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Synergistic interaction of hyperbranched polyglycerols and cetyltrimethylammonium bromide for oil/water interfacial tension reduction: A Molecular dynamics study.

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Abstract

Applying surfactants to reduce interfacial tension (IFT) on water/oil interfaces is a proven technique. The search for new surfactants and delivery strategies is an ongoing research area with applications in many fields, such as drug delivery through nanoemulsions and enhanced oil recovery. Experimentally, the combination of hyper-branched polyglycerol (HPG) with cetyltrimethylammonium bromide (CTAB) had reduced substantially the observed IFT of oil/water interface: 0.9 mN/m, while HPG alone was 5.80 mN/m, and CTAB alone IFT was 8.08 mN/m. Simulations in an aqueous solution showed that HPG is a surfactant carrier. Complimentary, in this work, we performed classical molecular dynamics simulations on combinations of CTAB and HPG with one aliphatic chain to investigate further the interaction of this pair in oil interfaces and propose the mechanism of IFT decrease. Basically, from our results, one can observe that the IFT reduction comes from a combination of effects that have not been observed for other dual systems: (i) due to the CTAB-HPG strong interaction, occurs a weakening of their specific and isolated interactions with the water and oil phases; (ii) the aggregates enlarge the interfacial area, a less ordered interface; and (iii) the spread of individual molecules' charge profiles, leads to the much lower interfacial tension observed with the CTAB+HPG systems.

Introduction

The search for new surfactants is an ongoing field of research with applications in a myriad of areas, such as drug delivery with nanoemulsions, medicine, agriculture, oil spill recovery, microfluidic, enhanced oil recovery, cleaning, among many other.¹⁻⁴ In particular, to answer to the yearly increasing oil production demand, mixtures of surfactants with other compounds like polymers and alkali have been used to flood existing reservoirs in the chemically enhanced oil recovery (EOR) process.⁵ Wang *et al.*⁶ used molecular dynamics (MD) to show that, when combined with the surfactant sodium dodecyl benzene sulfonate (SDBS),

the partially hydrolyzed polyacrylamide polymer (HPAM) that initially contributes to the formation and stabilization of foam produced by chemical flooding liquids, decreases the liquid film drainage rate upon a further increase in its concentration. Through numerical simulation, Zhong *et al.*⁷ found that the micro-displacement efficiency increases as the elasticity of a viscoelastic polymer increases during a two-phase flow in a micropore model. On the other hand, Fang *et al.*⁸ used photoetched glass model displacement experiments to correlate the increase in oil recovery in the high permeability model with increasing HPAM molecular weight, while for the low permeability model, the oil recovery first increases and then decreases upon increasing HPAM molecular weight.

The combination of different compounds has been based on each specific property, e.g., polymers increase the water viscosity inside the shale, decreasing its reactivity, while surfactants reduce the water-oil interfacial tension (IFT) or change the rock wettability. However, their coexistence in the mixture may result in antagonist or synergistic effects. Recently, several investigations addressing the synergistic behavior of different compound combinations have been conducted, not only from the experimental but also from the computational perspective. For example, Ciszewski *et al.*⁹ observed that the addition of hexanol as a cosurfactant along with CTAB further decreased the IFT compared to that of surfactant individually. The mechanism underlying the IFT reduction relies on increasing the surfactant adsorption at the interface by relieving their cationic head-group electrostatic repulsion when hexanol is placed between them. Thus, the synergistic effect would be due to the ability of alcohol molecules to interlink cationic surfactant molecules, shrinking the spaces among them, which, in turn, enables higher surfactant concentrations at the interface. Using similar methodology and techniques, Schabes *et al.*¹⁰ found that CTAB and polyacrylic acid (PAA) together can decrease the IFT by up to 5 times when the isoelectric ratio between them is reached. This effect is attributed to a charge coupling between the head groups of the adsorbed CTAB and the PAA carboxylate groups, uncoiling the PAA and allowing more polymer molecules to be added at the interface and hence bringing more surfactant

molecules to a subsequent charge neutralization. Numin *et al.*¹¹ investigated the effect of different concentrations of alkali-surfactant-polymer flooding on the water/oil IFT from experimental and theoretical approaches. Their results confirmed the major role played by the surfactant and the marginal effect on the IFT caused by the alkali or polymer addition. Spinning drop video tensiometer results show that when Na_2CO_3 and HPAM were added to the surfactant, the IFT slightly decreased. The interfacial thickness and the hydrogen bond analysis revealed that the ability of the surfactant to lower the IFT is affected by alkali or polymer similarly, by attracting surfactant molecules from the interface to the water-rich region and by suppressing hydrogen bond formation between the surfactant polar head and water molecules. So, essentially, the oil-water IFT further reduction observed for mixtures of surfactants comes from their ability to promote the concentration and organization of surfactants at the interface by alleviating their intermolecular repulsion.

On the other hand, in a recent work, Ferreira *et al.*¹² obtained a high performance in oil recovery by associating CTAB molecules with partially hydrophobic hyperbranched polyglycerol (HPG), a peculiar structure obtained by anionic, ring-opening multi-branching polymerization of glycidol^{13,14} or glyceryl carbonate.¹⁵ The authors proposed that the high density of functional groups available in the three dimensions for interaction/reaction in the structure of the HPG is one of the main factors for its superior performance in oil recovery when compared with linear polymeric structures^{16,17}

We have shown¹² that with more sites available to interact with the surfactant molecules, the HPG can act as a carrier. However, our simulations were then performed in aqueous solution. Here, we include the complex interfacial system to provide insight into the enhanced extraction mechanism. The understanding of the behavior of hyperbranched polyglycerols at the water/oil interface can contribute to the planning of the architecture of new hyperbranched polymers as surfactant carriers, with a performance superior to that observed before Ferreira *et al.*¹² Moreover, this knowledge can also contribute to the design of new compounds that could be applied in other systems, including drug carriers that act at bio-

logical water/oil interfaces.

Therefore, in this work, we employ molecular dynamics simulations to assess the synergistic effect of the CTAB and HPG on enhanced oil recovery since, as we have demonstrated before, the IFT reduction is of one order of magnitude. This strategy allows us to propose the atomistic interaction mechanism through density and charge profiles, order parameters, and radial distribution functions, deepening the understanding of this complex system.

Methodology

Simulations were conducted for CTAB ($\text{C}_{19}\text{H}_{42}\text{BrN}$) and HPG ($\text{C}_{54}\text{H}_{110}\text{O}_{27}$) individually and combined in the oil/water interfaces. As mentioned before, HPG is a hyperbranched polyglycerol whose structure, along with the other compounds' structures, is presented in Figure 1.

The oil model, as seen in figure 1, had the following composition: Hexane 11.15%, Heptane 14.03%, Octane 16.00%, Nonane 20.70%, Cyclohexane 7.26%, Cycloheptane 13.75%, Benzene 4.21%, and Toluene 12.90%, as already used in previous works.^{18–24}

The simulations were performed with the AMBER package^{25–28} using the TIP3P potential for water,²⁹ the GAFF2³⁰ and the Lipid14³¹ force fields for the oil and the surfactant molecules, respectively. The atomic charges were obtained using the RESP method³² together with the Antechamber software.³³ All the systems were assembled with Packmol.^{34,35}

The simulation of the HPG:CTAB agglomerate in water containing 100 molecules of each surfactant/polymer was run for 60 ns in an NPT ensemble. The agglomerate was then inserted in the oil/water/oil interface, and a new NPT simulation was run for 150 ns. The number of surfactant molecules at the interface, known as surface excess concentration (SEC), can be determined through sufficiently long simulations with molar excess.³⁶ The number of CTAB and HPG molecules that remain at the interface, individually and combined, were averaged from the final steps of isotropic NPT simulations of 150 ns at 300 K and 1 atm.

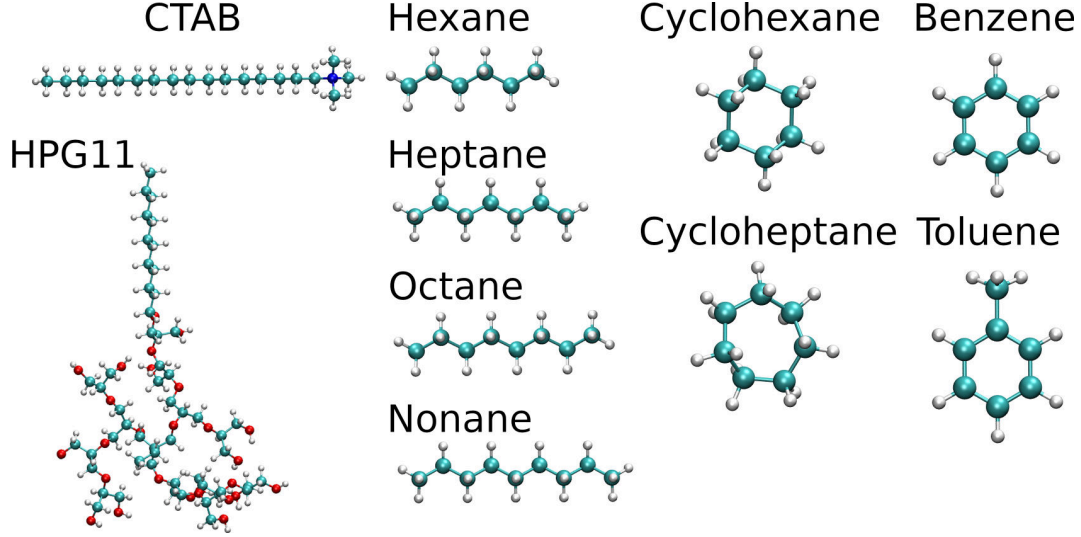


Figure 1: Molecules used in our simulations: HPG and CTAB and the oil model, which had a concentration of Hexane 11.15%, Heptane 14.03%, Octane 16.00%, Nonane 20.70%, Cyclohexane 7.26%, Cycloheptane 13.75%, Benzene 4.21%, and Toluene 12.90%. The white atoms are hydrogen, the blue are nitrogen, light blue carbon, and red oxygen.

Experimentally, the SEC, Γ , depends on the derivative of the interfacial tension, γ and the logarithm of the bulk concentration, C :³⁷

$$\Gamma = \frac{1}{nRT} \left(\frac{d\gamma}{d \ln C} \right). \quad (1)$$

Although a bulk concentration for the water solution can be set in the MD simulations, it has little meaning for the desired SEC because of the drastically different area/volume ratio compared to experiments. In the nanoscale simulations, most/all the surfactant molecules migrate to the interface; this leads to an SEC way lower than the experimental one for the same bulk concentration, simply due to the small number of molecules in the MD simulation cell and the high area/volume ratio. Moreover, it is not straightforward to infer the bulk concentration from an SEC value³⁸ without experimental data to compare. Nonetheless, besides the number of surfactant molecules at the interface obtained through MD simulations, the SEC values were also calculated for all systems investigated in this work. It should be mentioned that, for the HPG system, the optimized interfacial number of molecules was undetermined since any molecules left the interface even for simulations with high molecular

quantities.

Thereafter, new systems with the obtained number of molecules at the interface were further equilibrated with a simulation of 50 ns in an isotropic NPT ensemble followed by 50 ns of production runs. The total size of the simulated systems is shown in Table S1 of the supplementary material, although the sizes were around $100 \times 100 \times 250 \text{ \AA}$, and at least 200 thousand atoms.

The IFT was determined with the Irving-Kirkwood method,³⁹ as previously described.^{18,19,40} Since we have a liquid-liquid interface, the IFT (γ) can be obtained from the following equation:

$$\gamma = \frac{L_z}{n} \left(P_{zz} - \frac{P_{xx} + P_{yy}}{2} \right), \quad (2)$$

where γ is the IFT, L_z is the box length in the direction perpendicular to the interface, n is the number of interfaces, P_{zz} is the pressure normal to the interface, P_{xx} and P_{yy} are the pressure components parallel to the interface. The interfacial region widths were analyzed by fitting the water and oil density decays by hyperbolic tangents⁴¹ through the following function:

$$\rho(z) = \frac{1}{2}\rho_{water,oil} - \frac{1}{2}\rho_{water,oil}\tanh\left[\frac{2(z - z_0)}{d}\right], \quad (3)$$

where $\rho(z)$ is the fitted density, $\rho_{water,oil}$ is either the water or oil density, z_0 is a parameter that defines the center of the interface, and d is half the width of the interface. Hence, we fit the oil decay to obtain its z_0^{oil} and d^{oil} , then the water decay, and to obtain z_0^{water} and d^{water} . The starting position of the interface was defined as $z_0^{oil} - d^{oil}$, and the ending position as $z_0^{water} + d^{water}$, resulting in a total interface width of $z_0^{water} + d^{water} - z_0^{oil} + d^{oil}$.

We have also analyzed the S_2 order parameter for the different molecules in our systems. The S_2 is defined as follows:

$$S_2 = \frac{1}{2} (3\cos^2(\theta) - 1) \quad (4)$$

where θ is the angle between a molecular vector and the normal to the interface. For water, the vector is aligned along its dipole; for the benzene, toluene, cyclohexane, and cycloheptane, the vector is formed by taking the normal to the plane formed by their carbon rings; for the CTAB, the vector is obtained from its nitrogen atom and the second carbon of its chain; for the HPG, a fit to a plane is performed for all the atoms of the body (excluding the ones from the aliphatic chain), then the normal to this plane is taken as the reference vector. The lower limit for it is $S_2 = -0.5$, for which $\theta = 0$, and the reference vector is aligned along the normal to the interface. In the higher limit $S_2 = 1$, and $\theta = 90$, the reference vector would be perpendicular to the interface.

Results and Discussion

Carrier Effect

To investigate the HPG carrier effect observed by Ferreira, et al.,¹² we have simulated an HPG:CTAB agglomerate in water with 100 CTAB molecules and 100 HPG molecules. The agglomerate remained stable during all the simulations, as shown in Figure 2 a). This observation agrees with the DLS measurements of Ferreira et al.,¹² which shows the HPG:CTAB agglomerates to be stable in water solution.

After the insertion of the agglomerate between an oil/water/oil interface, as shown in Figure 2 b), 86 CTAB and 75 HPG molecules migrated to the interfaces, also corroborating the experimental results of Ferreira, *et al.*¹² that observed better oil recovery with CTAB and HPG combined than with each surfactant separately. The simulations show that it happens because the agglomerate, although stable in the water solution, disperses when it approaches the water/oil interface delivering surfactant molecules that lower the interfacial

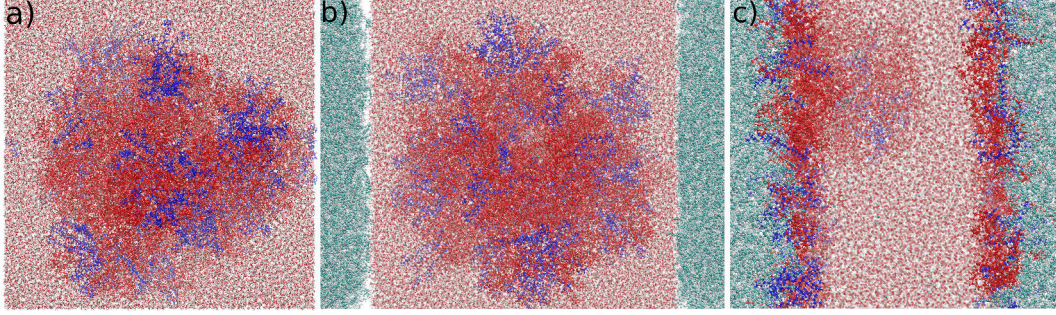


Figure 2: a) HPG:CTAB aggregate; b) initial steps of the aggregate near the water/oil interface; c) final step of the dissolved aggregate at the interface. Red—HPG11, blue—CTAB, light red—water molecules, and light blue—hydrocarbons.

tension, enhancing the oil recovery.

Interfacial Tensions

The surfactant concentrations at the interfaces were determined from runs with high amounts of surfactant, as described in the Methodology section. Figure 3 shows the initial interface of the HPG:CTAB system in a) and the final snapshot of the simulation in b), where one can see that some micelles are formed in the water phase, with the CTAB and HPG molecules also containing a few hydrocarbons inside.

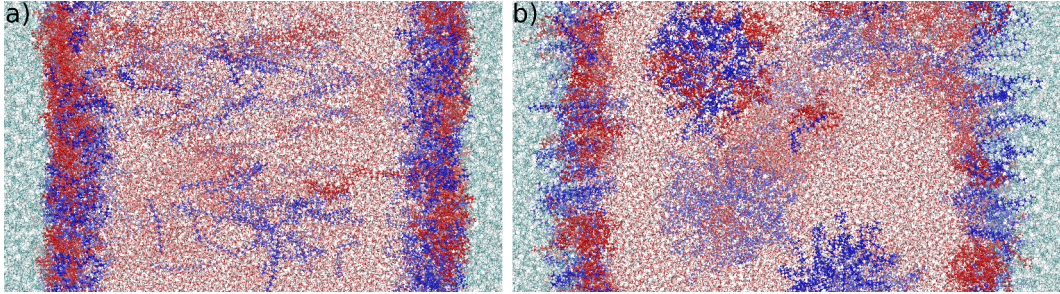


Figure 3: In a) the initial interface for HPG:CTAB saturation is shown, in b) the final snapshot is shown. The Red molecules are HPG11, blue are CTAB molecules, light red are water molecules, and light blue are hydrocarbon molecules.

Table 1 shows the systems investigated, the number of surfactant molecules at each interface together with the SEC (Γ), and the IFT (γ). The IFT of the CTAB combined with HPG, either in low or high concentration (last two rows of Table 1), is much lower than

the IFT of the Pure system (no surfactant/polymer), the IFT of the system with 150 HPG molecules, and even the IFT of the system with 133 CTAB molecules.

The system with 150 HPG molecules can reduce the IFT of the Pure system by almost two times, while the IFT of the CTAB system is ten times lower than that of the Pure system. However, when both surfactants are present, either CTAB+HPG(l) or CTAB+HPG(h), the IFT of the pure water/oil interface is reduced a hundred times, showing that the CTAB and HPG act synergistically to lower the interfacial tension, as observed experimentally by Ferreira, et al.¹²

Table 1: Interfacial tension for the various simulated systems. The surfactant load corresponds to the amount of surfactant molecules directly on the surface.

System Name	Amount of Surfactant	SEC Γ (10^{-6}mol/m^2)	IFT γ (mN/m)
Pure	No surfactant	-	39.30
HPG	150 HPG	2.58	19.16
CTAB	133 CTAB	2.29	3.89
CTAB+HPG(l)	108 CTAB + 16 HPG	1.86, 0.28 ¹	0.33
CTAB+HPG(h)	102 CTAB + 86 HPG	1.76, 1.48 ²	0.32

¹ SEC values for 108 CTAB and 16 HPG, respectively.

² SEC values for 102 CTAB and 86 HPG, respectively.

Interfacial Region Analysis

To better understand the interfacial phenomena, density profiles of all investigated systems were obtained. Figure 4 a) shows an aromatic accumulation near the interface of the Pure system, in agreement with previous studies^{19,24} attributed to the weak hydrogen bonding between aromatic rings and water molecules.²⁴

Although the aromatics can still be found in the interface of the HPG system, its accumulation is reduced by the presence of HPG molecules, as shown in Figure 4 c). The density profile of the CTAB system (Figure 4 b) also shows a hindering of the aromatic accumulation at the interface, although in a less pronounced extension.

The same aromatic accumulation hindering is found for the systems with CTAB+HPG at

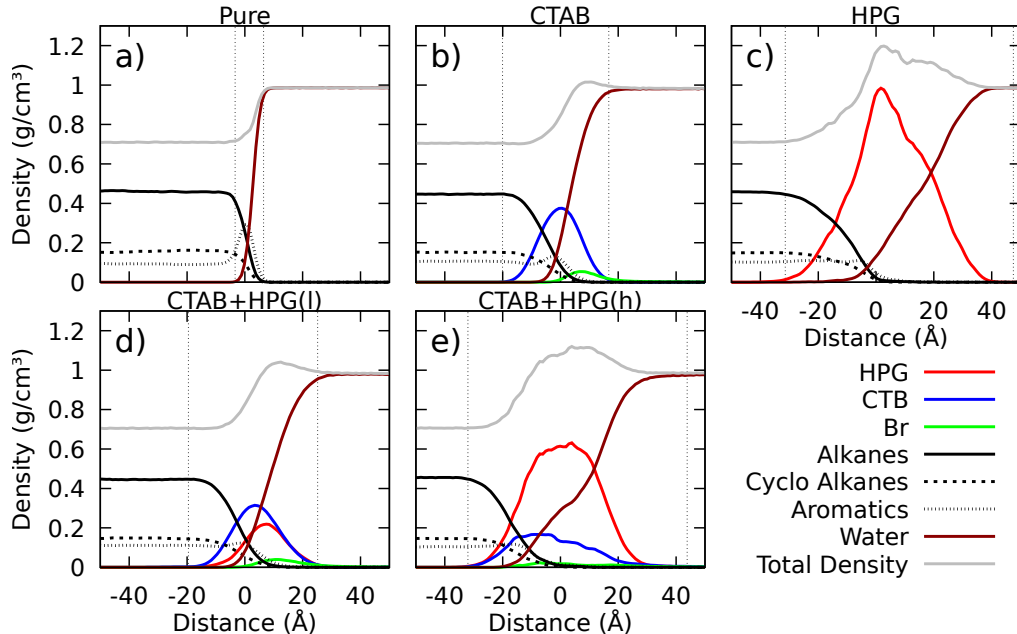


Figure 4: Density profiles for the simulated systems. The vertical dotted lines are the interfacial limits. The densities in the subpanels are shown as follows: a) Water/Oil interface, b) CTAB system, c) HPG system, d) CTAB+HPG(l) system, and e) CTAB+HPG(h).

the interface, as shown in Figures 4 d) and e). The CTAB+HPG(l) and CTAB+HPG(h) systems have similar amounts of CTAB molecules, differing by their amount of HPG molecules. In both cases, however, a small bump in the density profile of the aromatics at the interface can still be observed, similar to that found in the HPG system, indicating that the HPG seems to hinder the aromatic accumulation better than the CTAB. It is worth mentioning that the aromatic accumulation hindrance is not directly related to the IFT reduction, since the HPG system presents a high IFT compared to other surfactant systems.

Figure 4 also shows the interfacial limits and the respective interfacial widths are shown in Table 2. Obtained from the interfacial limits shown in Figure 4, the interfacial width presented in Table 2 is greatly increased for all systems containing surfactants either HPG, CTAB, or their combinations. However, the HPG and CTAB combined with a high number of HPG molecules (CTAB+HPG(h)) have the largest values of interfacial width.

Although some authors could relate the increase in the interfacial thickness to the lowering of the IFT,⁴² these quantities do not seem to correlate well in our work. Analyzing the effect

Table 2: Interfacial widths for the simulated systems

System Name	Interfacial Width (Å)
Pure	9.87
HPG	78.88
CTAB	36.71
CTAB+HPG(l)	44.72
CTAB+HPG(h)	75.81

of mixtures of surfactants on the IFT through the interfacial thickness is not as meaningful as varying a single surfactant concentration. When dealing with a single surfactant, as the SEC increases, the interfacial thickness increases, and the IFT decreases up to a critical concentration. The data presented in Table 2 shows that although the interface width increases as the amount of HPG increases, from CTAB+HPG(l) to CTAB+HPG(h) and HPG system, the IFT values (Table 1) follows a different trend explained by a synergistic interaction between the CTAB and HPG surfactants.

The data presented in Table 2 shows that the primary function of HPG is to increase the interfacial width and carry CTAB to this region. The CTAB and CTAB+HPG(l) can also enlarge the interfacial width. However, its effect is half of the one for HPG and CTAB+HPG(h). On the other hand, the presence of CTAB is the main responsible for breaking the interfacial organization, as evinced in Table 1 (and also in the following sections). Thus, that relation was not observed when comparing different surfactants or two mixed surfactants.

The charge profiles perpendicular to the interface are shown in fig. 5. As one can see, the systems do not present high total charge accumulations. However, when resolved by molecule, there are significant individual contributions from the CTAB and Br because of their charged nature. The Pure and HPG cases had the least charge changes at the interface and those with higher interfacial tension. However, the CTAB case has the highest individual molecule charge accumulations and does not show the lowest interfacial tension. The CTAB+HPG(l) and CTAB+HPG(h) cases have the CTAB molecules and Br atoms more spread, as the interface is thicker than the CTAB case, which lowers the charge peak. Hence, it seems the charged surfactants are essential to lowering the interfacial tension,

albeit the HPG molecules help to thicken the interface, as shown in Table 2, it appears that a combined effect of interface thickness and local charge organization leads to lower interfacial tensions.

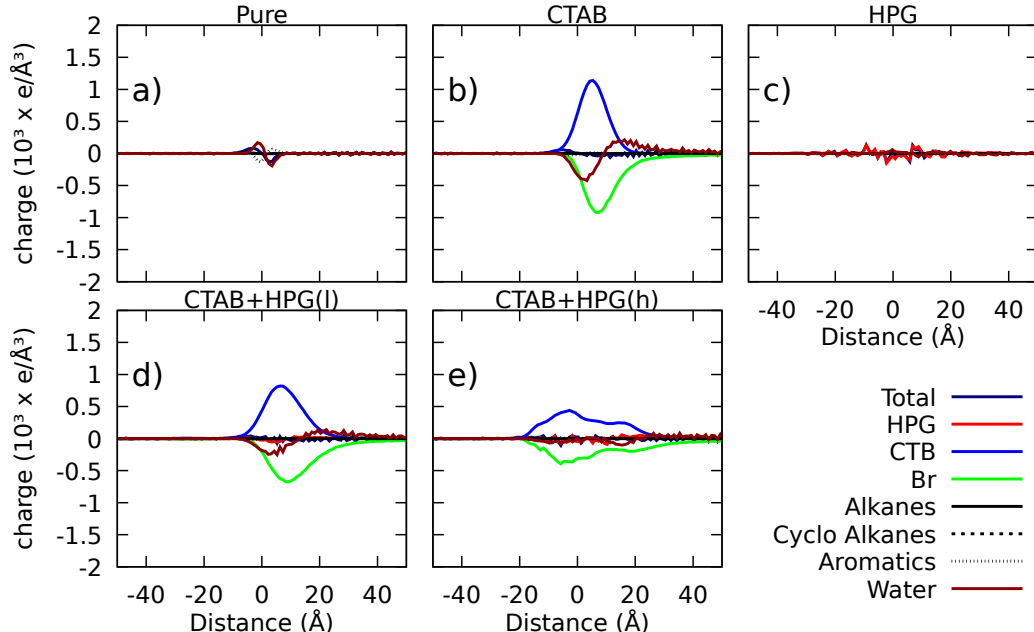


Figure 5: Charge profiles for the simulated systems. The charge profiles in the subpanels are shown as follows: a) Water/Oil interface, b) CTAB system, c) HPG system, d) CTAB+HPG(l) system, and e) CTAB+HPG(h).

Order Parameters

In fig. 6, the S_2 order parameter of the different molecules is shown to assess the molecule's orientation regarding the interface.

One can see that in the Pure case, the water order parameter differs from the other cases. The water molecules have negative S_2 values at the interface, meaning that the water dipole has an angle with the normal to the surface, likely to form weak hydrogen bonds with the aromatic molecules,²⁴ as can be seen in the inset of figure 6 a), with such hydrogen bond being observed in a snapshot from our simulation. Furthermore, the aromatic molecules in the interfacial region have positive S_2 values; thus, their normal vector tends to align with the interface's normal vector. For the CTAB and CTAB+HPG(l) cases, there is a change in

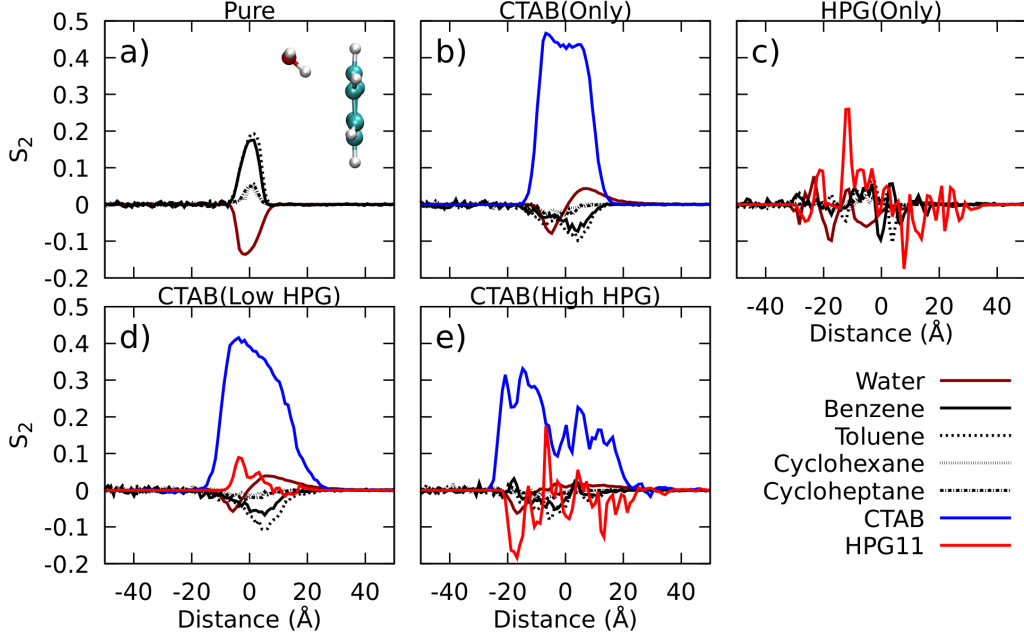


Figure 6: Order parameter S_2 for various simulated systems. The inset in a) illustrates the weak hydrogen bond formed between water and benzene, as extracted from a snapshot of our simulation. The order parameters in the subpanels are shown as follows: a) Water/Oil interface, b) CTAB system, c) HPG system, d) CTAB+HPG(l) system, and e) CTAB+HPG(h).

water's S_2 from only a negative peak to a double asymmetric peak. The water has multiple peaks for the HPG and CTAB+HPG(h) cases, as the interface is much wider. Thus, water significantly changes its organization near the interface, being disordered by high amounts of HPG molecules.

The considered oil components had also changed their order parameter from a positive peak in the Pure case to lower negative peaks (CTAB and CTAB+HPG(l)), or alternating values (HPG and CTAB+HPG(h)). Again, high amounts of HPG disorders the interface, influencing the order parameters. For the systems with no or low amounts of HPG, the aromatic molecules' normal vector now tends to have an angle with the interface's normal, in contrast with the Pure case, reflecting their lower accumulation near the interface. As fewer water molecules would be available to form weak hydrogen bonds, the preferred site should be the CTAB polar head.

The CTAB molecules are very aligned with the normal to the interface for the CTAB

system. This alignment is still very noticeable in the CTAB+HPG(l) system, although hindered for the CTAB+HPG(h) one. The HPG molecules seem disordered for the systems with high concentrations, although the CTAB+HPG(l) system shows a slight tendency to align its normal vector to the surface's normal. Therefore, the best that can be said is that there is no clear relation between the lower IFT for the double surfactant cases with the observed order parameters.

Radial Distribution Functions

In Figure 7 a), the RDF of the water molecules with the oil components are shown for the Pure and the CTAB systems. As one can see, the water interaction with the aromatic molecules is hindered in the CTAB system; this happens because of the surfactant layer, which places the water molecules further away from the oil, and the lower aromatic accumulation near the interface, as observed in the density profile (Figure 4 a) and b)).

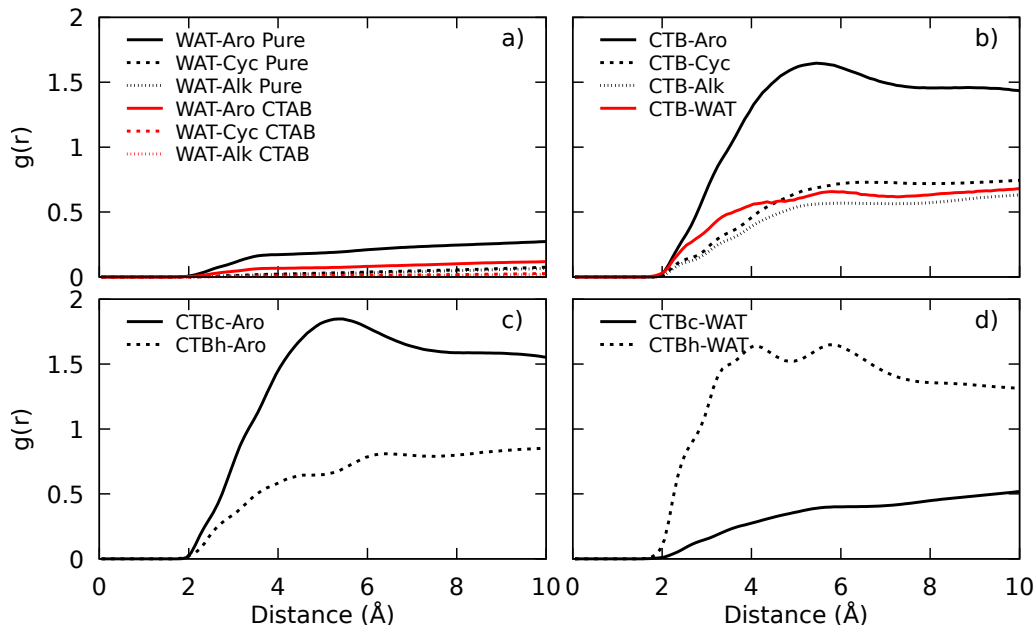


Figure 7: The radial distribution functions (RDF) are shown for the Pure system in a), and the CTAB system in a), b), c), and d). In c) and d), the RDF are resolved for the CTAB chain (CTBc), and CTAB head (CTBh).

Moreover, in Figure 7 b), the CTAB molecule interaction for the CTAB system is shown.

For shorter distances, the CTAB molecules interact strongly with the aromatic part of the oil, and then with water. As there is still a small aromatic molecule accumulation at the interface, the CTAB molecules interact with them now instead of with water, and this corroborates the inverse ordering observed for the S_2 order parameter shown in Figure 6. These interactions are resolved for the CTAB chain (CTBc) and CTAB head (CTBh), for the aromatic molecules in Figure 7 c), and water in d). Mostly the non-polar chain of the CTAB interacts with the aromatics and the polar head with the water.

The HPG system RDF is shown in Figure 8. In panel a), one can see that the HPG interacts more strongly with water, with a noticeable peak around 1.85 Å. In panel b), the RDF is resolved for the HPG chain (HPGc), and HPG body (HPGb); now, it can be seen that the 1.85 Å peak comes from the HPG body, as it has many hydroxyl groups available for hydrogen bonding; hence this peak should be the O-H hydrogen bond distance. Furthermore, a shoulder at around 2.8 Å coincides with the typical O-O hydrogen bond distance.⁴³ Thus, the water interaction with the aromatic molecules is weaker than in the Pure case, as the HPG body dominates this interaction due to its hydrophilic body, which provides stronger hydrogen bonds when compared to the aromatic molecules.

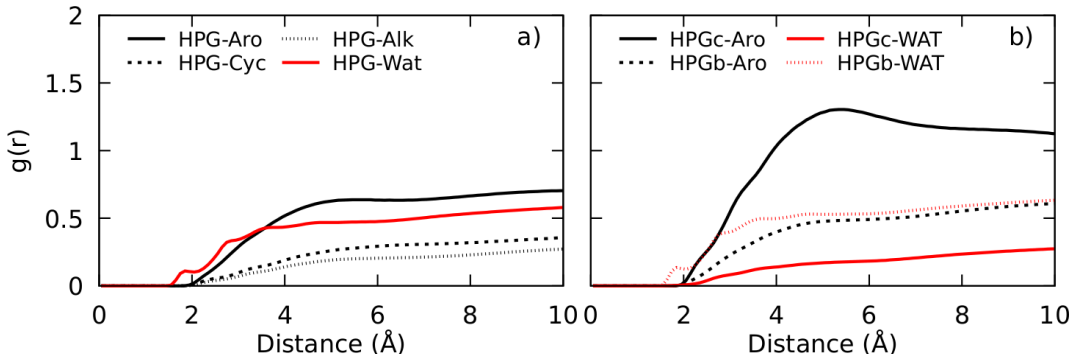


Figure 8: The RDF for the HPG system is shown in a) for the full molecule, in b) for the body (HPGb) and chain (HPGc) resolved RDF are shown.

The RDF for the CTAB+HPG(l) and CTAB+HPG(h) are shown in Figures 9, and 10 respectively. One can see in Figures 9 a) and 10 a) that in these systems, the CTAB molecules interact mainly with the HPG molecules, hindering its interaction with the water molecules,

in contrast with what was observed in the CTAB system. As can be seen in Figures 9 b) and 10 b) The CTAB interaction is dominated by its polar head with the HPG, closely followed by its chain with the HPG and the polar head with the water. There is still some interaction of the CTAB with aromatic molecules, although not significant, as there is little accumulation at the interface. The resolved CTAB and HPG interactions are shown in Figures 9 c) and 10 c), they are dominated by the CTAB chain with the HPG chain and the CTAB head with the HPG body, due to their non-polar and polar nature, respectively. In addition, one can see in Figures 9 d) and 10 d), that the HPG mainly interacts with water for shorter distances, with the same peaks at 1.85 Å and 2.8 Å, observed in the HPG only system, again showing the hydrophilicity of the HPG molecules. For longer distances, the CTB-HPG interactions dominate. Thus, as the surfactants interact among themselves, the CTAB interaction with water is hindered, and the HPG is the one that interacts more strongly with water.

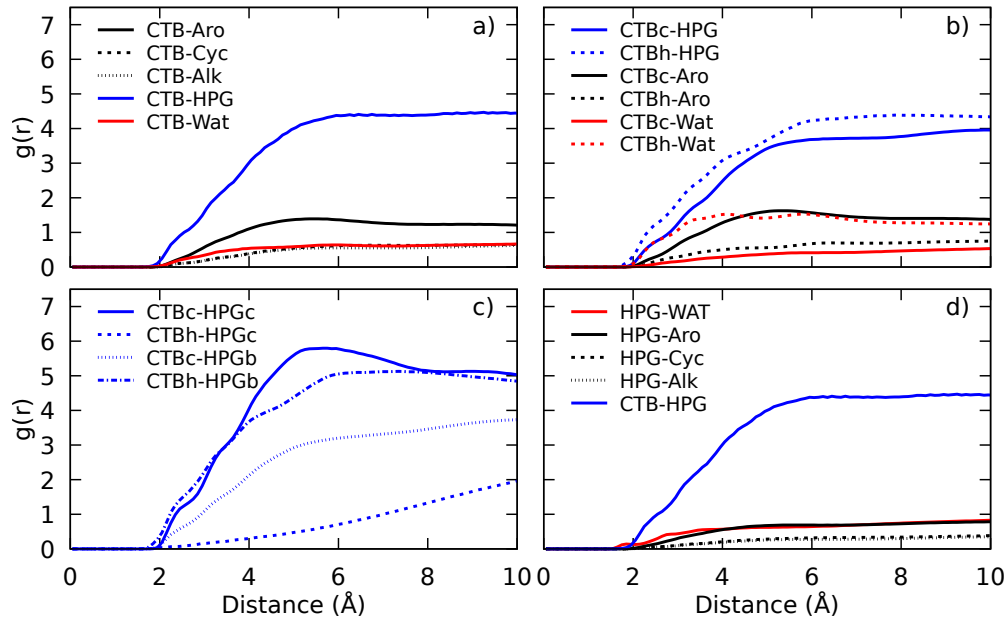


Figure 9: CTAB+HPG(l) system radial distribution functions. In a) the CTAB interactions with different molecules are shown, and in b) the CTAB head interaction with other molecules is shown. On panel c) the CTAB head and chain interactions with the HPG body and chain are shown. On panel d) the HPG interaction with other molecules is shown.

The RDFs for the combined surfactant systems are similar. One can see that the sur-

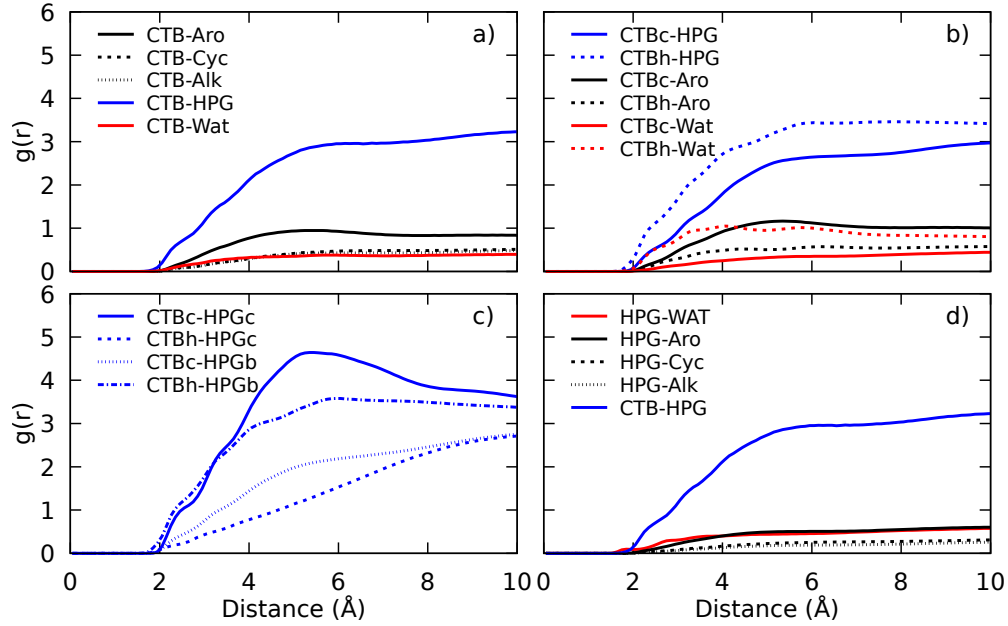


Figure 10: The CTAB+HPG(h) system radial distribution functions. In a) the CTAB interactions with different molecules are shown, and in b) the CTAB head interaction with other molecules is shown. On panel c) the CTAB head and chain interactions with the HPG body and chain are shown. On panel d) the HPG interaction with other molecules is shown.

factants interact strongly between them, reducing their interactions with the oil and water phases. Hence, this could lead to weaker interfacial tensions, as the interfacial region is wider, the charge peaks are more spread, and not as ordered as in the CTAB system. The interaction among co-adsorbed surfactants is critical for their synergetic effects, as pointed out in the literature,^{44–47} an effect we observe for CTAB and HPG.

This explanation of the surfactant interactions for interfacial tension lowering, developed by Rosen et al.,^{44,45} is related to a coefficient β that represents the deviation of the mixture from ideality. However, this coefficient depends on the concentration of the surfactants in the solution, which is not represented correctly in simulations, as discussed in the methodology section of this work. Although, we had evidence of this stronger interaction by analyzing the radial distribution functions among the surfactants and water/oil.

Hence, the surfactant-surfactant interaction is essential, there is no silver bullet to explain the reduced interfacial tension for the combined surfactants, as many effects come together

for this achievement.

Conclusion

In this work, we used classical molecular dynamics simulations to explore the combination of cetyltrimethylammonium bromide (CTAB) and hyperbranched polyglycerols with one aliphatic chain (HPG) as surfactants at a water/oil interface. We have shown that an agglomerate of both CTAB and HPG is stable in a water solution. After placing the CTAB-HPG agglomerate was then placed it near an oil/water/oil interface, most of the CTABs migrated to the interface in the simulation time, thus corroborating the HPG carrier behavior already observed experimentally.

We have also simulated the interfacial tensions (IFT), between water and a light oil model. The obtained interfacial tensions showed significant effects of the combination of CTAB and HPG, lowering the IFT by one order of magnitude compared to pure CTAB as a surfactant. Then, we analyzed the density profiles, charge profiles, order parameters, and radial distribution functions. From those analyses, we concluded that the IFT reduction effects come from a combined effect, mainly due to the CTAB-HPG strong interaction, weakening the interactions with the water and oil phases. The latter, combined with an interface widening, less ordering, and spread of individual molecules' charge profiles, leads to the much lower interfacial tension observed in the CTAB+HPG systems.

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Supporting Information Available

The following files are available free of charge:

- Supplementary-Material.pdf: Contains a table with the number of atoms and simulation box sized for all simulated systems.
- HPG.mp4: Video of the simulated HPG structure.

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