Reversible double water in oil in water (W/O/W) emulsions were developed to contain subsurface hydrocarbon spills during their remediation using surfactant flushing. Double emulsions were prepared by emulsifying CaCl₂ solutions in canola oil, and subsequently by emulsifying the W/O emulsions in aqueous sodium alginate solutions. The formation of double emulsions was confirmed with confocal and optical microscopy. The double emulsions reversed and gelled when mixed with the surfactants sodium dodecyl sulfate (SDS) and cocamidopropyl betaine (CPB). Gels can act as ‘emulsion locks’ to prevent spreading of the hydrocarbon plume from the areas treated with surfactant flushing, as shown in sand column tests. Shear rheology was used to quantify the viscoelastic moduli increase (gelation) upon mixing the double emulsion with SDS and CPB. SDS was more effective than CPB in gelling the double emulsions. CPB and SDS could adsorb at the interface between water and model hydrocarbons (toluene and motor oil), lowering the interfacial tension and rigidifying the interface (as shown with a Langmuir trough). Bottle tests and optical microscopy showed that SDS and CPB produced W/O and O/W emulsions, with either toluene or motor oil and water. The emulsification of motor oil and toluene in water with SDS and CPB facilitated their flow through sand columns and their recovery. Toluene recovery from sand columns was quantitated using Gas-Chromatography Mass-Spectroscopy (GC-MS). The data show that SDS and CPB can be used both for surfactant flushing and to trigger the gelation of ‘emulsion locks’. Ethanol also gelled the emulsions at 100 mL/L.

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electrokinetics (Chowdhury et al., 2017), slow release oxidizers (Liang and Chen, 2017), oxidizing nanoparticles (Mosmeri et al., 2017) and ferrate (Minetti et al., 2017), and surfactant enhanced oxidation (Dahal et al., 2016). Pump and treat has also been used for hydrocarbon treatment (Stefanakis et al., 2016). However, capillary forces trap contaminant residuals in the soil pores, causing the concentrations of contaminants in groundwater to rebound when pumping stops (De Gisi and Notarnicola, 2016). Surfactant flushing involves the injection of surfactants to promote the removal of hydrocarbon residuals from the subsurface (Jousses et al., 2017; Pensini et al., 2018). Solubilization using co-solvents (e.g., ethanol) can also promote hydrocarbon removal (Karaoglu et al., 2019). An important risk associated with surfactant flushing or injection of co-solvents is the uncontrolled migration of contaminant plumes. Uncontrolled contaminant plume migration worsens the pollution problem, endangering downstream receptors (e.g., drinking water wells).

The injection of viscous polymer solutions around the polluted zones has been proposed to mitigate the risk of uncontrolled plume migration during surfactant flushing (Heymans and Obernolte, 1991; Gioia and Urciuolo, 2004; Ahn et al., 2017). Contaminant containment can also be achieved with colloidal gels (Apps et al., 1998; Kim and Corapcioglu, 2002). Previously developed gels have either constant, significant viscoelasticity or contain delayed crosslinkers, which trigger gelation with a fixed time delay (Heymans and Obernolte, 1991; Apps et al., 1998; Kim and Corapcioglu, 2002; Gioia and Urciuolo, 2004; Ahn et al., 2017). High viscoelastic moduli impede pumping to the polluted zones. Also, in low permeability soils with slow groundwater flow, delayed crosslinkers may gel the fluids before they reach the polluted zones.

An alternative to gel barriers are cutoff walls (Malusis et al., 2003) and permeable reactive barriers, which contain and treat hydrocarbon plumes. Permeable reactive barriers can be permanent, semi-permanent, or replaceable, and they are placed downstream of contaminant plumes (Guerin et al., 2002). In all cases, barriers need to be constructed and installed in the subsurface. The advantage of permeable barriers is that they allow the in situ treatment of contaminants through physical (e.g., sorption), chemical (e.g., oxidation) and biological (e.g., degradation using bacteria) methods (Guerin et al., 2002). Sorbent materials used for subsurface barriers include zeolites (Vignola et al., 2011), organoclays modified with surfactants (Zhao et al., 2017), and waste reclaimed adsorbents laden with oxidizing agents (Do et al., 2011). Examples of oxidizing barriers are blends of sodium or potassium persulfate, cement, sand, and water (Barcelona and Xie, 2001; Liang et al., 2011a; Liang et al., 2011b), concrete briquets able to release oxygen and nitrate (Borden et al., 1997), or barriers containing oxygen releasing compound to enhance hydrocarbon biodegradation (Lin et al., 2010).

The disadvantage of the cutoff walls and barriers described above is their high cost and the complexity of their installation, especially for deep contamination. This is because the installation of the barriers requires that the soil is excavated, or else that high-pressure grouting is used. Our ‘emulsion lock’ technology was developed in response to the need for economic barriers that can be easily injected around the polluted zones during surfactant flushing. ‘Emulsion locks’ are obtained with reversible double emulsions, which have low viscoelasticity in the clean zones but gel upon contact with surfactants. The emulsification of model hydrocarbons (toluene and motor oil) with SDS and CPB was studied with bottle tests, interferential tension measurements, optical microscopy and Langmuir trough experiments. Toluene and motor oil were selected for this study because they are important environmental contaminants (Baker et al., 2002; Alkoai and Ghaly, 2006; Winderl et al., 2007). The applicability of the technology to treat other organic contaminants should be the objective of future work. Enhanced flow of toluene and motor oil through sand upon injection of SDS and CPB was verified through sand column experiments. While surfactants (e.g., SDS and CPB) injected in the center of the hydrocarbon plumes promote hydrocarbon extraction by emulsifying them, ‘emulsion locks’ injected around the contaminant plume ensure contaminant containment. The low viscoelasticity of ‘emulsion locks’ before mixing with surfactants should facilitate pumping around the polluted zones. ‘Emulsion locks’ gelation upon mixing with SDS and CPB was verified with shear rheology experiments. Gelation of the double emulsions was also studied upon mixing with ethanol, which can solubilize hydrocarbons in water. Our previous study showed that switchable double emulsions could gel upon mixing with sufficient concentrations of toluene, benzene or hexane (Lamont et al., 2019). Our previous study envisioned a large plume contamination, where gelation was triggered by contact with model contaminants (toluene, benzene or hexane) (Lamont et al., 2019). The focus of our previous study was to use switchable double emulsions for trapping hydrocarbons, but not for treating them. The current study expands on our previous research, investigating emulsion reversal and gelation upon mixing with selected surfactants. Since emulsion reversal can be triggered by selected surfactants, the current study shows that the double emulsions can be used for any contaminant concentration.

The effectiveness of surfactants to reverse emulsions was not investigated in our previous study. Also, our previous study did not analyze the emulsification of model contaminants (e.g., toluene and motor oil) and the effectiveness of selected contaminants in facilitating contaminant transport through porous geological media (and hence their remediation). In summary, the current study demonstrates the use of ‘emulsion locks’ for the safe remediation of sites contaminated by hydrocarbons, combining surfactant flushing with economic barriers, at any contaminant concentration. This technology was never proposed before and has the potential of revolutionizing the safety standards achieved during hydrocarbon remediation using surfactant flushing.

1. Materials and methods

1.1. Reagents

SDS (technical grade) was purchased from Sigma Aldrich. CPB (Candora Soap brand) and canola oil (Selection brand) were purchased from local markets. Calcium stearate and fluorescent Nile Red (technical grade) were purchased from Sigma
Aldrich. Sodium alginate (alginic acid, sodium salt, Acros Organics), calcium chloride anhydrous (Desiccant ACS, EMD Millipore), NaCl salt (Acros Organics), Tween 20 (Ultrapure, Thermo Scientific) and ethylcellulose (EC, 48% ethoxyl content, 10 cP, Acros Organics) were purchased from Fisher Scientific. Experiments were conducted using either deionised (DI) or ultra-pure water with a resistivity of 18.2 MΩ-cm, treated using a Milli-pore system (milli-Q water). The pH of water was 6. Anhydrous ethyl alcohol (Commercial Alcohol) was purchased from Fisher Scientific. Toluene (HPLC grade, Fisher Chemical) was purchased from Fisher Scientific and motor oil (Motomaster Formula 1, SAE 5W-20) was purchased from a local market. Based on the product safety data sheet, the motor oil used was comprised by lubricating oils (C20-C30), heavy paraffinic distillates and anti-wear agents. While surfactants are not listed in the safety data sheet, they are typically present in motor oil as dispersants and to create a skin on the surface of the oil, reducing volatility losses in the engine (Reick, 1980).

1.2. Emulsion preparation

Emulsions were prepared as previously described (Lamont et al., 2019). Briefly, EC (10 g/L) and calcium stearate (2.5 g/L) were dissolved in canola oil at 150°C. Calcium chloride solutions (250 mL of 0.36 mol/L CaCl2 in DI water) were first mixed with 1 L of canola oil containing 10 g/L EC and 2.5 g/L calcium stearate, to form water in oil (W/O) primary emulsions. A Cole Parmer Hand-Held Homogenizer, 110 V was used at high speed (speed setting 2) to mix the primary emulsions. The primary emulsions (100 mL) were then hand-mixed with 0.75% sodium alginate in DI solutions (1 L), with 10 g/L NaCl (added to balance the osmotic pressure) and the surfactant Tween 20. Mixing the primary emulsions with sodium alginate, NaCl and Tween 20 produced double emulsions (W/O/W).

1.3. Bottle tests

Bottle tests were conducted to evaluate the effectiveness of SDS and CPB in emulsifying toluene and motor oil in DI water. In bottle tests 20 mL of DI water were hand-shaken for 30 sec with 5 mL of either toluene or motor oil. The surfactant concentrations in water were 2.5 g SDS/L DI and 25 mL of CPB/L DI. Emulsions were also prepared without surfactants for comparison. After shaking the emulsions were allowed to settle on the bench and observed for 2 hr.

1.4. Sand column tests: contaminant mobilization

Sand column tests were conducted to assess the effectiveness of SDS and CPB in mobilizing toluene and motor oil in sandy soils. A copper column (7 cm diameter and 1.5 m height) was filled with Ottawa sand (purchased from BEI/PECAL, Stake Technology Ltd.). The porosity (0.4) was determined by as indicated in Section 1.4. Before each experiment the permeameter was saturated with simulated groundwater (1 mmol/L CaCl2, 0.5 mmol/L MgCl2, 1 mmol/L KCl and 1 mmol/L NaCl), either with 5 g/L SDS or without SDS. Each experiment was comprised of two parts. In the first part of the experiment, flow was determined by filling a 100 mL burette with aqueous solution (simulated groundwater, with or without SDS) and measuring the time required for the water to drain from 50 to 40 mL, from 40 to 30 mL, and finally from 30 to 20 mL. Before starting the second part of the experiment, the permeameter was opened and 55 mL of double emulsion was pipetted on top of the sand. The permeameter was then sealed and the flow measured by determining the time required for the burette to drain, as described above. The flowrate measured was compared with and without emulsion, and with and without SDS.

1.5. Sand column tests: ‘emulsion locks’ barriers

Sand column tests were conducted to assess the effectiveness of double emulsions to form ‘emulsion locks’ (i.e., barriers) upon contact with SDS. A permeameter (Ele Ltd.) having a height of 13 cm and a diameter of 9 cm was filled with Ottawa sand (purchased from BEI/PECAL, Stake Technology Ltd.). The porosity (0.4) was determined by as indicated in Section 1.4. Before each experiment the permeameter was saturated with simulated groundwater (1 mmol/L CaCl2, 0.5 mmol/L MgCl2, 1 mmol/L KCl and 1 mmol/L NaCl), either with 5 g/L SDS or without SDS. Each experiment was comprised of two parts. In the first part of the experiment, flow was determined by filling a 100 mL burette with aqueous solution (simulated groundwater, with or without SDS) and measuring the time required for the water to drain from 50 to 40 mL, from 40 to 30 mL, and finally from 30 to 20 mL. Before starting the second part of the experiment, the permeameter was opened and 55 mL of double emulsion was pipetted on top of the sand. The permeameter was then sealed and the flow measured by determining the time required for the burette to drain, as described above. The flowrate measured was compared with and without emulsion, and with and without SDS.

1.6. GC-MS

The concentrations of toluene in the water at the outlet of the sand column were determined using a 7890A Agilent GC system and an Agilent 5975C inert XL EI/CI MSD with triple-axis detector. The column used was an HP-5MS. Water samples were diluted with 50% ethanol and analyzed using liquid injection. An external standard calibration was used. The R2 values of the calibration curves were 0.98 or greater. The toluene peaks were quantified using ChemStation software.

1.7. Confocal and optical microscopy

The primary emulsions and the double emulsions were imaged using confocal and optical microscopy, as previously described (Lamont et al., 2019). An optical VHX-5000 digital microscope (Keyence) was used. For confocal microscopy imaging, fluorescent Nile red was added to the oil phase, which hence appeared bright. The water phase was instead
black. Confocal microscopy imaging was conducted using an upright Leica TCS SP5 Laser Scanning Microscope (Leica, Mannheim, Germany) equipped with a 20x glycerol objective and an Argon laser with excitation at 476 nm, emission range 555–620 nm.

1.8. Dynamic interfacial tension

Dynamic interfacial tension measurements were conducted over a 15 min time period using the pendant drop method and the Young-Laplace model (Lopez de Ramos et al., 1993), with a Theta Lite optical tensiometer (Biolin Scientific). Experiments were conducted with either motor oil or toluene, with 0.5 g/L SDS and 10 mg/L (volume based) CPB solutions in milli-Q.

1.9. Compressional isotherms

Compressional isotherms were measured at the interface between oil (toluene or motor oil) and milli-Q, with SDS (2 g/L) and CPB (2 mL/L and 10 mL/L), to determine the compressional rigidity of surfactant films. The Langmuir trough used (Microtrough G1, Kibron) had an area of 16,500 mm² and was equipped with symmetric mobile barriers, which were used to compress the interfacial surfactant films while monitoring the interfacial pressure exerted on a Wilhelmy plate. The Langmuir trough was cleaned with ethanol, acetone and milli-Q water prior to each test. The trough was considered clean when the interfacial pressure increased by less than 0.5 mN/m when the barriers were compressed to an area of 1600 mm² when the trough was filled with milli-Q water only. The bottom compartment of the trough was filled with surfactant solutions in milli-Q water (50 mL). Toluene or motor oil were then carefully pipetted onto the top phase, and the barriers compressed to an area of 1600 mm² at a speed of 20 mm/min.

1.10. Shear rheology

The shear viscoelastic behavior of the double emulsions before and after mixing with surfactants was determined at 23°C, using a rotational torque-controlled (i.e., combined-motor-transducer type) rheometer (MCR302 Anton Paar, Graz, Austria) with parallel plate geometry (diameter = 50 mm). Slip during measurements was minimized by using sand paper (600 grit). The frequency was 3 rad/sec in all measurements and the strain was ramped from 0.01% to 100%. Measurements probed the effect of mixing time, waiting time after mixing, and surfactant (SDS or CPB) concentration on the shear viscoelasticity of double emulsions.

1.11. Diffusion tests

Diffusion tests were conducted to investigate the possible diffusion of model contaminants (motor oil and toluene) through ‘emulsion locks’. Gastight vials (20 mL volume) were filled with 10 mL of double emulsion, to which SDS was added (2.5 g/L). The emulsion was mixed with SDS for 60 sec and then the vials were filled to the top with motor oil or toluene dyed with Nile Red for visual contrast. The vials were then tilted horizontally and left on the bench for three weeks, during which diffusion of the dyed contaminants into the gel was qualitatively assessed with the naked eye.

2. Results and discussion

2.1. Effectiveness of SDS and CPB in enhancing flushing of model hydrocarbons from sand

Hydrocarbon removal from polluted soil using surfactant flushing relies on the emulsification of hydrocarbons in water. Dynamic interfacial tension data show that SDS and CPB adsorbed at the oil-water interface, lowering the interfacial tension (Fig. 1). The decrease of the interfacial tension between the toluene-water interface with SDS is in agreement with previous studies (Addison and Hutchinson, 1948; Sain and Akbari, 2006). The critical micelle concentration (CMC) for SDS is 8.3 mmol/L (2.4 g/L) (Bales et al., 1988). In this study, the interfacial pressure at the oil-water interface was not measured at the CMC using the pendant drop method, because the droplet streamed out of the needle at very high surfactant concentrations. Measurements of the interfacial tension at high surfactant concentrations using alternate methods (e.g., Du Nuoy ring) will be the objective of future research. The adsorption of CPB at the toluene-water interface was not previously reported, but previous studies demonstrated CPB adsorption onto crude oil coated sands (Dai et al.,...
and its effectiveness in mobilizing hexadecane and heptane from model porous media (Yarveicy and Haghtalab, 2018). The interfacial tension of motor oil decreased even without SDS or CPB. This result indicates that interfacially active species were present in motor oil. Surfactants are typically present in motor oil to create a skin on the surface of the oil, reducing volatilization losses in the engine (Reick, 1980). Detergents can also prevent carbon deposition on metal surfaces.

Surfactants can stabilize emulsions by imparting compressional rigidity to the oil-water interface (2013). Compressional experiments conducted with a Langmuir trough using motor oil showed that CPB was able to rigidify the oil-water interface even at small deformations (i.e., large areas) at either 2 mL/L (6 × 10⁻³ mol) or 10 g/L (3 × 10⁻² mol) (Fig. 2). The rigidity of the CPB at the motor oil–water interface was evident from the increase of the interfacial pressure upon compression of the films. SDS at 2 g/L (7 × 10⁻³ mol) produced interfaces with negligible rigidity at small deformations, and rigidified the motor oil-water interface only at areas smaller than approximately 5800 mm² (Fig. 2). The negligible increase in interfacial pressure at small deformations (i.e., large areas) has been previously reported for surfactants (Aka’a et al., 2012) and interfacially active molecules (Wang et al., 2017). The region where the increase in pressure is negligible corresponds to the so called gas phase, and here the interfacially active molecules are not fully packed at the oil-water (or air-water) interface (Minones et al., 2009; Yu et al., 2018). It is reported that the critical micelle concentration for SDS is 2 g/L area of the SDS polar head is 66 Å² (Bonfillon and Langevin, 1993). Accepting this estimate, approximately 9 × 10¹⁵ SDS molecules were adsorbed at the motor oil-water interface at the transition from the gas phase to the liquid phase, where the pressure increased with decreasing surface area. It is noted that in Langmuir trough experiments the interfacial pressure was zeroed before each compression, and is not correlated to the interfacial tension.

Without SDS or CPB, the motor oil–water interface had negligible rigidity (data not shown). The toluene-water interface also had negligible rigidity, either with or without surfactants in milli-Q water (data not shown).

Compressional rigidity of interfacial film is not the only factor controlling emulsion stability. Previous studies showed that the compressional elastic moduli of SDS at dodecane-water interfaces decreased when increasing the SDS concentrations in the bulk water phase from 0.03 to 0.2 g/L (Bonfillon and Langevin, 1993). Similarly, our previous research showed that films formed at the toluene-water interface by amphiphilic ethylene oxide–propylene oxide co-polymers were softer with higher polymer concentrations (Pensini et al., 2014).
Fig. 4 – Optical microscopy observations of water in oil (W/O) or oil in water (O/W) emulsions obtained by mixing DI water with either motor oil or toluene, with either CPB or SDS. Images were taken 15 min after hand-shaking. All scale bars are 100 μm.
However, emulsion stability increases with increasing concentrations of SDS and amphiphilic polymers, up to a benchmark concentration. Emulsion stability depends on a complex interplay of diverse mechanisms. In addition rigidifying the oil-water interface, surfactants can stabilize emulsions through Marangoni effects and electro-steric repulsive forces (2013). SDS is an anionic surfactant (Marques et al., 1993) and it should impart a negative charge to oil droplets in water. Bottle tests demonstrated that 2.5 g SDS/L and 25 mL of CPB/L produced both water in oil and oil in water emulsions after 30 sec hand-shaking motor oil or toluene with DI water (Fig. 3). In the presence of CPB or SDS, the water phase remained turbid over 120 min, indicating the presence of oil in water emulsions. Optical microscopy images confirmed the formation of oil in water and water in oil emulsions with SDS or CPB added (Fig. 4). With motor oil, water in oil and oil in water emulsions also formed without SDS or CPB. However, the water phase was more turbid in the presence of surfactants, as qualitatively assessed with the naked eye. Also, water in motor oil emulsions were more stable with CPB than with SDS, possibly due to the greater compressional rigidity of CPB films (Fig. 2). Toluene separated from water almost immediately without surfactants. The formation of emulsions with SDS and CPB suggest that these surfactants have the potential to promote the mobilization of model hydrocarbons (toluene and motor oil) in porous media, facilitating their remediation through surfactant flushing. In this study, we have not determined the minimum concentration at which SDS and CPB could form emulsions of toluene or motor oil in groundwater, and this should be the objective of future research.

Column experiments were conducted to confirm the effectiveness of SDS and CPB in flushing toluene and motor oil from sand columns. The data show that toluene recovery was greater with surfactants (Fig. 5). When sand columns contaminated with toluene were flushed with DI water (without surfactants), 17% of the toluene could be recovered. Flushing with 0.008 M SDS or CPB solutions (i.e., 2.5 g/L SDS and 2.7 g/L CPB) at 6 mL/min increased toluene recovery from 17% to 31% (with CPB) and 74% (with SDS). Anionic SDS may be more effective than zwitterionic CPB in flushing toluene from sand (which is negatively charged at neutral pH (Pensini et al., 2012)) due to the electrostatic repulsion between emulsified toluene droplets and the solid matrix (sand). When sand columns contaminated with motor oil were flushed with DI, flow was impeded and a constant flowrate could not be maintained. The pump had to be stopped at regular intervals to allow the water to drain slowly from the column, indicating that motor oil had scarce mobility and impeded water flow. When sand columns contaminated with motor oil were flushed with either SDS or CPB solutions, a constant flow of 6 mL/min could be maintained. Also, samples exiting the column flushed with SDS or CPB were visibly turbid after approximately 15 min, suggesting the presence of motor oil emulsified in water. These results qualitatively indicate that flushing with CPB and SDS solutions promoted motor oil recovery from sand columns.

2.2. Double ‘emulsion locks’

Surfactants can mobilize hydrocarbons, facilitating their recovery using pumping wells. For instance, SDS and CPB can facilitate the recovery of toluene and motor oil spills in sand, as discussed in the previous section. An important risk associated with surfactant flushing is the uncontrolled spreading of hydrocarbons, due to their emulsification in groundwater. ‘Emulsion locks’ were developed to prevent this risk, as schematized in Fig. 6.

Confocal and optical microscopy images of W/O/W double emulsions (aqueous CaCl₂ solutions in EC and calcium stearate in canola oil, emulsified in sodium alginate in water with Tween 20) were taken prior to mixing with surfactants, and are given in Fig. 7. The observed structure of the double emulsions is in agreement with our previous study (Lamont et al., 2019). Before mixing with SDS and CPB, the double emulsions had low viscoelastic moduli (\( G’ = 2.67 \pm 0.58 \) Pa and \( G’’ = 1.69 \pm 0.24 \) Pa in the linear region, which extended up to strains \( \approx 2.5\% \)). The low shear elastic moduli of the double emulsions are desirable, because they should promote pumping and transport to the contaminated areas.
Mixing with either CPB or SDS triggered the gelation of the ‘emulsion locks’, increasing their viscoelastic moduli (Figs. 8-9). These results suggest that ‘emulsion locks’ pumped in the subsurface around the polluted regions can be used as barriers to prevent hydrocarbon plume migration during surfactant flushing. With the proposed ‘emulsion locks’ technology, hydrocarbons can be safely mobilized and pumped from confined areas, outside of which they cannot migrate because of the gel barriers.

Gelation is caused by the double emulsion reversal, which releases CaCl₂ into the sodium alginate solution. CaCl₂ crosslinks sodium alginate, forming an elastic network (gel). Emulsion reversal was attributed to the increase in the HLB (hydrophilic lipophilic balance) number. The HLB number of surfactants increases with increasing hydrophilicity (Jin et al., 2008). HLB numbers can also be computed for double emulsions. The HLB number of double emulsions is given by the weighted average of the HLB numbers of the surfactants added to each phase (Schmidts et al., 2010). A study reports that inversion of W/O/W emulsions obtained with paraffinic oil and water occurred when the HLB of the system approached 10 (Frenkel et al., 1983). It is speculated that SDS (with HLB = 40, (Mohamed and Mahfoodh, 2006)) and CPB (with HLB = 15, (Yarveicy and Haghtalab, 2018)) destabilized the double emulsions by increasing the HLB number of the system.

With 30 sec mixing, SDS increased the viscoelastic moduli at concentrations as low as 1.25 g/L (Fig. 8). With SDS

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**Fig. 7** – Optical microscopy image of the double water in oil in water emulsions, prior to mixing with surfactants (a) and confocal microscopy images (b, c). In image (b) the oil phase is bright because of Nile Red dye, and the water phase is black. The scale bar is 100 μm.
concentrations between 1.25 and 5 g/L, the viscoelastic moduli increased over time, when gels were allowed to set after mixing. With 2.5 g/L SDS, $G'$ increased from 165.7 to 254.6 Pa and $G''$ increased from 7.14 to 15.2 Pa, from immediately after mixing to 105 min after mixing. The viscoelastic moduli also increased upon waiting 20 min, as shown for 1.25 and 5 g/L SDS (Fig. 8). The shear viscoelastic moduli measured immediately after 30 sec mixing increased with increasing SDS concentrations up to 2.5 g/L SDS, above which they decreased (Fig. 8). These results suggest that SDS concentrations of 2.5 g/L or above were effective at rapidly reversing the double emulsion, but high SDS concentrations weakened the gels. This is because SDS associates with calcium ions, likely preventing them from crosslinking sodium alginate chains. Previous studies showed that positive calcium ions can form bridges between the anionic SDS heads (Sammalkorpi et al., 2009), and that they associate with SDS micelles (Baviere et al., 1983).

Higher CPB concentrations and longer mixing times were required to trigger the gelation of double emulsions (Fig. 9). The viscoelastic moduli of the double emulsions increased with 10 g/L CPB after mixing for 60 sec or longer, while shorter mixing times did not trigger gelation (Fig. 8). The HLB of CPB is lower (HLB = 15, (Yarveicy and Haghtalab, 2018)) than the HLB of SDS (HLB = 40, (Mohamed and Mahfoodh, 2006)), likely explaining why emulsion reversal required higher CPB concentrations and longer mixing times. Specific effects due to difference in the chemistry of the CPB and SDS cannot be discounted (Schmidts et al., 2010). Similar to SDS, waiting 20 min after 60 sec mixing with 10 g/L CPB increased the viscoelastic moduli, e.g., from $G'$ 220 Pa and $G''$ 11 Pa.

In addition to surfactants, solvents such as ethanol can be used to mobilize hydrocarbons, by enhancing their solubility in water. Ethanol could also trigger gelation, but only at fairly high concentrations (100 mL/L) and with 1 min mixing (Fig. 10). Due to its scarce effectiveness in reversing double emulsions, ethanol is not the preferred candidate to enhance the mobility of hydrocarbons when used in combination with ‘emulsion locks’.

Shear rheology showed that SDS was more effective than CPB in triggering the gelation of ‘double emulsions’ in DI
water. The effectiveness of SDS and double emulsions in forming barriers was verified with diffusion tests and in flow tests using a permeameter. Future research may focus on the combined effect of SDS and CPB on double emulsion gelation. Diffusion tests conducted over a three-week period in gas-tight vials showed that motor oil and toluene could not diffuse through double emulsions prepared with DI and gelled by mixing with SDS, as shown in Fig. 11. Qualitative observations showed that gelation also occurred when mixing 2 mL of simulated groundwater (1 mmol/L CaCl₂, 0.5 mmol/L MgCl₂, 1 mmol/L KCl, 1 mmol/L NaCl) and SDS (1 mL of 1 g/10 mL) with 5 mL of emulsion for 30 sec. The picture was taken 20 min after mixing.

Fig. 11  — Gas tight vials filled first with gelled double emulsions and then with motor oil (bottom) and toluene (top), dyed with Nile Red to enhance visual contrast. The vials were laid flat on a counter and images taken over time. This image was taken three weeks after the start of the experiment.

Fig. 12  — Gel obtained by mixing 2 mL of simulated groundwater (1 mmol/L CaCl₂, 0.5 mmol/L MgCl₂, 1 mmol/L KCl, 1 mmol/L NaCl) and SDS (1 mL of 1 g/10 mL) with 5 mL of emulsion for 30 sec. The picture was taken 20 min after mixing.

flow was retarded by 76% ± 2% with 5 g/L SDS. Since Ca²⁺ crosslinks sodium alginate, high CaCl₂ concentrations interfere with gelation. Concentrations comparable to those present in the primary emulsions cause gelation even without SDS addition. Excessively high CaCl₂ concentrations (e.g., 1 mol/L) overcrosslink sodium alginate, decreasing gel quality (as assessed through visual observations). Our current research is focusing on the development of barriers for aquifers with high calcium concentrations, e.g., in limestone aquifers.

3. Conclusions

Our study demonstrated that double W/O/W emulsions prepared with CaCl₂ solutions in canola oil (with EC and calcium stearate) in sodium alginate (with Tween 20) can be gelled with SDS and CPB, which reversed the emulsions and increased their shear viscoelastic moduli. Emulsion reversal was caused by an increase in the HLB number of the oil/water mixture. SDS (HLB = 40) could reverse the double emulsions at lower concentrations than CPB (HLB = 15), likely because of its high HLB number. Diffusion tests conducted in gas-tight vials showed that once double emulsions prepared with DI water gelled due to mixing with SDS, they did not allow the diffusion of either motor oil or toluene over a three-week period. Qualitative observations also showed that gelation also occurred when mixing 2 mL of simulated groundwater (1 mmol/L CaCl₂, 0.5 mmol/L MgCl₂, 1 mmol/L KCl, 1 mmol/L NaCl) and SDS (1 mL of 1 g/10 mL) with 5 mL of emulsion. Flow tests conducted with a permeameter using simulated groundwater and SDS confirmed that the double emulsions could impede flow through sand. The proposed double emulsions can therefore act as ‘emulsion locks’ around hydrocarbon polluted areas remediated with surfactant flushing. The effectiveness of CPB and SDS in emulsifying model hydrocarbons (toluene and motor oil) was demonstrated by bottle tests and by optical microscopy observations. Both CPB and SDS adsorbed at the oil-water interface (with either toluene or motor oil), decreasing the interfacial tension. CPB could also impart rigidity to motor oil-water interfaces, promoting their stability. The emulsification of motor oil and toluene in water with SDS and CPB enhanced their recovery and flow through saturated sand columns, used to mimic sandy aquifers. Our study demonstrates the potential usefulness of ‘emulsion locks’ for the safe treatment of sites contaminated by hydrocarbons, combining surfactant flushing with economic, pumpable barriers. The testing conducted was limited to a lab setting, and to sandy aquifers. Different soils must be studied, and real groundwater samples originating from the field should be used for gel preparation. When using DI water in the lab, gels were stable for three weeks (longer observations were not conducted). The stability of the gels should be analyzed over longer time periods, using real groundwater originating from polluted sites.

Declaration of Competing Interest

We hereby declare that there is none of the co-authors are in conflict of interest. Erica Pensini on behalf of all co-authors.
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