and oil samples in MARTINI 2.2

With the aim to overcome the limitations of MARTINI 2.2\cite{2} to reproduce compounds based on poly(ethylene oxide) (PEO), Grunewald et al.\cite{3} developed a new set of parameters that were able to capture significant physico-chemical aspects of aqueous solutions of PEO-based nonionic surfactants or polystyrene (PS)-PEO copolymers. Later, Crespo et. al.\cite{4} demonstrated that this model can reproduce very well the phase behaviour of different Poly(oxyethylene) alkyl ethers (C\textsubscript{i}E\textsubscript{j}). Figure A1 show the CG mapping scheme for C\textsubscript{12}E\textsubscript{6} surfactant as an example. Apolar C\textsubscript{1} beads were selected to map the alkyl groups, the new EO bead (which includes the OCH\textsubscript{2}CH\textsubscript{2} group)\cite{3} was chosen for the ethylene oxide and the terminal hydroxyl group was mapped with the SP\textsubscript{2} polar bead. The CG model for C\textsubscript{16}TAB was taken from MARTINI 2.2\cite{2} in which tetramethyl ammonium moieties are mapped with Q\textsubscript{0} (charged with no hydrogen donor/acceptor character) and C\textsubscript{1} beads for the alkyl chain. Consequently, dodecane and eicosane are also represented by C\textsubscript{1} beads as shown in Figure A1. The silica surface was modelled with the CG bead type chosen by Perrin et al.\cite{5} where the N\textsubscript{d} (non-polar bead with donor hydrogen bond capability) was selected to study the interactions between surfactants and a rigid surface formed by silanol groups.

![MARTINI 2.2 Coarse-Grained Framework](image)

Figure A1. MARTINI 2.2 CG mapping for C\textsubscript{12}E\textsubscript{6} \cite{3,4} C\textsubscript{16}TAB \cite{6} the silica model from Perrin et al.\cite{5} and the oil samples besides the water models were taken from MARTINI 2.2\cite{2}
A.2. Molecular modelling and coarse-grained model validation

The AA-MD simulations carried out by Tang et al.[1] inspired us to model our CG-MD framework to tackle the interactions between silica-based surfaces and oils. Tang et al. addressed the detachment of oil from a hydroxylated silica surface using aqueous solutions of three different surfactants (nonionic, ionic and anionic), including the nonionic surfactant octylphenol polyoxyethylene ether. Their AA-MD consisted in randomly arrange 130 dodecane molecules over a silica surface and the simulation was run for 10 ns, revealing the arrangement of the dodecane molecules over the silica surface. They obtained the density profile of dodecane along the direction normal to the silica surface and compared with previous reports.[1] Taking this configuration as a reference, we constructed a silica surface containing 5000 silanol groups and 1664 molecules of dodecane (to maintain the same silica/dodecane ratio used in Tang et al.) were randomly arranged over the silica surface. The CG parameters used in the simulations are summarised in Figure A1, and the simulation box consisted of a silica surface at the bottom of a triclinic box (23 x 17.25 x 30 nm) where a dodecane layer of 1664 molecules was placed over it. After an energy minimisation/equilibrium steps, the NVT production run was run for 500 ns. Figure A2.1 shows the number density of dodecane in the normal direction to the silica surface, exhibiting three layers as found by Tang et al. Even though the location and intensity of the peaks were different, caused by the different scales and the different of the degree of detail between AA and CG simulations, both profiles are in a reasonable qualitative good agreement. In fact, the three main peaks displayed similar distances and the dodecane layer width was 1 nm in both, AA, and CG.
Tang et al. also reported AA-MD simulations including water, concluding that even though the dodecane molecules were dislocated at the top layer, the water molecules could not penetrate the dodecane. We reproduced the same scenario where 100000 water molecules (25000 CG water beads) were included in our CG system. Figure A2.2a compares the simulation snapshots at 100 and 1000 ns, displaying a different scenario that it was found by Tang et. al. The water was completely frozen revealing the limitations of the MARTINI 2.2 water model. In fact, when MARTINI 2.2 was developed, Marrink et. al.[2] recommended the addition (10%) of special “anti-freeze” water beads (BF₄) to avoid unrealistic freezing of water under conditions that must be liquid.[2] The dodecane detachment and frozen water observed in our simulation was likely caused by the poor energy landscape of the MARTINI 2.2 water model. Analysing the trajectory of the simulation from 100 to 1000 ns, the freezing of water occurred at the dodecane-water interphase nor at the liquid-vapor.
Figure A2.2. a) CG-MD simulation snapshots for the silica surface (yellow) and dodecane (grey) layer in contact with water (blue) at 100 and 1000 ns of simulation time. b) CG-MD simulation tests for silica-water (left), graphene-water (centre) and silica-polarisable water[7] (right) performed to evaluate the silica or graphene interaction with water.

Additional CG-MD simulations were carried out entailing different concentrations of “anti-freeze” water beads, unfortunately yielding the same “frozen water” scenario. Furthermore, three CG-MD simulations with water in contact with the silica or graphene (graphene is widely studied entailing a hydrophobic character, in contrast with the polar silica surface) surfaces were carried out along 1000 ns. Figure A2.2b displays the simulation tests carried out with the silica-water (left), graphene-water (centre) and silica-polarizable water[7] (right). Figure A2.2b illustrates how the water was quickly frozen over the surface with silica (left) or graphene (centre) when the MARTINI 2.2 regular water was used (more noticeable in the silica surface due to its polar character). It must be noticed that researchers also reported similar issues when describing the interactions between water and a graphene surface, arguing the limitations of the MARTINI 2.2 water model to describe surface-water interphase.[8] Conversely, the MARTINI 2.2 polarizable
water (right) was not frozen over the silica surface pointing towards the best scenario to construct our CG-MD simulation framework. Unfortunately, polarizable water requires a complete re-parameterisation of the surfactants and oils used in this study since, as far as we know, no models were reported yet. In fact, a test was performed for the systems disclosed in Table 1 and the polarisable water displayed very low micelle size distributions (half in average) compared with the systems using the regular MARTINI 2.2 water (Table 1) and experimental estimates.

The issues found with the water model of MARTINI 2.2 urged us to attempt the recently released MARTINI 3.0 which entails an important improvement in terms of the energy landscape of water (details can be found in the main manuscript) besides a more sophisticated parameterisation. Therefore, the silica-dodecane validation test previously performed was recapped by attempting a new parameterisation for silanol (C₂ CG beads are still used in MARTINI 3.0 to map the dodecane). The SN₁dq CG bead in MARTINI 3.0 was initially chosen since entails similar interaction energies when compared with the Nd MARTINI 2.2 version. In fact, Figure A2.3a compares the number density profile of dodecane in the normal direction to the silica surface for MARTINI 2.2 and 3.0 versions, exhibiting very similar profiles. Analogous CG beads for silanol were attempted (interaction energies values near to SN₁dq) and compared with the MARTINI 2.2 reference (analysis not shown) but the selected SN₁dq parameterisation yielded the best result.

Once the MARTINI 3.0 model for the silica surface was validated, the silica-dodecane was brought in contact with water, resembling the test done in MARTINI 2.2 (Figure A2.2b) to ensure that the water is not frozen. The tiny water model (TW) of MARTINI 3.0 encloses two water molecules per CG bead (2:1) and it is more computational demanding. However, it was selected since is more realistic and closer to the AA scale, offering a much better energy landscape compared with the W (4:1) and SW (3:1) models available in MARTINI 3.0. The silica-dodecane-water system was run along 1000 ns and the dodecane remained at the silica surface whilst the water was no frozen as it can be seen in Figure A2.3b.
Figure A2.3. a) Comparison between the number density of the dodecane in the normal direction to the silica surface for MARTINI 2.2 (black) and MARTINI 3.0 (red). b) CG-MD simulation snapshot after 1000 ns for the silica-dodecane-water system.

A.3. Silica-oil-water and surfactant-oil-water interactions

The simulation boxes used in the 8 %wt., 13 %wt., 30 %wt. surfactant concentration solutions shown in Figure 2 were repeated without surfactants to evaluate the stability of the dodecane or eicosane above the silica surface. Figure A3.1 displays the CG-MD simulation snapshots after 2000 ns where the dodecane (Figure A3.1a) remained completely attached to the silica surface overall concentrations whereas the eicosane was partially detached (Figure A3.1b). The impact of the surfactant can be clearly explored in the systems with dodecane since remained in equilibrium with water at least for 2000 ns of simulation whereas the water disrupted the eicosane layer, reaching the silica surface (Figure A3.1b). However, in presence of surfactants, the eicosane denoted more difficulties to be detached from the silica surface. Interestingly, when the above results are compared with their counterparts with surfactants, the C₈E₆ seems to have a weak impact in the eicosane detachment (Figures S1), being partially detached overall concentrations. Similarly, when the hydrophilic content is increased, the eicosane was partially detached from the silica surface with C₈E₁₂ (Figure 2). Conversely, if only the hydrophobic content is increased with the C₁₂E₆ surfactant or both with the C₁₆E₁₂ (Figure 2) (when compared with C₈E₆) the surfactant somehow hampered the detachment, in contrast with the systems without
surfactant (Figure A3.1b) which still attached to the silica surface at least for 2000 ns. The above results emphasize the impact of the surfactant concentration since the phase behaviour clearly impacts the detachment of oil. For instance, at relatively high hydrophilic balance HLB (Table 2), as C₈E₆ or C₈E₁₂, the surfactants mainly formed micelles or prolate shaped aggregates, yielding a total (dodecane) or partial oil detachments. However, only partial detachment or no detachment at all were obtained for low HLB systems as in C₁₂E₆ or C₁₆E₁₂ in which rod-like, hexagonal or gyroid phases were found. Conversely, the HLB has a lower impact in the detachment of oil when charged surfactants are used. The C₁₆TAB possesses the higher HLB of all the surfactant evaluated in this study (21.4). However, the dodecane and the eicosane remained densely packed and close to the silica surface where gyroid-like phases were formed overall concentrations (Figure 3) despite some water reached the silica surface as denoted in the density profiles shown in Figure S14.

**Figure A.3.1.** CG-MD simulation snapshots after 2000 ns using the 8 %wt., 13 %wt. and 30 %wt. surfactant concentration runs but without surfactants for a) dodecane and b) eicosane. Dodecane and eicosane are shown in grey, silica in yellow and water in blue.
References:


