Molecular Simulations of NAPL Removal from Mineral Surfaces using **Microemulsions and Surfactants**

Evan Lowry, Mohammad Sedghi, Lamia Goual*

Department of Chemical and Petroleum Engineering, University of Wyoming, 1000 East

University Avenue, Laramie, Wyoming 82071, United States

ABSTRACT

Remediation of petroleum contaminants from aquifers is an ongoing and environmentally relevant challenge. Non-aqueous phase liquids (NAPLs) can infiltrate groundwater reservoirs and pollute the water source leading to health and public safety concerns. NAPLs such as asphaltenes and naphthenic acids possess high adsorptive potential making removal difficult with conventional pump-and-treat techniques. As a result, surfactants and microemulsions have been posited as a means of mobilizing and solubilizing these heavy contaminants for safe and effective removal. Experiments have shown that microemulsions with nonionic surfactants are effective for removing aquifer contaminants, although the exact molecular level mechanism is not clear. To this aim, molecular dynamics simulations were carried out with water, surfactant, and microemulsion solutions. These simulations were compared to determine the effects of surfactants and microemulsions on contaminant removal from calcite mineral surfaces. Results indicate that polar molecules serve as a base layer upon which further non-polar molecules could adsorb. Microemulsions were effective at swelling the oil phase and reducing the overall percentage of polar components, leading to easier removal. In addition, the dissociation of microemulsion micelles at the contaminant-water interface was shown to be a thermodynamically favorable process.

1. INTRODUCTION

The persistence of groundwater contaminants after a significant chemical spill is an ongoing problem since hydrocarbon-based contaminants can pose a significant threat to public safety and environmental health.¹ Crude oil based-NAPLs can become trapped in pore space due to capillary forces and alter the wettability of rock surfaces even after traditional remediation techniques have been utilized. This is especially true when the major fraction of contaminant is composed of highly adsorptive species such as asphaltenes and other polar petroleum derivatives.²

Surface morphology and chemistry affect how well molecules can adsorb to mineral surfaces. Calcite is a very common reservoir rock mineral characterized by ordered, sheet-like structures of carbonate and calcium ions. Due to its ionic nature, it is generally more adsorptive of polar components than siliceous minerals and can undergo wettability alteration relatively easily.³ Tabrizy et al. showed that stearic acid and other hydrocarbon based polar molecules can strongly adsorb to calcite due to its ionic surface.⁴

Several studies have upheld the idea of contaminant deposition taking place as a result of the prior adsorption of highly polar components. Highly polar components such as carboxylic acids and even low molecular weight alcohols have been shown to adsorb to mineral surfaces, enabling co-adsorption of less polar hydrocarbons. Keleşoğlu et al. showed that naphthenic acids readily adsorb and are retained by calcite, even after a desorption sequence.⁵ Molecular dynamics simulations (MD) revealed that alcohols can adsorb strongly to the calcite surface, effectively altering its wettability.⁶ Gomari and Hamouda concluded that medium chain fatty acids are able to alter the wettability of calcite, even when a thin water film is present.⁷ It was posited that this is likely due to increased solubility of the polar functional groups in water,

allowing their diffusion to adsorption sites. Previously, van Duin and Larter used MD simulations to show that highly polar hydrocarbon components can compete with water layers at the calcite surface and may aid in altering the wettability to allow further adsorption of less polar molecules.⁸

Asphaltenes in oil are also known to be adsorptive species that can alter rock wettability. Marczewski and Szymula measured adsorption isotherms for asphaltenes in toluene onto various mineral surfaces using the BET adsorption technique.⁹ They determined that quartz had significantly less adsorption of asphaltenes as compared to calcite, kaolinite, titanium dioxide and dolomite. Further, silica-coated quartz crystals will desorb significant quantities of asphaltene in the presence of saline water, indicating a thermodynamically unfavorable adsorption of asphaltenes to quartz-like minerals.¹⁰ This again was confirmed in dynamic tests by Saraji et al.¹¹ Asphaltenes in toluene were deposited onto various crushed mineral packs through continuous flow experiments. The results indicated that the type of mineral is critical in asphaltene adsorption and that calcite induces the most adsorption when compared to dolomite and quartz. The importance of mineral type on asphaltene adsorption is emphasized by other studies available in the literature.^{12,13} These studies all concluded that silica is not a strong adsorber of asphaltenes and that calcite and other carbonate or clay-like minerals tend to be better substrates for adsorption.

The removal of contaminants from aquifers is often performed using surfactant enhanced aquifer remediation (SEAR) techniques, which are considered a chemical enhancement to pump and treat methods. There are two major mechanisms responsible for removal of contaminants by surfactants: mobilization and micellar solubilization. Mobilization involves reduction of interfacial tension between the contaminant and aqueous phase,¹⁴ and is primarily assumed to be

responsible for the bulk removal of trapped oil during remediation operations.¹⁵ Micellar solubilization, on the other hand, is a less understood phenomenon. It is believed that surfactant micelles dissociate near the contaminant-water interface and then re-form around the contaminant, essentially partitioning the hydrocarbons into the aqueous phase.¹⁶ Micellar solubilization of this type leads to a Winsor type I, oil-in-water emulsion.^{14,17,18} Thus, the solubility of NAPL increases largely when the surfactant concentration is well above the critical micelle concentration (CMC).¹⁹ Although the exact mechanism of solubilization has not been completely elucidated, several models have been proposed, a few of which are described in detail by Zhong et al.²⁰

Previous studies have been carried out to quantify the amount of contaminant solubilized by micellar solutions of nonionic surfactants. Javanbakht and Goual demonstrated that environmentally friendly, nonionic surfactants are an effective means of mobilizing as well as solubilizing oil based-NAPLs.²¹ Imbibition tests indicated that the trapped oil was mobilized and solubilized in a ratio of approximately 6:1, indicating that solubilization does indeed play a role in the removal of contaminants. Edwards et al. showed that the amount of solubilization of polycyclic aromatic hydrocarbons into the aqueous phase was linearly related to the concentration of nonionic surfactant, with more solubilization at higher concentrations.²² Multiple laboratory tests have executed surfactant-enhanced solubilization of NAPL contaminants and many surfactants have been identified as good candidates for this process.^{19,20,23-25}

More recently, interest has centered on special mixtures known as microemulsions that may be useful for removal of contaminants. Microemulsions are mixtures of water, oil, and surfactants that form a solution with dispersed nanometric micelles. Specifically, in an oil-in-

water (O/W) microemulsion, the micellar capsules are considered to be thermodynamically stable, enabling usage in field applications.²⁶ Thermodynamically stable O/W microemulsions with nanosized micelles can be created by taking advantage of the phase inversion temperature, the temperature at which a water-in-oil emulsion transitions to an oil-in-water emulsion.²⁷ The oil phase may be an organic solvent that can be delivered to the contaminant via the microemulsion, allowing the solvent to assist in breaking up the adsorbed contaminant. Oliveira et al. found that the microemulsion was able to effectively reduce soil contamination by varying concentration and flow rate.²⁸ Mandal and others conducted experiments with nonionic surfactant-stabilized microemulsions to prove that microemulsions can recover up to 30% more trapped oil phase than traditional water-flooding.²⁹ On the molecular level, the understanding of the driving forces of microemulsion-aided contaminant removal is vague. Several studies have demonstrated the formation and stability of microemulsion micelles under standard conditions.³⁰⁻
³² Bui et al. used molecular dynamics to study microemulsions in the presence of adsorbed *n*-heptane layers. They showed that the organic solvent from the microemulsion is able to penetrate the organic layer after dissociating onto the hydrocarbon layer.³³ Microemulsions were found to effectively reduce the interfacial tension between the water and hydrocarbon and improve the shear profile at the interface during an induced flow. Despite showing that microemulsions do indeed form under specific conditions and that the solvent is critical in penetrating the oil layer, this study did not reveal the mechanism by which a microemulsion interacts with, desorbs, and partitions a contaminant droplet. Also, fully atomistic simulations of microemulsion systems in the presence of mineral surfaces have not been conducted to date.

The objective of this work is to explain the possible mechanisms associated with surfactant and microemulsion assisted NAPL recovery. A molecular dynamics methodology is explained

for studying oil adsorption and desorption from a model calcite surface in the presence of surfactants and microemulsions. Conclusions are drawn and novel insights are gained about the action of microemulsions in the presence of oil contaminants.

2. METHODS

In order to simulate a calcite surface, carbonate bonding parameters were taken from Raiteri et al. and non-bonded parameters were taken from the CHARMM36 force field.³⁴ These parameters have previously been used for calcium and carbonate ions.³⁵ At first, a periodic slab of calcite mineral with a surface parallel to $\{1\ 0\ \bar{1}\ 4\}$ plane and a thickness of 12 molecular layers was created using CrystalMaker software.³⁶ This plane is well studied and known to be the most commonly occurring and energetically favorable surface of calcite mineral.^{37,38} Positional restraints were applied for calcium and carbon within the calcite surface in order to prevent dissolution of the surface into the solvent. The final slab dimension used for all the simulations was $14.568 \times 3.5 \times 11.972\text{ nm}^3$.

All MD simulations were carried out using GROMACS 5.1.1 software and all the organic molecules were parameterized using the CHARMM36 Force Field and the SPC/E model was used for water. To maintain a consistent temperature of 298 K throughout the simulations, the Nose-Hoover thermostat was used since it produces a thermodynamically accurate ensemble throughout the simulation time.³⁹ The system pressure was maintained at 100 bar through the use of a piston constructed from hard-sphere Lennard-Jones particles, placed at the top of the simulation box, above the fluid phase solvent. In all the *NVT* simulations, the pressure was maintained at 100 bar through the use of the piston. The piston particles were calculated with a

constant downward acceleration along the axis of the simulation box that produced the desired fluid pressure.

In order to investigate the effects of polar oil components on the adsorption/desorption behavior, naphthenic acids were added to mixtures of other hydrocarbon components. [Figures 1 and 2](#) show the molecules used for the simulations on calcite. Several simulations with different proportions of polar and non-polar components were conducted until the oil mixture was found to adsorb to the surface in the presence of water. The design of the mixtures was based in part on the work of Crocker and Marchin who showed that polar components are critical in adsorption and wettability alteration of rock cores.⁴⁰

The model asphaltene molecules were based on previous work by Sedghi et al.⁴¹ Two asphaltene structures were chosen with different functional groups, as shown in [Figure 1](#). ANO asphaltenes contain both pyridinic and hydroxyl groups in their polyaromatic core and thus have hydrogen bonding abilities. On the other hand, AN asphaltenes are non-hydrogen bonding species since they contain only a pyridinic group in their cores. The model naphthenic acids were taken from two previous works and, together with ANO asphaltenes, constitute the polar fraction of oil. *n*-Dodecane was chosen to represent the saturated fraction of the oil while toluene was chosen to represent the aromatic portion.^{42,43} The weight percentages of these fractions were similar to the ones used by Crocker and Marchin.⁴⁰ The average molecular weight of the final oil mixture was 248 g/gmol and the specific gravity was 0.857, corresponding to a medium-light hydrocarbon composition.

The oil mixture shown in [Table 1](#) was initially pressurized in an *NPT* simulation to 150 bar at 298 K in order to estimate its density. The Berendsen pressure coupling algorithm and thermostat were used to bring the system to equilibrium. To initialize the simulations, the oil mixture was

distributed randomly in the space 5 nm above the calcite surface. After energy minimization, this system was allowed to equilibrate for 10 ns under vacuum conditions to adsorb the oil mixture. After adsorption of the oil mixture, the system was solvated with SPC/E model water and allowed to equilibrate for an additional 25 ns at a piston pressure of 100 bar. After solvation, three different production simulations were performed for 100 ns at a pressure of 100 bar, using this equilibrated system as the initial condition. [Table 2](#) shows the weight percentages of additives used for solvents in each 100 ns simulation run.

In order to construct the microemulsion that was used for the third simulation, the microemulsion micelle was equilibrated separately then added to the calcite surface simulation as a solvent. Limonene is an environmentally friendly terpene solvent and was chosen as the hydrocarbon solvent phase. 2-Propanol was used to enhance the solubility of the microemulsion mixture in water. A $10 \times 10 \times 10 \text{ nm}^3$ box was filled with 150 limonene molecules and 53 surfactant molecules before being solvated with water. The system was equilibrated at *NPT* conditions for 25 ns in order to allow the surfactant and limonene to form a micellar microemulsion. Once equilibrated, the micelle was removed and inserted as a solvent above the pre-equilibrated oil droplet on the calcite surface. The remaining void space was filled with 2-propanol and water as the continuous phase. [Figure S1](#) of the Supporting Information shows a snapshot of the equilibrated microemulsion micelle where surfactant molecules (in red) surround the limonene droplet (in yellow).

After all three simulations were allowed to equilibrate for 100 ns, the simulation cells were subjected to another 100 ns simulation trial. During this second simulation set, the water molecules were imparted with a constant acceleration of $2.5 \times 10^{-6} \text{ nm/ps}^2$ in order to simulate

isotropic flow. This method of simulating induced flow is similar to that used by previous studies.^{33,44}

3. RESULTS AND DISCUSSION

3.1 Equilibrium Simulations

Prior to simulations with the various solvent types, multiple oil mixtures were tested in order to determine the composition that would remain adsorbed to calcite in the presence of water. The polarity and asphaltene concentrations were varied to find an adsorptive composition (see [Table S1](#), Supporting Information). It was noted that about 20% of the mixture was required to be polar molecules for the adsorption of oil onto calcite. The presence of the polar molecules was critical for the further adsorption of the bulk, non-polar oil phase onto the calcite mineral surface. This is consistent with the findings of Crocker and Marchin.⁴⁰ Due to its strong adsorption; oil mixture 5 was used for all the subsequent simulations. [Table S1](#) also illustrates the importance of the limonene solvent in altering the ratio of the polar to non-polar components in the oil mixture.

After the initial 25 ns equilibration of oil mixture 5 in water, it was visually estimated that the oil droplet formed an acute contact angle with the water phase but remained adsorbed on the surface of the calcite. The acute contact angle estimate is indicative of a weakly water-wet surface.⁴⁴ [Figure S2](#) of the Supporting Information presents a snapshot of the equilibrated oil droplet on the surface and highlights the position of the polar hydrocarbon molecules. Most of the polar molecules migrated to the calcite surface and adsorbed strongly while others were positioned with their polar groups facing outward, in contact with the water phase.

[Figure 3b-d](#) shows snapshots from the end of simulation trials in three solvents and an image of the initial condition for comparison ([Figure 3a](#)). The first of the three solvents tested with the

oil droplet on calcite was pure water. This system was allowed to equilibrate for 100 ns before observing the trajectory to determine the effects on adsorption. The water phase was unable to desorb any of the oil molecules, although it did cause a slight change in the droplet shape. The polar naphthenic acids and ANO asphaltenes were primarily responsible for anchoring the droplet onto the surface, as shown in [Figure 3b](#).

For the second simulation trial, 15% surfactant was added to the water solvent. The surfactant rapidly dissociated from micelles and attached onto the oil droplet with the hydrophilic head groups facing outward toward the water phase. The surfactant was able to disrupt the structure of the oil droplet and cause some desorption as is evidenced by the snapshot in [Figure 3c](#) and the average interaction energies in [Table 3](#). The surfactant caused a fairly significant reduction in the energy between the calcite surface and the non-polar oil components but was unable to significantly reduce the interaction energy between the calcite surface and the polar oil components when compared to the simulations without additives.

In the third simulation trial, microemulsions were added to the water solvent in the proportions shown in [Table 2](#). The microemulsion micelles completely dissociated onto the oil droplet after only 15 ns, releasing the limonene solvent and allowing the break-up of the tightly packed oil structure, as depicted in [Figure 3d](#). The decrease in the total energy profile in [Figure 4](#), as compared to water alone, reveals that the microemulsion micelles undergo a thermodynamically favorable transition when going from micelles to the dissociated state. It is appropriate to note that the energies reported in [Figure 4](#) are not normalized on a molecular basis and therefore the total energy of the microemulsion simulation is higher than that of the simulation with water. However, the primary purpose of [Figure 4](#) is to demonstrate the decreasing energy trend observed in the microemulsion simulation that indicates the path to a

more thermodynamically favorable state. This is perhaps due to the increased entropy gained by the limonene solvent molecules after dissociation.

The limonene solvent was responsible for the large dispersive effect caused by the microemulsion. Once released from the micelle, the limonene swelled the oil phase drastically, breaking up any nanoaggregate structures formed by asphaltenes and allowing the oil to become more mobile. This finding is consistent with Bui et al.³³ In order to quantify this effect, the total accessible volume of the oil droplet was calculated using the double cubic lattice method (DCLM) with a probe radius of 0.14 nm.⁴⁶ The surfactant induced a 13% increase in droplet volume while the microemulsion caused a 34% increase in the total droplet volume due to the infiltration of the limonene solvent (see Figure 5, Supporting Information). This swelling may make removal of the droplet under flow conditions more favorable due to the commensurate increase in hydrodynamic radius after introduction of limonene. Given that many subsurface flow situations are characterized by relatively low Reynolds numbers, the droplet radius may be critical for the further desorption and transport of contaminants from mineral surfaces.⁴⁷ The Stokes flow model, valid for very low Reynolds numbers, states that the hydrodynamic force experienced by a spherical particle is directly proportional to the particle radius.

The interaction energy between the oil droplet and the calcite surface was used as a quantitative measure of thermodynamic desorption. The average Van der Waal's and Coulomb energy between the oil phase and the calcite surface was calculated for the last 50 ns and tabulated in Table 3. As expected, the total interaction energy between oil molecules and the surface decreased with the microemulsion. Interestingly, the surfactant did not reduce this energy. The surfactant may have curbed the ability of the oil molecules to reach a minimum energy state with the calcite surface by preventing the polar components from effectively

rearranging on the surface. The positive Van der Waal's energies are a result of the anchoring of the oil droplet to the surface by the dominating Coulombic forces.

3.2 Flow Simulations

After the initial 100 ns simulations, flow was introduced to the simulation cell to determine how the equilibrated droplets would behave. A constant acceleration of $2.5 \times 10^{-6} \text{ nm/ps}^2$ was imparted to each water molecule in order to simulate flow under laminar flow conditions. [Figure 6](#) provides snapshots of the oil droplet at the beginning and end of 100 ns induced flow for water, surfactant, and microemulsion. The oil droplet remained roughly the same in the simulation with no additives. At the start of simulation, the microemulsion had completely encapsulated the oil droplet and effectively dispersed the oil molecules throughout the micellar structure. The simulation with no surfactant or microemulsion showed very little lateral displacement after being subjected to the 100 ns flow sequence. The polar molecules effectively anchored the non-polar bulk of the droplet via the polar-nonpolar Van der Waal's forces, as can be noted from the energies tabulated in [Table 4](#). The surfactant was able to lessen the amount of attraction between polar and non-polar components but not to the same degree as the microemulsion.

In order to quantify the mobility of the oil droplet when subjected to flow, the distance between the droplet center of mass and the calcite center of mass was recorded for each simulation frame. [Figure 7](#) shows the lateral droplet displacement versus time for each solvent type. The data only extends to 45 ns due to the non-relevance of the calculation once the droplet crossed the periodic boundary, shortly after 45 ns. The microemulsion allowed for the largest lateral displacement of the oil droplet, followed by the surfactant. The simulations with surfactant and with water alone do not display a definite displacement trend due to the fact that

the non-polar bulk of the droplet remained anchored to the calcite surface via the polar molecules. It is worth noting that in all the simulations, the majority of the polar molecules remained irreversibly adsorbed to the surface.

3.3 Molecular Mechanism of Contaminant Removal by Microemulsions

From these simulations, it is postulated that the effectiveness of the microemulsion relies on the reduction in the percentage of polar adsorptive molecules achieved by the addition of a nonpolar solvent. The nonpolar solvent, limonene in this case, swells and dilutes the composition of the bulk, nonpolar oil phase. This allows both greater volume and mass of the droplet to be acted upon by any flow that is present in the system and decreases the polar to non-polar ratio, reducing the available adsorptive molecules per unit mass. In addition, the microemulsion solvent can effectively reduce the Van der Waal's interactions between the polar and non-polar oil components, allowing the droplet to move more freely. Once mobilized, the oil droplet would be protected by the surfactant, which accumulates around the droplet periphery in micellar fashion. In this way, the droplet could be effectively **dispersed** into the water phase once dislodged from the mineral surface. The total mechanism may be summarized in [Figure 8](#) as the diffusion of the micelles to the contaminant droplet, infiltration of the microemulsion solvent, swelling of the contaminant phase and finally solubilization induced by flow. These simulations suggest that microemulsions may be a better option than surfactant alone for removal of oil-based contaminants from mineral surfaces.

4. CONCLUSIONS

In this study, the ability of surfactants and microemulsions to desorb oil-based contaminants from mineral surfaces was studied using MD simulations. A model oil mixture was used as a representative contaminant phase containing polar and non-polar asphaltenes, polar acids, and non-polar saturates and aromatics. In the first sequence of simulations, the pre-equilibrated adsorbed oil droplet was subjected to 100 ns of simulation with three different solvent types. Pure water was used as a control solvent while an ethoxylated alcohol surfactant and a microemulsion were used for the other two trials. The oil was unable to be desorbed in the presence of water only, mostly due to the large Coulomb interactions between the polar molecules and the calcite surface. The polar molecules served as a base layer upon which further non-polar molecules could adsorb. The addition of surfactant molecules to water was able to reduce the interaction between the droplet and the surface more than the water, but to a lesser extent than the microemulsion. Indeed, the microemulsion effectively dispersed the oil droplet due to the nonpolar limonene solvent. It was demonstrated that the dissociation of the microemulsion micelles onto the oil contaminant droplet caused a decrease in the system energy, indicating a thermodynamically favorable change. In addition, the limonene caused a significant swelling in the volume and, consequently, the hydrodynamic area of the oil droplet, leading to easier removal when subjected to a water flow.

The effect of water flow was further investigated by inducing flow through the simulation cell, perpendicular to the droplet. As expected, the microemulsion allowed a larger lateral displacement of the droplet, likely due to the larger surface area of the droplet. In addition, the microemulsion effectively reduced the restrictive Van der Waal's interactions between the polar and non-polar oil components, allowing the droplet to move more freely.

These simulations suggest that microemulsions may be a better option than surfactant alone for removal of oil-based contaminants from mineral surfaces. The combination of the surfactant with the limonene solvent allows the micelles to dissociate and swell the oil phase. Also, by reducing the interaction between the near irreversibly adsorbed polar molecules and the bulk oil phase, the microemulsion can increase the mobility of otherwise adsorbed non-polar molecules.

5. ACKNOWLEDGEMENT

The authors would like to thank the National Science Foundation (Career Award #1351296) and Enhanced Oil Recovery Institute for financial support. The authors are also grateful to Dr. Mohammad Piri for providing access to his computer cluster.

6. REFERENCES

- [1] Paria, S. Surfactant-Enhanced Remediation of Organic Contaminated Soil and Water. *Advances in Colloid and Interface Science* **2008**, 138 (1), 24–58.
- [2] Fountain, J. C.; Starr, R. C.; Middleton, T.; Beikirch, M.; Taylor, C.; Hodge, D. A Controlled Field Test of Surfactant-Enhanced Aquifer Remediation. *Ground Water* **1996**, 34 (5), 910–916.
- [3] Graue, A.; Viksund, B. G.; Eilertsen, T.; Moe, R. Systematic Wettability Alteration by Aging Sandstone and Carbonate Rock in Crude Oil. *Journal of Petroleum Science and Engineering* **1999**, 24 (2), 85–97.
- [4] Tabrizy, V. A.; Denoyel, R.; Hamouda, A. A. Characterization of Wettability Alteration of Calcite, Quartz and Kaolinite: Surface Energy Analysis. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2011**, 384 (1), 98–108.
- [5] Kelesoglu, S.; Volden, S.; Kes, M.; Sjoblom, J. Adsorption of Naphthenic Acids onto Mineral Surfaces Studied by Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D). *Energy & Fuels* **2012**, 26 (8), 5060–5068.

- [6] Okhrimenko, D. V.; Nissenbaum, J.; Andersson, M. P.; Olsson, M. H. M.; Stipp, S. L. S. Energies of the Adsorption of Functional Groups to Calcium Carbonate Polymorphs: The Importance of -OH and -COOH Groups. *Langmuir* **2013**, 29 (35), 11062–11073.
- [7] Gomari, K. R.; Hamouda, A. A. Effect of Fatty Acids, Water Composition and pH on the Wettability Alteration of Calcite Surface. *Journal of Petroleum Science and Engineering* **2006**, 50 (2), 140–150.
- [8] van Duin, A. C.; Larter, S. R. A Computational Chemical Study of Penetration and Displacement of Water Films near Mineral Surfaces. *Geochemical Transactions* **2001**, 2 (1), 35.
- [9] Marczewski, A. W.; Szymula, M. Adsorption of Asphaltenes from Toluene on Mineral Surface. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2002**, 208 (1), 259–266.
- [10] Farooq, U.; Sjöblom, J.; Øye, G. Desorption of Asphaltenes from Silica-Coated Quartz Crystal Surfaces in Low Saline Aqueous Solutions. *Journal of Dispersion Science and Technology* **2011**, 32 (10), 1388–1395.
- [11] Saraji, S.; Goual, L.; Piri, M. Adsorption of Asphaltenes in Porous Media under Flow Conditions. *Energy & Fuels* **2010**, 24 (11), 6009–6017.
- [12] Dudášová, D.; Simon, S.; Hemmingsen, P. al V.; Sjöblom, J. Study of Asphaltenes Adsorption onto Different Minerals and Clays: Part 1. Experimental Adsorption with UV Depletion Detection. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2008**, 317 (1), 1–9.
- [13] de la Cruz, J. L. M.; Castellanos-Ramírez, I. V.; Ortiz-Tapia, A.; Buenrostro-González, E.; Durán-Valencia, C. de los A.; López-Ramírez, S. Study of Monolayer to Multilayer Adsorption of Asphaltenes on Reservoir Rock Minerals. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2009**, 340 (1), 149–154.
- [14] Baran, J. R.; Pope, G. A.; Wade, W. H.; Weerasooriya, V.; Yapa, A. Microemulsion Formation with Chlorinated Hydrocarbons of Differing Polarity. *Environmental science & technology* **1994**, 28 (7), 1361–1366.
- [15] Duffield, A. R.; Ramamurthy, R. S.; Campanelli, J. R. Surfactant Enhanced Mobilization of Mineral Oil within Porous Media. *Water, Air, and Soil Pollution* **2003**, 143 (1-4), 111–122.

- [16] West, C. C.; Harwell, J. H. Surfactants and Subsurface Remediation. *Environmental Science & Technology* **1992**, 26 (12), 2324–2330.
- [17] Winsor, P. A. Binary and Multicomponent Solutions of Amphiphilic Compounds. Solubilization and the Formation, Structure, and Theoretical Significance of Liquid Crystalline Solutions. *Chemical reviews* **1968**, 68 (1), 1–40.
- [18] Jackson, R. E. Surfactant-Enhanced Remediation of DNAPL Zones in Granular Aquifer Systems. *Remediation Journal* **1993**, 4 (1), 77–91.
- [19] Sabatini, D. A.; Knox, R. C.; Harwell, J. H.; Wu, B. Integrated Design of Surfactant Enhanced DNAPL Remediation: Efficient Supersolubilization and Gradient Systems. *Journal of Contaminant Hydrology* **2000**, 45 (1), 99–121.
- [20] Zhong, L.; Mayer, A. S.; Pope, G. A. The Effects of Surfactant Formulation on Nonequilibrium NAPL Solubilization. *Journal of contaminant hydrology* **2003**, 60 (1), 55–75.
- [21] Javanbakht, G.; Goual, L. Mobilization and Micellar Solubilization of NAPL Contaminants in Aquifer Rocks. *Journal of Contaminant Hydrology* **2016**.
- [22] Edwards, D. A.; Luthy, R. G.; Liu, Z. Solubilization of Polycyclic Aromatic Hydrocarbons in Micellar Nonionic Surfactant Solutions. *Environmental Science & Technology* **1991**, 25 (1), 127–133.
- [23] Martel, R.; Lefebvre, R.; Gélinas, P. J. Aquifer Washing by Micellar Solutions: 2. DNAPL Recovery Mechanisms for an Optimized Alcohol–surfactant–solvent Solution. *Journal of Contaminant Hydrology* **1998**, 30 (1), 1–31.
- [24] Butler, E. C.; Hayes, K. F. Micellar Solubilization of Nonaqueous Phase Liquid Contaminants by Nonionic Surfactant Mixtures: Effects of Sorption, Partitioning and Mixing. *Water Research* **1998**, 32 (5), 1345–1354.
- [25] Zhou, M.; Rhue, R. D. Screening Commercial Surfactants Suitable for Remediating DNAPL Source Zones by Solubilization. *Environmental science & technology* **2000**, 34 (10), 1985–1990.
- [26] McClements, D. J. Nanoemulsions versus Microemulsions: Terminology, Differences, and Similarities. *Soft matter* **2012**, 8 (6), 1719–1729.

- [27] Förster, T.; Schambil, F.; Tesmann, H. Emulsification by the Phase Inversion Temperature Method: The Role of Self-Bodying Agents and the Influence of Oil Polarity. *International journal of cosmetic science* **1990**, 12 (5), 217–227.
- [28] Oliveira, P. F.; Oliveira, T. M.; Spinelli, L. S.; Mansur, C. R. Development and Evaluation of Solbrax-Water Nanoemulsions for Removal of Oil from Sand. *Journal of Nanomaterials* **2014**, 2014.
- [29] Mandal, A.; Bera, A. Surfactant Stabilized Nanoemulsion: Characterization and Application in Enhanced Oil Recovery. **2012**.
- [30] Lee, S.-J.; Olsen, B.; Schlesinger, P. H.; Baker, N. A. Characterization of Perfluorooctylbromide-Based Nanoemulsion Particles Using Atomistic Molecular Dynamics Simulations. *The Journal of Physical Chemistry B* **2010**, 114 (31), 10086–10096.
- [31] Rahman, M. B. A.; Huan, Q.-Y.; Tejo, B. A.; Basri, M.; Salleh, A. B.; Rahman, R. N. Z. A. Self-Assembly Formation of Palm-Based Esters Nano-Emulsion: A Molecular Dynamics Study. *Chemical Physics Letters* **2009**, 480 (4), 220–224.
- [32] Abdul Rahman, M. B.; Latif, M. A. M.; Basri, M.; Salleh, A. B.; Abdul Rahman, R. N. Z. Molecular Dynamics Simulation of Oleyl Oleate Swollen Micelles System. *Molecular Simulation* **2010**, 36 (5), 403–407.
- [33] Bui, K.; Akkutlu, I. Y.; Zelenev, A.; Saboowala, H.; Gillis, J. R.; Silas, J. A. Insights into Mobilization of Shale Oil Using Microemulsion; Society of Petroleum Engineers, 2015.
- [34] Raiteri, P.; Gale, J. D.; Quigley, D.; Rodger, P. M. Derivation of an Accurate Force-Field for Simulating the Growth of Calcium Carbonate from Aqueous Solution: A New Model for the Calcite- Water Interface. *The Journal of Physical Chemistry C* **2010**, 114 (13), 5997–6010
- [35] Huang, J.; MacKerell, A. D. CHARMM36 All-Atom Additive Protein Force Field: Validation Based on Comparison to NMR Data. *Journal of computational chemistry* **2013**, 34 (25), 2135–2145.
- [36] CrystalMaker Computer Software LTD, Oxford, UK (2015).
- [37] de Leeuw, N. H.; Parker, S. C. Surface Structure and Morphology of Calcium Carbonate Polymorphs Calcite, Aragonite, and Vaterite: An Atomistic Approach. *The Journal of Physical Chemistry B* **1998**, 102 (16), 2914–2922.

- [38] Stipp, S. L. S.; Gutmannsbauer, W.; Lehmann, T. The Dynamic Nature of Calcite Surfaces in Air. *American Mineralogist* **1996**, *81* (1-2), 1–8.
- [39] Hoover, W. G. Canonical Dynamics: Equilibrium Phase-Space Distributions. *Physical Review A* **1985**, *31* (3), 1695.
- [40] Crocker, M. E.; Marchin, L. M.; others. Wettability and Adsorption Characteristics of Crude-Oil Asphaltene and Polar Fractions. *Journal of petroleum technology* **1988**, *40* (04), 470–474.
- [41] Sedghi, M.; Goual, L.; Welch, W.; Kubelka, J. Effect of Asphaltene Structure on Association and Aggregation Using Molecular Dynamics. *The Journal of Physical Chemistry B* **2013**, *117* (18), 5765–5776.
- [42] Rogers, V. V.; Liber, K.; MacKinnon, M. D. Isolation and Characterization of Naphthenic Acids from Athabasca Oil Sands Tailings Pond Water. *Chemosphere* **2002**, *48* (5), 519–527.
- [43] Varadaraj, R.; Brons, C. Molecular Origins of Heavy Crude Oil Interfacial Activity Part 2: Fundamental Interfacial Properties of Model Naphthenic Acids and Naphthenic Acids Separated from Heavy Crude Oils. *Energy & fuels* **2007**, *21* (1), 199–204.
- [44] Koplik, J.; Banavar, J. R.; Willemsen, J. F. Molecular Dynamics of Fluid Flow at Solid Surfaces. *Physics of Fluids A: Fluid Dynamics (1989-1993)* **1989**, *1* (5), 781–794.
- [45] Anderson, W.; others. Wettability Literature Survey-Part 2: Wettability Measurement. *Journal of Petroleum Technology* **1986**, *38* (11), 1–246.
- [46] Eisenhaber, F.; Lijnzaad, P.; Argos, P.; Sander, C.; Scharf, M. The Double Cubic Lattice Method: Efficient Approaches to Numerical Integration of Surface Area and Volume and to Dot Surface Contouring of Molecular Assemblies. *Journal of Computational Chemistry* **1995**, *16* (3), 273–284.
- [47] Holmes, D. W.; Williams, J. R.; Tilke, P. Smooth Particle Hydrodynamics Simulations of Low Reynolds Number Flows through Porous Media. *International Journal for Numerical and Analytical Methods in Geomechanics* **2011**, *35* (4), 419–437.

Table 1. Oil mixture composition

Fraction	Species	No. Molecules	Wt. %
Saturates	Dodecane	103	47%
Aromatics	Toluene	121	29%
Non H-bonding Asphaltenes (Non-polars)	AN	1	2%
H-bonding Asphaltenes + Naphthenic Acids (Polars)	ANO	8	22%
	NA1	6	
	NA2	5	

Table 2. Weight percent of additives used for solvents in each simulation

Simulation	Solvent	BS25-9	Limonene	2-Propanol
1	Water	-	-	-
2	Water + Surfactant	15%	-	-
3	Water + Microemulsion	15%	13%	6%

Table 3. Average interaction energy ($\text{kJ mol}^{-1} \text{S}^{-1}$) over the last 50 ns of simulation between the oil droplet and calcite surface

Simulation	Van der Waal's Energy	Coulomb Energy	Total Energy
No Additive	51.9	-1430	-1383
Surfactant	47.2	-1605	-1559
Microemulsion	68.9	-1318	-1260

Table 4. Average interaction energy ($\text{kJ mol}^{-1} \text{S}^{-1}$) between the polar oil components and the non-polar oil components from the last 50 ns of the flow simulation

Simulation	Van der Waal's Energy	Coulomb Energy	Total Energy
No Additive	-1524	54	-1470
Surfactant	-743	23.6	-719
Microemulsion	-336	10.8	-325

Figure 1. Model structures used to simulate oil

Figure 2. Model structures used for microemulsion and surfactant

Figure 3. Oil droplet at (a) the beginning of simulations in water, and at the end of 100 ns simulation in different solvents: (b) water, (c) surfactant, and (d) microemulsion. Surfactant is shown in red and limonene is in yellow. Water and 2-propanol not shown for clarity

Figure 4. Total energy profile of simulation with (a) water and (b) microemulsion solvent. The water-water interaction energy has been removed for noise reduction

Figure 5. Oil droplet volume throughout the simulation time for each solvent type

Figure 6. Images of the oil droplet at the beginning and end of 100 ns induced flow (left to right) for (a) water only, (b) surfactant and (c) microemulsion. Solvent not shown for clarity

Figure 7. Lateral droplet displacement (along x-coordinate), as a function of time, during flow simulation. Due to periodic boundary condition effects, only the first 45 ns of data are shown

Figure 7. Proposed mechanism of microemulsion interaction with NAPL on mineral surface

Table of Content Graphic

Molecular Simulations of NAPL Removal from Mineral Surfaces using Microemulsions and Surfactants

Evan Lowry, Mohammad Sedghi, and Lamia Goual