

Effectiveness of Polysorbate Polyester on Separation of Emulsions Made by Green Surfactants

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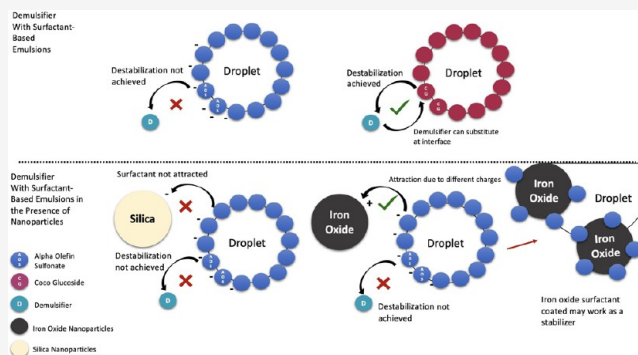


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ABSTRACT: The surge of new technology in the oil industry with nonpollutant/green surfactants, new brines, and the addition of nanoparticles to emulsion systems imposes a question on how these systems are separated and if the current most commonly used method is still applicable to them. This paper showcases the study on the performance of a green demulsifier (polysorbate polyester) up to a maximum concentration of 1000 ppm in the separation of crude oil emulsions with different compositions. These emulsions varied from light to medium crude oil with three surfactants, Coco Glucoside (sugar-based), Greenzyme (enzymatic-based), and alpha olefin sulfonate (synthetic). These emulsion systems contained two environmentally friendly brines, sodium and potassium formate, and the results were compared with sodium chloride. Some compositions consider the addition of 0.25 wt % silica and magnetite nanoparticles. The demulsification efficacy was evaluated with a bottle test at 60 °C. The demulsifier produces a full separation with Coco Glucoside with light crude oil with any composition; however, a high concentration is needed. Emulsions with medium crude were more difficult to separate as the demulsifier was slower to act due to the viscosity increase and in some cases even presented no considerable changes in separation, like for 7 g/dL potassium formate salt. The demulsification with particle presence was dependent on the interaction between the surfactant–particle interaction. Emulsions containing silica decreased the demulsification between 10 and 20% with a stronger effect observed for the samples with magnetite between 10 and 40% depending on the surfactant type.



1. INTRODUCTION

Emulsions are normally created during the production process in the oil and gas industries; this happens when oil has contact with water through a turbulent flow to the surface.¹ Oil and water are produced separately; however, the turbulence produces a high shear force that deforms and disperses one phase into the other while it flows from well connections to pipelines.² The higher the flow velocity, the smaller the droplet size of the emulsion, and therefore, the tighter and stable the emulsion phase.³ The source of the brine contained in the emulsion could be either formation brine or treatment brine. However, for this paper, only brine that originated from well treatments will be considered. This operational aqueous phase usually contains surfactants, as they are used for well cleaning or workover operations. The surfactant content in them tends to create a more stable emulsion phase than the one produced by just shear mixing.⁴ The emulsion presence in the hydrocarbon production could hinder this process in several ways; it can constrain the flow line pressure, diminish production, and cause pipeline corrosion problems, refinery catalyst poisoning, and extra-expense for additional equipment, among other issues.^{2,4} Another problem to consider is that the solids and water presence needs to be less than 1% to be able to sell the crude.^{5,6} To separate these phases, several methods

are used, which can be used by themselves or combined: thermal, mechanical, electrical, and chemical.⁷

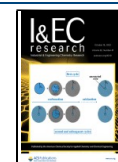
One of the most common methods of emulsion dehydration is the use of chemical demulsifiers,⁸ and one of the mostly used is the thermochemical process.^{9,10} A chemical demulsifier is a surface active agent that tends to adsorb to the water–oil interface to influence the formation of flocs, aggregation, and coalescence of the water droplets.^{7,11} There are water- and oil-soluble demulsifiers, with the former being the most widely applied at the wellhead to use the temperature to make the process faster. These demulsifiers are preferred as they act quickly, lower doses are needed, they are easily prepared, and they present a long shelf life. The effectiveness of the demulsifier depends on how fast it achieves the interfacial tension relaxation.¹² Most of the demulsifiers are polymerized surfactants having ethylene and propylene oxide; alkyl,

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ethoxylated, or propoxylated phenol formaldehyde resins; oxyalkylated alkyl resin; and polymerized polyols, alcohols, and amines, to name a few.^{1,6,7,13}

The application of demulsifiers has caused some environmental concerns due to their usage. However, the potential impact is controversial. A study tested several biocides, corrosion inhibitors, and demulsifiers (phenol formaldehyde, cationic–anionic blend, and oxyalkylated alkylphenol formaldehyde resins and polyoxyalkylated glycols in hydrocarbons). It concluded that the three demulsifiers tested presented a nondetectable level of toxicity in the aqueous phase for the marine bacterium *Vibrio fischeri*.¹⁴ However, two of these demulsifiers were classified as highly toxic by the Offshore Chemical Notification Scheme (OCNS).¹⁵ Currently, most demulsifiers registered on the OCNS for completion, work-over, and production operations are classified with a hazard quotient (HQ) between 0 and 30, corresponding to gold and silver bands indicating low toxicity. Only a few demulsifiers are marked as belonging to the List of Chemicals of Priority Action (LCPA), therefore prohibiting their discharge.

Nowadays with the mounting environmental concerns, the petroleum industry is proactively seeking more sustainable solutions, prompting a shift toward the utilization of environmentally friendly alternatives, including readily biodegradable chemicals. Commonly employed surfactants, such as sodium dodecyl sulfate, alpha olefin sulfonate, and alkyl benzenesulfonate, are petroleum-based and raise ecological apprehensions.^{16,17} Therefore, the industry has perceived the appearance of a new wave of eco-conscious surfactants, many of which are biosurfactants, plant-derived, or sugar-based.¹⁸ Biosurfactants like rhamnolipids and surfactin, plant-derived interfacial agents such as saponins and lecithin, and sugar-based surfactants including alkyl polyglucosides and sorbitan esters are among these innovative alternatives.^{19–22} This broader industry transition has also represented a change in the adoption of use of brines, to more environmentally friendly brines like sodium, potassium, and cesium formate, known for their biodegradability and reduced toxicity to marine life.²³

However, the integration of these environmentally friendly surfactants and innovative oil industry technologies, such as surfactant flooding, low-salinity water flooding, and nanoparticle fluid flooding, introduces an intriguing challenge—the potential formation of emulsions due to the dynamic nature of fluid movement.²⁴ Along these advancements, demulsifiers are also progressing. While new “green” demulsifiers are being introduced to align with the new biodegradability standards, questions linger about their efficacy in efficiently separating these emulsion phases.

Particularly, as the presence of injected surfactants and inorganic solids in the oil phase enhances emulsion stabilization, understanding how these new green demulsifiers interact with such complex samples becomes important for the energy industry.²⁵ This study aims to address this elaborate question, focusing on polysorbate polyester as the test subject. Polysorbate polyester is a polymeric nonionic surfactant that serves as an environmentally friendly alternative to petroleum-based demulsifiers. Nonionic surfactants in general are the most commonly used for this technique. A study using 52 nonionic surfactants with different functional groups found that a water removal of about 70 to 100% can be achieved with these demulsifiers. They performed demulsification tests at 80 °C for diluted bitumen emulsions with a concentration of 400 ppm and gravitational separation; these results increased with

centrifugation.⁷ However, no surfactant-based emulsion was tested.

In essence, the always changing landscape of the petroleum industry, marked by a shift toward greener surfactants and more sustainable demulsifiers, raises vital questions about their effectiveness with cutting-edge technologies and the intricate interplay of these agents with complex oil compositions. The search for this knowledge is essential to ensuring the environmental responsibility and efficiency of these new approaches within the industry.

2. METHODOLOGY

2.1. Materials. The salts used for the brine composition were sodium formate (NaCOOH, SF) 98% pure, potassium formate (KCOOH, PF) 99% pure with water less than 2%, and sodium chloride (NaCl) 99.5% pure, which were bought from Fisher Scientific. Concentrations used were 1 and 7 g/dL for either of the brines (when the brine description presents a number in front of the abbreviation indicating the concentration of such brine phase). Deionized water (DIW) was obtained from a Barnstead Smart2Pure water system by Thermo Fisher Scientific. Condensate was used for the light crude oil (LCO) spectrum obtained from North Sea offshore wells and was used without further treatment. Medium crude oil (MCO) was obtained from a mixture of heavy crude oil and 20% petroleum ether for dilution. The demulsifier that was utilized for the tests is polysorbate polyester, generously provided by CRODA from its environmentally friendly line. Alpha olefin sulfonate (AOS), the commercial surfactant, was purchased from Prime Surfactants, a supplier of Hansanyl OS by Enaspol; the environmentally friendly surfactant Coco Glucoside (CG) was bought from Naturallythinking; and the enzymatic-based Greenzyme (GZ) was kindly supplied by Biotech Processing Supply Solutions. All the surfactants were used at 2 wt %. Barazan D (xanthan gum, XG) was used as obtained from Halliburton. Dichloromethane (DCM) was used for the liquid–liquid extraction. Silica oxide nanoparticles (SiO₂ NPs) of 20 nm were purchased from Sigma-Aldrich as the negative surface-charged particle. Magnetite (Fe₃O₄) nanoparticles (MNPs) of 20 nm were purchased from GetNanoMaterials as the positively charged nanoparticle. Both nanoparticles were used without further modification.

2.2. Crude Oil and Brine Specification. The viscosity and density of the condensate and MCO and brines were measured with an Anton Paar SVM 3001 kinematic viscometer, following ASTM D-445 (Table 1). In order to

Table 1. Oil Properties at 25 °C

oil type	density (g/cm ³)	kinematic viscosity (mm ² /s)	dynamic viscosity (mPa·s)	°API
light crude oil	0.7840	1.8073	1.4367	48
medium crude oil	0.9231	177.90	163.47	21

obtain the American Petroleum Institute (API) gravity, which relates the oil density to that of water, the following formula was used:

$$\text{API} = \frac{141.5}{\text{specific gravity}} - 131.5 \quad (1)$$

The percentages of saturates, asphaltenes, resins, and aromatics (SARA) for the two types of crude oil, which were determined by liquid chromatography are detailed in Table 2. Table 3 describes the concentration conversions for the brine compositions.

Table 2. SARA Analysis

crude oil	percentage %			
	asphaltene	resin	aromatics	saturates
light crude oil	2.58	30.79	30.90	35.73
medium crude oil	0.26	6.55	16.15	77.04

Table 3. Brine Concentration Conversions to mM/L

concentration	NaCl (mM/L)	NaCOOH (mM/L)	KCOOH (mM/L)
1 g/dL	182.21	147.03	118.87
7 g/dL	1275.51	1029.26	832.14

2.3. Chemical Demulsification. The ability of the chemical demulsifier to break a 50/50 vol % water–oil emulsion was determined with a bottle test method. Two oils were tested, one LCO and the other considered as MCO. Brines were prepared first in 100 mL volumetric flasks with either 1 or 7 g/dL of sodium formate, potassium formate, and sodium chloride; these salts were mixed thoroughly with DIW on a magnetic stirrer and then decanted to a beaker for easier access. Two concentrations of XG were tested, 0.1 and 0.5 g/dL, also mixed with a magnetic stirrer overnight to ensure complete hydration of the polymer. The emulsion was prepared in 15 mL bottles with only 5 mL in total volume for the emulsion phase, and it was mixed in a Fisher Scientific Vortex Mixer at 3000 rpm for 1 min. After mixing, the demulsifier was added and the bottles were shaken manually to avoid overmixing; immediately after, the samples were placed in the thermostatic bath at 60 °C for a running test length of an hour.⁸

Tested concentrations for the demulsifier were 250, 500, and 1000 ppm to maintain it in the range used in the industry^{8,26}; the highest concentration was considered as the emulsions presented commercial surfactants already mixed into the

emulsion phase. Demulsifiers were added after the emulsion was mixed to simulate emulsions getting to the surface and applying treatment afterward. The demulsification tests were only using gravitational settling and heating, and the amount of separated water and oil was recorded every minute during the first 5 min and every 5 min until the 1 h mark.

$$\text{water demulsification}(v\%) = \frac{C_{t0}}{C_t} \times 100 \quad (2)$$

where C_{t0} is the original water volume before the bottle test and C_t is the water content released from the emulsion phase after the demulsification process.^{7,26} The bigger the water demulsification, the better the performance of the used demulsifier.

For the emulsions containing silica and magnetite, 0.25 wt % of the nanoparticles was added to the emulsion phase and mixed in a vortex mixer for 1 min at 3000 rpm, after the emulsions were already created. The demulsifier was added just before the test for demulsification. Droplet size analysis was conducted with an Olympus BX60 M microscope, and the micrographs were further analyzed with Fiji and MATLAB to identify the droplets and sizes.

In order to validate the results of the visual recordings captured on video, three separate experiments were run for the LCO samples with DIW. The first experiment was weighting on a scale the extracted oil and water separated from the emulsion. With the extracted phases, it was possible to recalculate the emulsion composition. The second experiment was performed with a TRACE 1300 gas chromatograph–flame ionization detector (GC-FID). A calibration standard was run with pure condensate phases diluted in DCM (Supporting Information). Liquid–liquid extraction was required to obtain the pure oil phase from the emulsion samples in order to run them in the GC-FID. Identical extraction methodology was used for the third method to obtain diluted oil samples to attain a calibration standard for the refractive index (Supporting Information). The samples were analyzed in an Abbat 3200 Refractometer by Anton Paar. It is important to acknowledge that despite the rigorous nature of these methods, none can be deemed 100% unailing, as all of them have either

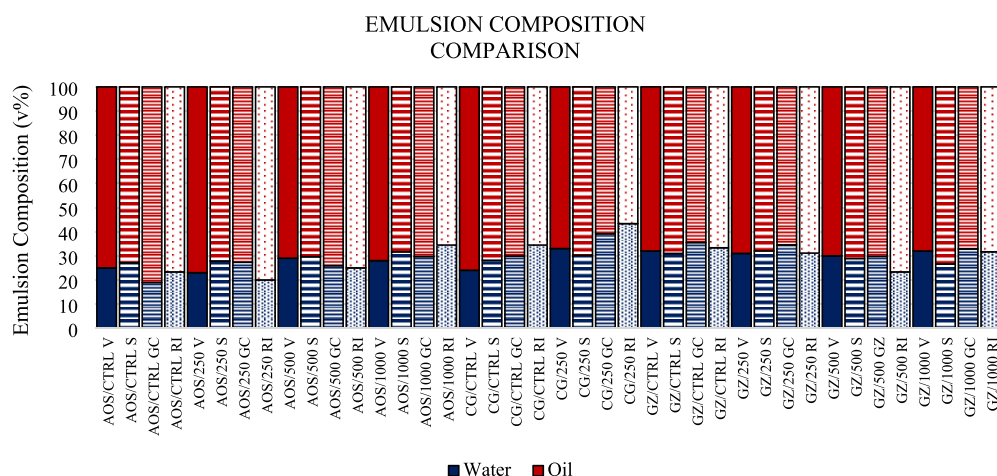


Figure 1. Emulsion composition comparison with several measuring methods. V: visual inspection, S: scale measurement, GC: GC-FID measurement, RI: refractive index. *Water details for GC-FID and RI measurements were obtained by subtracting the oil percentage from 100% (AOS emulsions: control, 250, 500, and 1000 ppm. CG emulsions: control, 250 ppm. GZ emulsions: control, 250, 500, 1000 ppm. CG emulsions: control, 250 ppm. GZ emulsions: control, 250, 500, 1000 ppm).

human or chemical/equipment error. For instance, with the simple scale method, by extracting the oil and water phase with the aid of a syringe, part of the emulsion phase could inadvertently be removed along and the recalculated composition could present some error. In the case of the GC-FID, the sample can be quickly overestimated if the emulsion sample presents a high concentration of oil. Extra dilution was needed to facilitate the chromatographic analysis. This could potentially introduce errors during the recalculation of the composition by integration. While the refractometer exhibits consistency and precision, the attainment of the measurements proved to be considerably intricate due to the susceptibility to any alterations in composition. During the measurement procedure, it became evident that the volatility of DCM posed a consistent, though not overly significant challenge. Evidently, the visual method presents some human error in it. Despite these noted considerations and circumstances, Figure 1 shows that the composition of the remaining emulsion phase is analogous throughout the different methods tested supporting the findings.

3. RESULTS AND DISCUSSION

3.1. Effect of Demulsification in LCO. LCO emulsions with AOS, CG, and GZ were examined with several aqueous phases in the presence of polysorbate polyester as the demulsifier.

3.1.1. AOS. The effect of temperature was not enough to separate the emulsion created with AOS and DIW with the LCO, as the maximum water separation was 69% with only 12.5% oil separation on the control sample (Figure 2). The

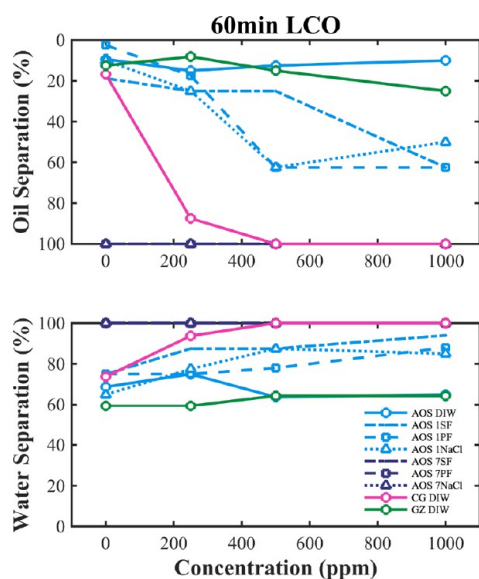


Figure 2. Demulsification of LCO emulsions with AOS, CG, and GZ with different aqueous phase compositions. Demulsifier concentrations of 0, 250, 500, and 1000 ppm.

addition of the demulsifier still has a positive impact in the separation. The demulsifier tested increased the water separation from 69 to 75%, and the oil separation from 9 to 15% with the lowest concentration of the demulsifier compared with the control sample. Increasing the demulsifier concentration further than 250 ppm was detrimental to the water separation as the separation decreased; as it can be observed in Figure 2, the droplet size does not change

considerably from the control sample to the 1000 ppm concentration and it can be observed in

Figure 3 micrographs. This reaction has been reported before where an increase of demulsifier concentration from 500 to 1000 ppm reduced the water removal from 80 to 10%.⁷ This is known as overdosing, and the demulsifier tends to make the emulsion stronger due to the higher concentration added to the sample.

Where emulsion control samples containing brines are compared with the DIW control, the water separation is considerably similar to just a slight increase of 6% for the formate brines. Water separation was substantially higher for samples containing a demulsifier as it ranged between 88 and 94%, being the highest for 1SF. The maximum overall separation corresponded to 1SF, and the biggest variability between control and demulsifier samples corresponded to 1NaCl. A previous analysis has reported the demulsification of an LCO of 43.4 API, slightly higher density than that used in the current study, and 2% KCl brine without the use of surfactant as an emulsion stabilizer.²⁵ They observed a complete water separation with a commercially available nonionic surfactant used as demulsifier at 2000 ppm in 10 min at 20 °C. They utilized double of the maximum concentration used in this study, which is considerably high for the industry standards.^{8,26} However, this concentration was successful. In comparison, the presence of AOS in the demulsification for LCO emulsions with polysorbate polyester, being also a nonionic demulsifier, increased the demulsification time around five times and reduced the water removal between 6 and 10%.

From

Figure 3, it can be observed that the increase in the demulsifier concentration represents a substantial change from the control samples having, for example, in the case of 1SF, droplets with sizes over 100 μm (Supporting Information), making the emulsion considerably more unstable. The salt presence just increases water separation in 10%. Although no full separation was reached, the salt presence enhances the emulsion instability, which favors separation with the increase of demulsifier concentration. For all brines tested, the maximum oil separation reached 62%, an increase of 42, 59.5, and 52% for 1SF, 1PF, and 1NaCl, respectively.

A higher concentration of salt was tested to be 7 g/dL, yet no emulsion was obtained with condensate, and the mixture presented a full phase separation after a few minutes, the same response as for CG and GZ at low salinity (1 g/dL).

3.1.2. CG. The control sample of the environmentally friendly CG emulsion with DIW and LCO appears to be more unstable than that of AOS as it destabilizes completely (Figure 2). Water separation for the control sample obtained 73% with oil separation only at 18%, very similar to AOS. The application of the demulsifier had a significant impact on the emulsion separation. Full demulsification is achieved in 55 min (Supporting Information) when the medium and highest concentrations are used. It appears that the rigidity of the interface produced by this surfactant is being affected and therefore reduced by the application of temperature, that with the addition of the demulsifier the film is disturbed, further allowing the droplets to floc and then collide.⁹ This rate of collision increases with the increased thermal energy since the temperature decreases the viscosity of the emulsion phase.

The disturbance on the droplets can be observed in Figure 4 where from being droplets completely packed and with a size

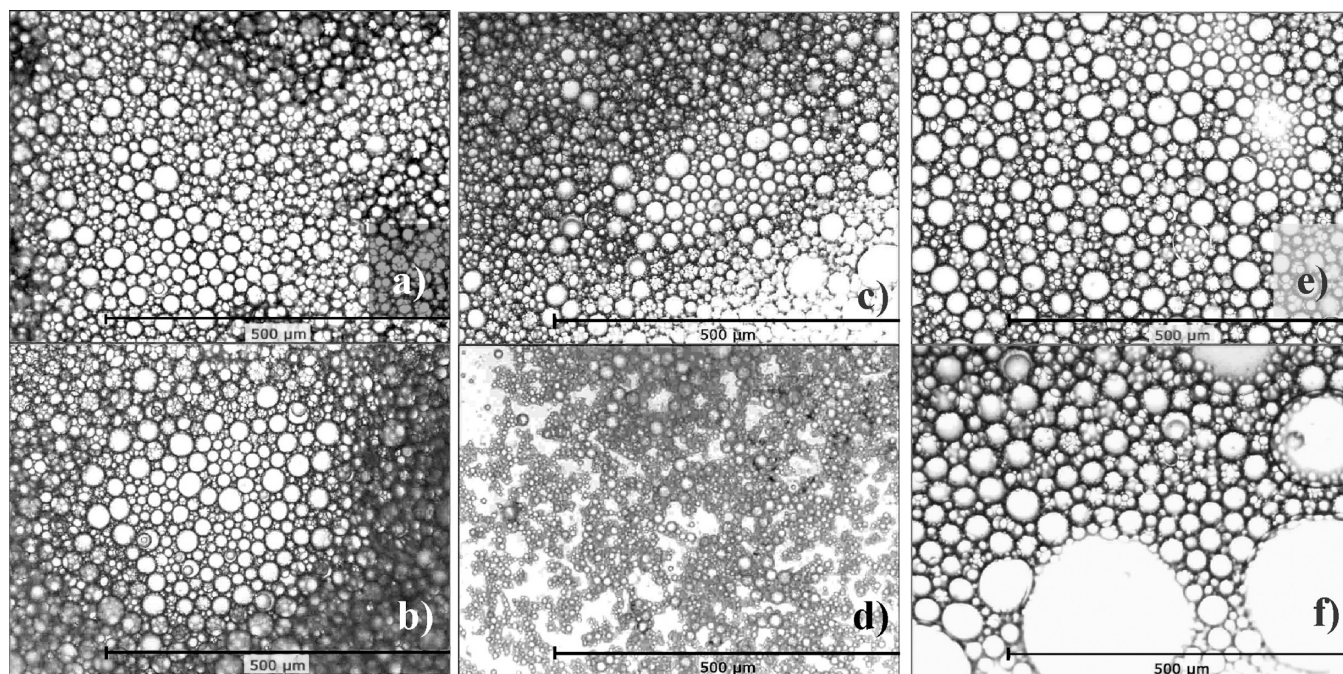


Figure 3. Micrographs of AOS emulsion samples with LCO: (a) DIW/control, (b) DIW/1000 ppm, (c) 1PF/control, (d) 1PF/1000 ppm, (e) 1SF/control, and (f) 1SF/1000 ppm.

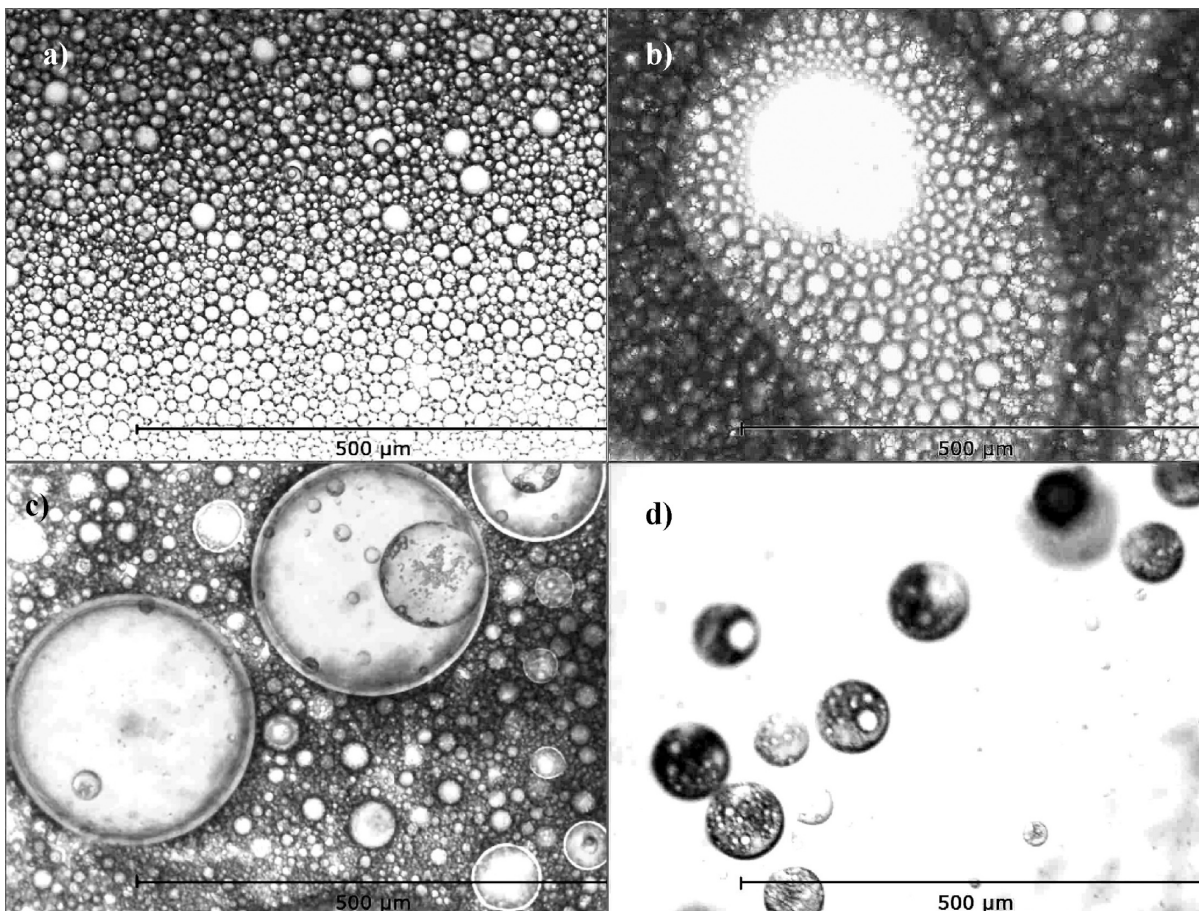


Figure 4. Droplet image samples at 500 μm for CG with DIW (measured 10 min after application of demulsifier) and 1SF emulsions (measured immediately after mixing). (a) CG/DIW/control, (b) CG/DIW/1000 ppm, (c) CG/1SF/control, and (d) CG/1SF/1000 ppm

of 20 μm and a volume frequency of 66% (Supporting Information) there is a decrease in the frequency of 23%,

indicating that the number of droplets of that size has been reduced considerably. The emulsion under the microscope

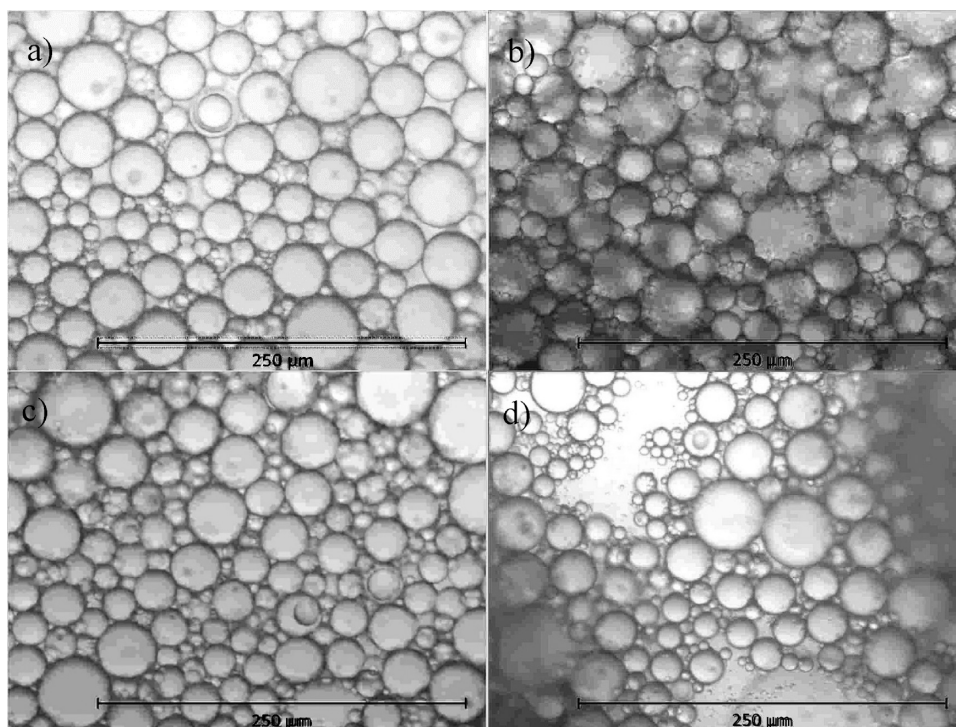


Figure 5. Microimages of the emulsion systems with LCO/DIW after chemical demulsification: (a) control, (b) 250 ppm, (c) 500 ppm, and (d) 1000 ppm.

appears to be more unstable as the droplets tend to coalesce quickly, forming pockets of empty space on the plate. Emulsions with a low-salinity concentration of 1 g/dL were also tested, and in comparison with AOS, they were not stable. These emulsions were more susceptible to the salt presence as a full phase separation was obtained at 5 min for the control sample. In Figure 4, it can be observed that there is a considerable change between the control DIW emulsion and the one with 1000 ppm. The salt presence yields a mix of big and small droplets, with the former reaching 200–250 μm , considerably more unstable than those observed for DIW (Supporting Information). CG emulsions can be considerably stable and maintain the emulsion phase for a day at room temperature at low-salinity conditions²⁷ with heptane as the oil phase. Nonionic surfactants are not as susceptible to reacting to salinity increases, yet CG has a slight tendency to work as an anionic surfactant. However, LCO appears to be quite unstable and volatile, rendering the emulsion phase more prone to react to the salt content; this behavior was not observed with heptane, which was unstable only with the higher salt composition (7 g/dL).

3.1.3. GZ. GZ presented a water separation with LCO for the control sample of 59% and an oil separation of 13%, which is considerably similar to that observed for AOS under the same conditions. However, when polysorbate polyester was added, the demulsifier appears to have no significant impact on the separation of this surfactant; the increase was only 5% for water separation and 12% for oil separation. In comparison with CG, this surfactant presents a good stability with LCO, yet it was only tested with DIW as the presence of salts made the emulsion highly unstable.²⁷

As observed in Figure 5, the droplet size remains similar even when the demulsifier increases (Supporting Information),

confirming what was observed macroscopically. The droplet size is fairly small, also indicating a good stability.

When the demulsifiers are added, they also tend to move to the droplet interface²⁸ (

Figure 6). They perform by a total or partial displacement of the original stabilizing film components that are enclosing the

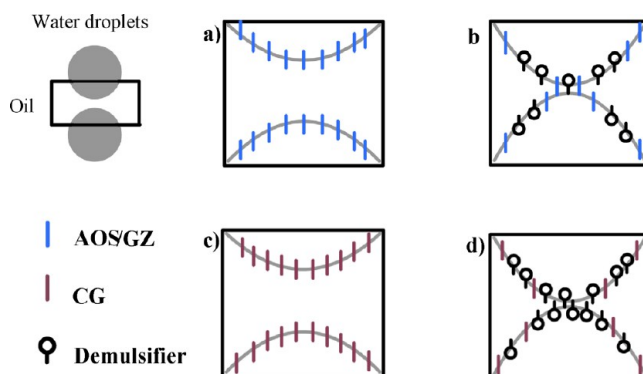


Figure 6. Emulsion water droplets in LCO. (a) AOS/GZ surfactant molecules surrounding droplets. (b) AOS/GZ surfactant molecules being partially substituted by the demulsifier. (c) CG surfactant molecules surrounding droplets. (d) CG surfactant molecules being mostly substituted by the demulsifier.

emulsion droplets. When natural surfactants (asphaltenes, resins) are the stabilizing components, an increase in water removal with an increase in demulsifier concentration can be justified by a displacement surge of the natural surfactants with a monolayer of the demulsifier, which is incapable of stabilizing the droplets. In this case, the original stabilizing components are commercial surfactants, AOS, CG, and GZ, that compete with the demulsifier, polysorbate polyester, that is also a

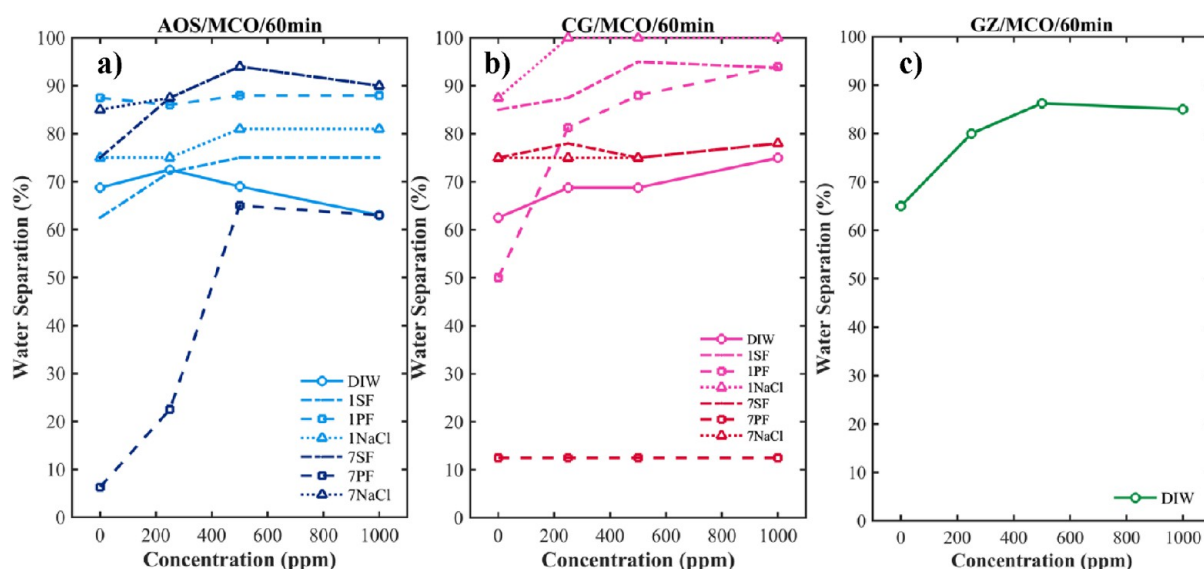


Figure 7. Demulsification of MCO emulsions with different brines as aqueous phases with MCO at 60 min: (a) AOS, (b) CG, and (c) GZ.

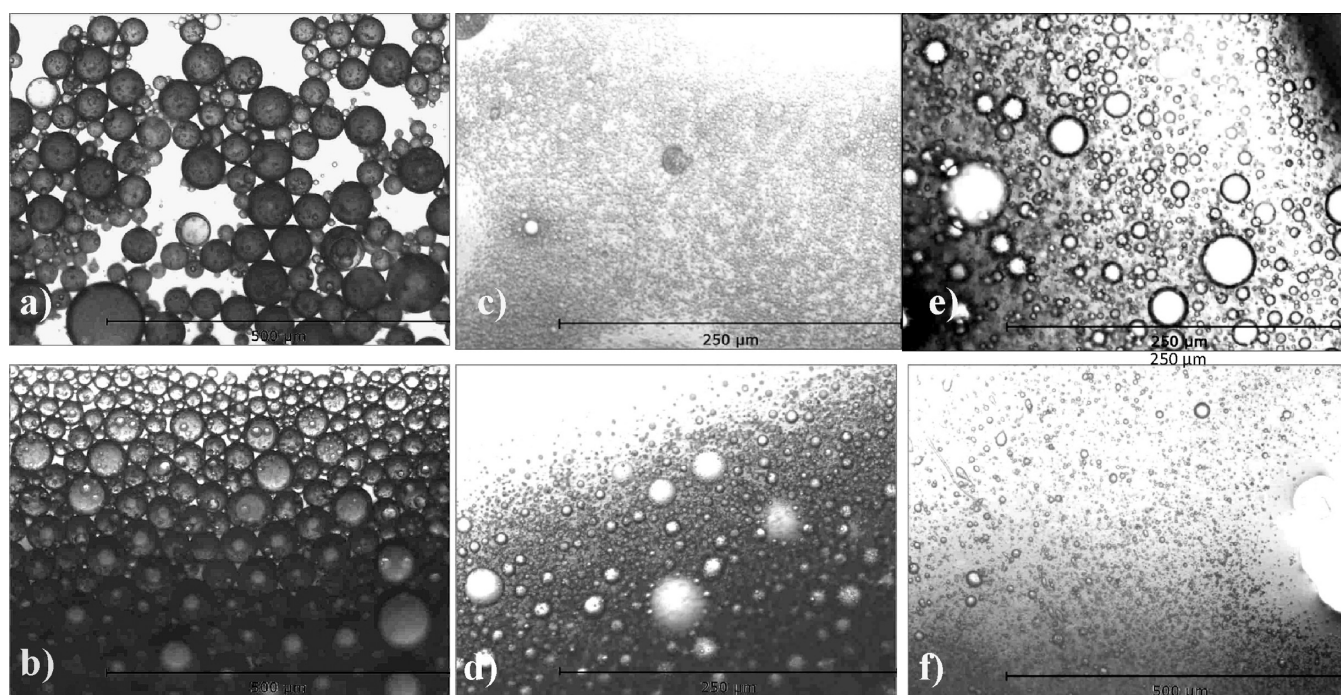


Figure 8. Micrographs of emulsion samples with AOS and MCO: (a) DIW/control, (b) DIW/1000 ppm, (c) AOS/7PF/control, (d) 7PF/1000 ppm, (e) 7NaCl/control, and (f) 7NaCl/1000 ppm.

surface-active species. This competition for the adsorption follows, attaining and forming a mixed film for which the composition varies depending on the solution constituents. Surfactants are highly adsorbed and therefore a low degree of displacement of this original species is likely, in comparison with natural surfactants that are weakly and slowly adsorbed.²⁹ From the results obtained, the displacement of AOS or GZ from the interface appears to be more difficult than the displacement of CG, as less water removal was obtained when the demulsifier was used, this difference was illustrated in

Figure 6 in which the demulsifier covers more part of the droplet when the emulsion is based with CG. CG and GZ seem to be affected considerably by the salt content, and CG is also affected by the oil type.

While AOS, CG, and GZ have been shown to present a decrease in surface and interfacial tension with the presence of these brines at high concentrations of salt,²⁷ the stability in this case is more affected by the type of oil phase that is present in the system. When the surfactants were tested with heptane, the surfactants achieved a considerably stable emulsion phase, although with high water separation. Thus, a similar emulsion phase could have been expected with condensate; however, a rapid separation was observed. This is due to the high content of toluene and benzene, aromatic components that provide less stability to the emulsion phase as they have less structural strength.³⁰

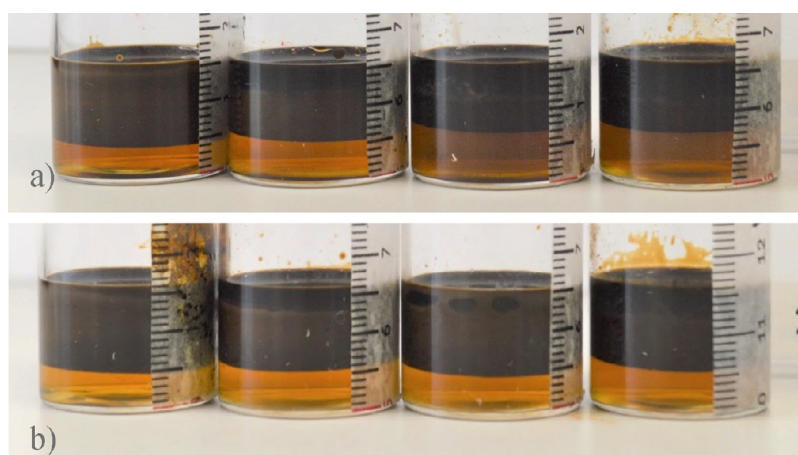


Figure 9. Emulsion samples of AOS and MCO with demulsifier concentrations from left to right of 0, 250, 500, and 1000 ppm: (a) 1PF and (b) 1SF

3.2. Effect of Demulsification in MCO. MCO emulsions were tested with different aqueous phases with the demulsifier addition for all of the surfactants.

3.2.1. AOS. When the demulsification efficiency is compared to that of the LCO emulsions, the demulsifier application is more effective in separating the lower viscosity crude. This implies that the emulsion made with MCO is definitely more stable than that of condensate (Figure 7). Nevertheless, full demulsification could not be achieved for AOS.

The AOS/MCO control sample presents the same water separation as the AOS/LCO control, with 69%. Water separation seemed to be reducing slightly while the demulsifier concentration is increasing; 250 ppm is the only concentration that increased the separation by 3%, which is negligible. AOS emulsion with DIW and condensate presented a similar response of overdosing at greater than 250 ppm. Lower concentrations were not tested, as comparable values were needed with the other surfactants tested. Droplets appear to be slightly bigger than those observed for LCO (Supporting Information), and the increase in concentration made them more compacted, as it can be observed in Figure 8a,b.

Water and oil demulsification for low-salinity emulsions was tested (Figure 7a). Control samples for these emulsions obtained no oil separation for any of the brines tested (Figure 9). Control water demulsification for brine-based emulsions ranged from 62, 75, to 87% for 1SF, 1NaCl, and 1PF, respectively, being just slightly higher for 1PF and 1NaCl and decreased by 13% for 1SF. The presence of the demulsifier did not produce a considerable difference between the control and the demulsifier samples. Water separation ranged between 81 and 88%, with the biggest increase being 19% for 1SF and the lowest belonging to 1PF with no increase. Water separation is noticeably lower than that for LCO samples, indicating that an increase in oil viscosity and density yields emulsions more difficult to separate.

Emulsions with a higher brine concentration (7 g/dL) were examined as well (Figure 7). Control samples indicate a minor increase in water separation for 7SF and 7NaCl, with just 12.5 and 10%, respectively. These two brines behave similarly with an increase in water separation with an increase in the demulsifier dosage. Droplet sizes for emulsions with 7NaCl ranged between 10 and 20 μm with the increase shown for the demulsifier application (Supporting Information). For 7PF, there is a decrease of around 80%; however, this is a result of

the change in the brine pH as this increases up to 11, which has an effect on the heavy particles of the oil aiding in the emulsification stabilization.²⁷ However, the demulsifier addition and the rise in temperature in the system for 7PF emulsions have a beneficial effect helping with the water separation reaching 68%, which was not observed before at room temperature. This enhances the coalescence of the droplets by decreasing the film thickness or film drainage. The droplet size increased slightly and the spacing between droplets increased, indicating that the demulsifier affected the stability, as it can be observed on Figure 8. In the case of the other two brines, the demulsifier effect in water separation produced a positive effect in all of the samples, with the best results with 500 ppm. The separation with 1000 ppm was similar, just off by 3–4%. The strongest effect in water separation was observed with 7PF attaining a 65% change of 59% when compared to the control sample. An increase of 19 and 9% for water separation was noted for 7SF and 7NaCl, correspondingly. It needs to be noted that the 500 ppm concentration left only 5–6% of water in these emulsion phases, which would most likely tend to separate if left longer in the thermal bath.

A previous study presented emulsions with oil of 28 API and a NaCl brine concentration of 50 g/L, similar to the concentrations of this research, obtaining a full separation in 20, 15, 7, and 6 min for 20, 30, 40, and 60 ppm demulsifier concentrations at 60 °C, respectively.³¹ However, this study did not use a surfactant as an interface stabilizer. The surfactant presence for the emulsions studied here made the separation considerably more difficult even when the salt content is slightly higher. Maximum separation was achieved between 50 and 55 min, for emulsions with 7 g/dL (Supporting Information), and for 1 g/dL emulsions, the time was in the range of 35 and 45 min more than double of the time for the mentioned study and it had still between 5 and 35% water content remaining.

It needs to be noted that the demulsifier effectiveness is decreased just by the change from LCO to medium crude. This could be attributed to the viscosity change for the LCO at a higher temperature being more drastic and tend to become more mobile. This would aid the demulsifier molecules to position themselves faster in the interface.²⁹ The change is not as drastic with MCO, but it also must be considered that the demulsifier also needs to compete with the presence of natural

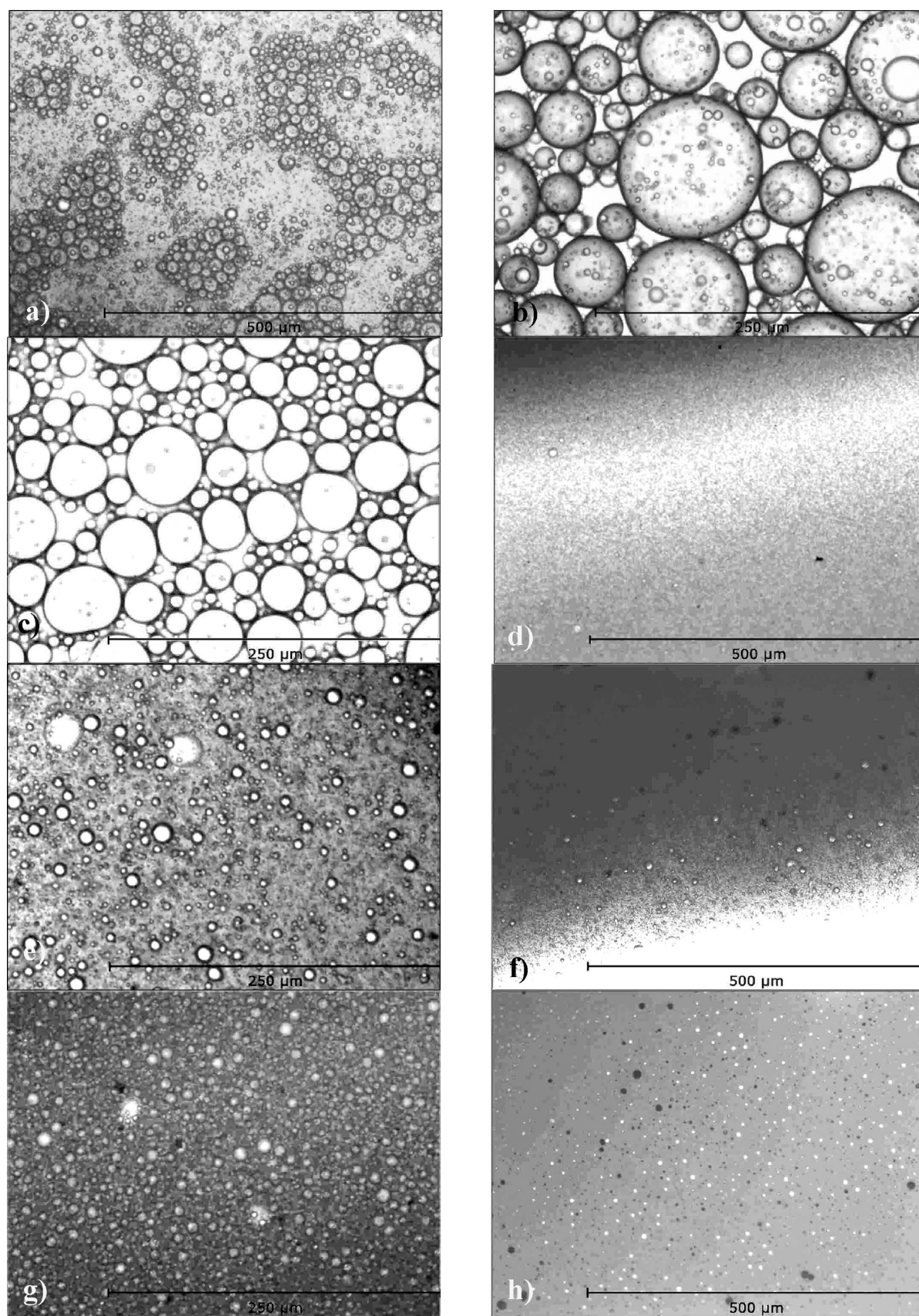


Figure 10. Micrographs of emulsion samples with CG/MCO (a) DIW/control, (b) DIW/1000 ppm, (c) 1NaCl/control, (d) 1NaCl/1000 ppm, (e) 7NaCl/control, (f) 7NaCl/1000 ppm, (g) 7PF/control, and (h) 7PF/1000 ppm.

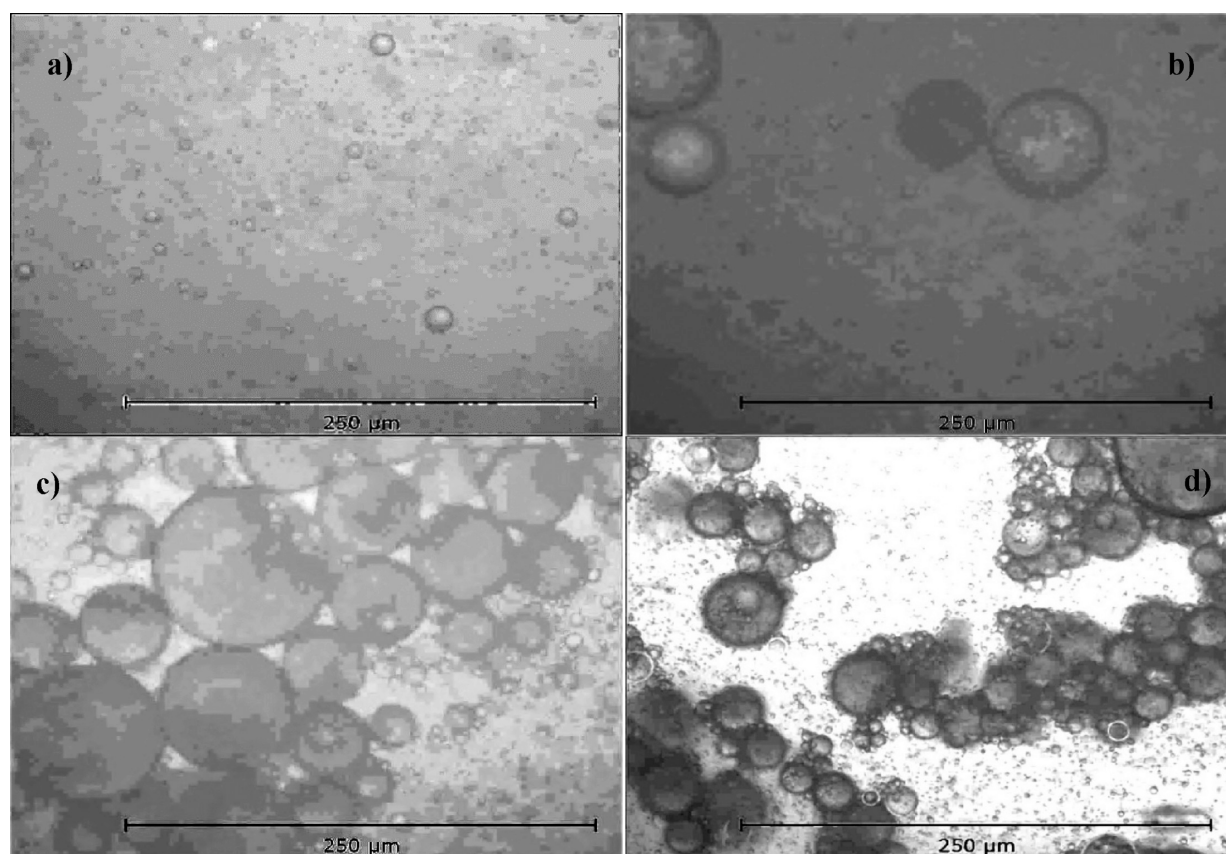


Figure 11. Micrographs with GZ/MCO emulsions with (a) control, (b) 250 ppm, (c) 500 ppm, and (d) 1000 ppm. Scale 250 μm .

surfactants as well as synthetic surfactants added to the emulsion phase.

3.2.2. CG. CG emulsions with MCO were investigated to determine whether current demulsifiers work on these emulsion phases (Figure 7 b).

As shown with AOS, CG had a similar response; the demulsifier is more effective in separating the emulsion produced when LCO is the oleic phase in comparison with MCO. The water separation of the control sample with DIW decreased from 74 to 63% with no oil removal when compared to the LCO emulsions. The application of demulsifier increased water demulsification by 12%, from 63 to 75%, and oil separation reached 38%. As it can be seen in Figure 10, there is a mixture of very small and considerably bigger droplets for both the control sample and the sample with 1000 ppm, with more prevalence in the latter, with the peak for the control on 30 μm and for the demulsifier sample on 120 μm (Supporting Information). This indicates that there is some destabilization in the emulsion phase; however, it is not sufficient to separate the phases completely.

An increase in salt concentration in conjunction with the demulsifier seems to have a good effect for CG emulsions with low salt concentration brines, as seen in Figure 7. Control samples appear to have a considerably good separation in the case of 1SF and 1NaCl, followed by 1PF. Water separation for the control samples ranged between 50 and 88%.

Emulsions made with NaCl were demonstrated to be considerably more unstable than those with the other two brines. Due to this, full separation was achieved with the highest concentration of the demulsifier in a minute and for the other two concentrations, in 35 min (Supporting

Information). This can be observed in Figure 10d, as there are just very few droplets observed on the right side of the image after separation, which can be considered as separated. Most of the droplets for this emulsion fall in the range of 3 to 80 μm with the peak on 50 μm . Emulsions with 1SF also appeared to be quite unstable, as they almost completely separated just with 2% water and oil left into the emulsion phase, which could be considered as full separation. However, these emulsions took longer time for the demulsification; at a 20 min mark, they were able to reach this state. Emulsions with 1PF were slightly more resilient to the process; it took 35 min for the water separation to reach 94% and 45 min for the oil separation to reach its maximum.

As with the LCO, the demulsifier seems to have a high impact on these low-salinity medium crude emulsions. It appears that CG is more easily replaceable in the interface by the polysorbate polyester, having a greater effect on the demulsification as the film is less firm tending to rupture and therefore coalesce.²⁹

Coco Glucoside emulsions with a higher salt concentration were tested, and the results can be observed in red in Figure 7b. Control samples for 7SF and 7NaCl had identical responses with water separation of 75%. In the case of 7PF, there was no water separation. The use of the demulsifier had no significant impact in the separation of these emulsions as the water separation increase only ranges between 2 and 10%, being the biggest increase for 7SF. In addition, the lowest demulsifier concentration appeared to be the most effective for 7SF. This response on the demulsification is considerably peculiar. CG emulsions, in comparison with AOS, at high salinity obtained less water removal. It is peculiar since

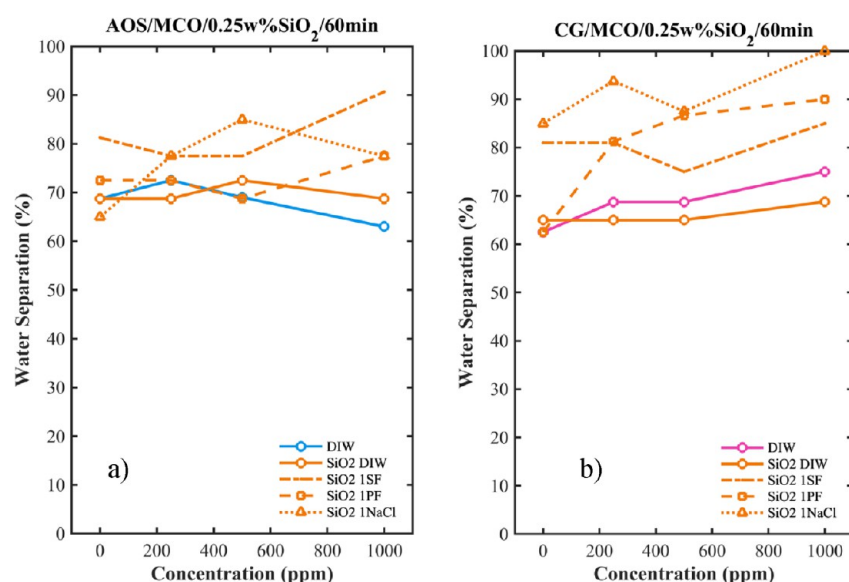


Figure 12. Demulsification of AOS (a) and CG (b) emulsions with medium crude oil and 0.25 wt % of SiO₂ nanoparticles with DIW and low-salinity brines.

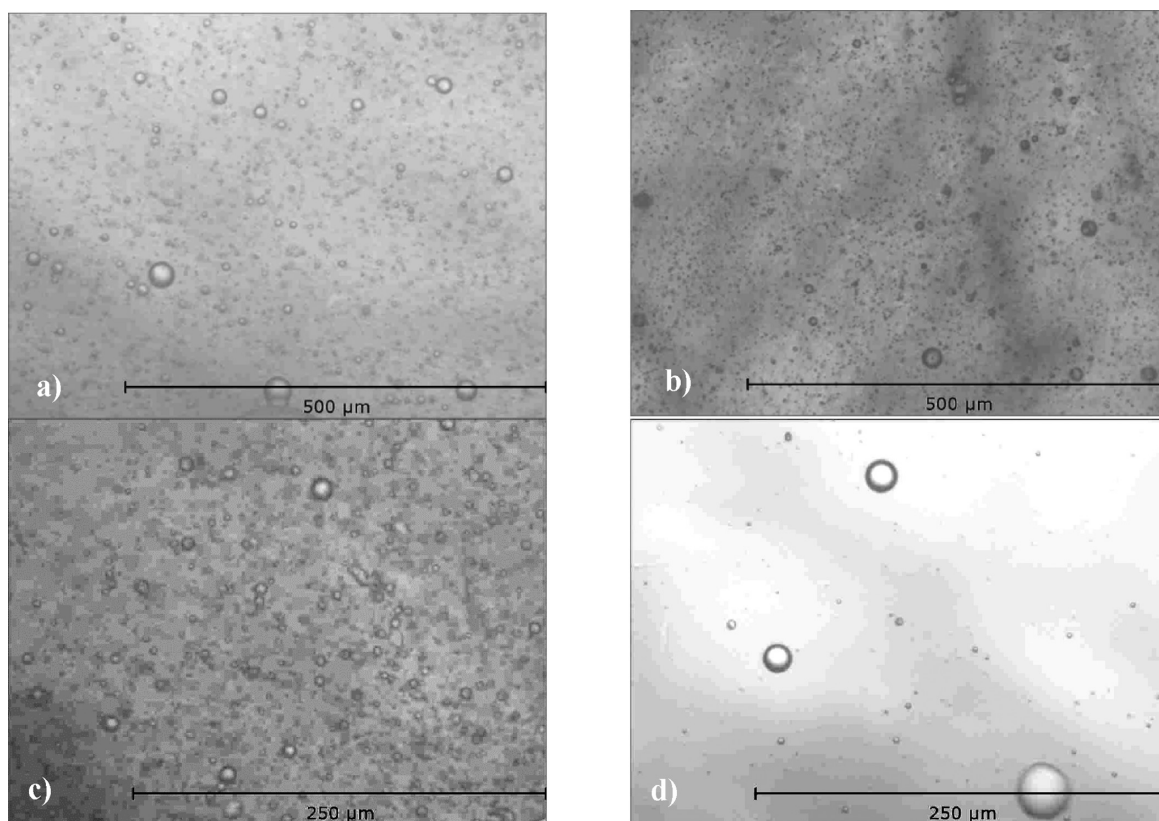


Figure 13. Micrographs of emulsion samples with AOS and MCO with 0.25 wt % SiO₂ nanoparticles: (a) DIW/control, (b) DIW/1000 ppm, (c) 1SF/control, and (d) 1SF/1000 ppm. Scale: 250 and 500.

emulsions with LCO at high salinity separated in a few minutes and emulsions with AOS presented more water separation under these conditions. This reaction for CG emulsions may be attributed to overdose, and in here, the demulsifier aided CG to make the emulsion more stable; therefore, the addition of the demulsifier is detrimental for separation. Another possible reason is that the demulsifier cannot compete with CG and thus being unable to substitute it at the rigid film, with

the addition having no effect on the separation. The last possible reaction could be that the demulsifier could not move as easier as in the LCO emulsion to reach the interface of all the droplets due to a difficulty in mobility that the increase in viscosity generates.

3.2.3. Greenzyme. In comparison with the LCO results, MCO presented a slightly higher water separation, with the control sample reaching 65%. The addition of demulsifier to

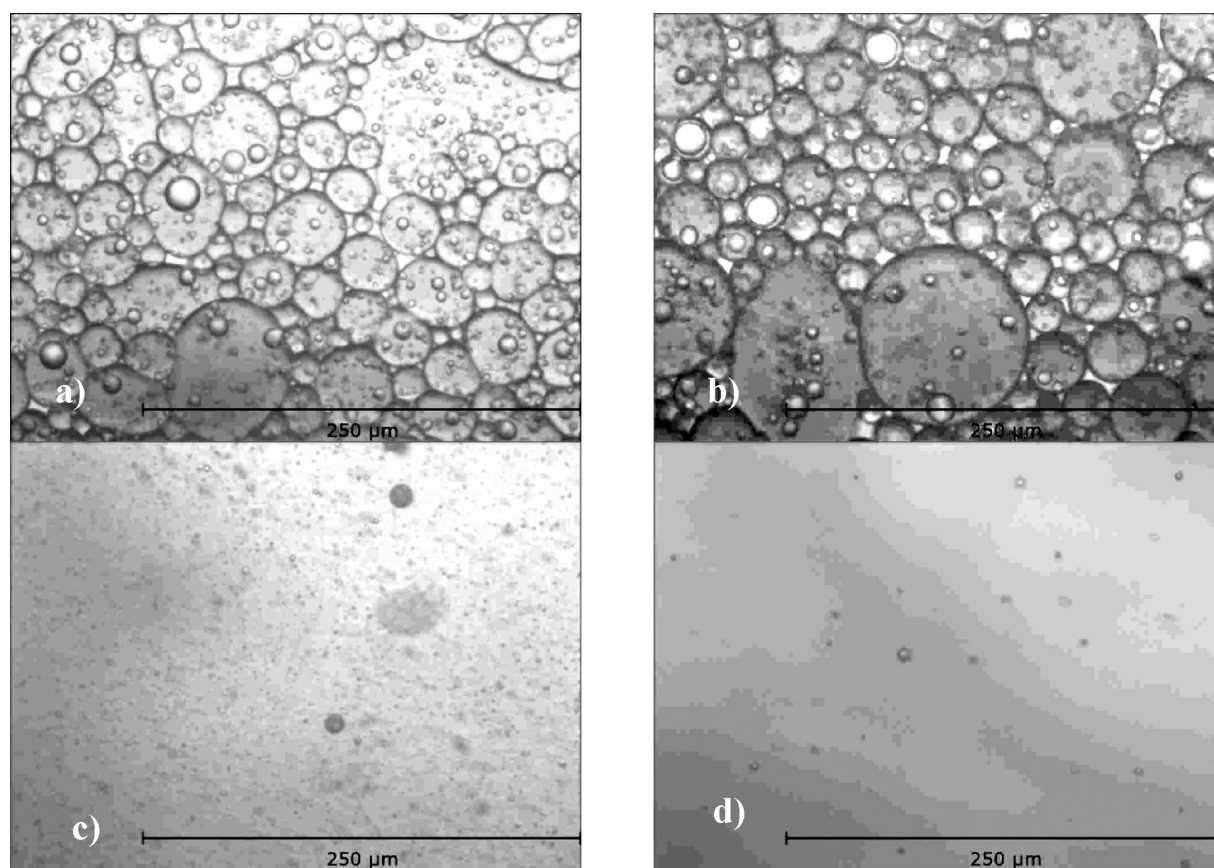


Figure 14. Micrographs of CG emulsions with MCO and 0.25 wt % of SiO₂ nanoparticles: (a) DIW/control, (b) DIW/1000 ppm, (c) 1NaCl/control, and (d) 1NaCl/1000 ppm. Scale 250 μm.

the sample had a better response, having an increase of 20% for the highest and second highest concentrations. Although no full separation was observed, polysorbate polyester presented a better response in comparison with AOS and CG. As GZ presents a higher interfacial tension when compared to the other two surfactants at the same conditions, it can be assumed that the surfactant is not sufficiently strong to properly emulsify the aqueous phase into a thicker oil phase presented by the MCO.

Analyzing the micrographs (Figure 11), it can be observed that the size is increasing as the concentration of the demulsifier was increased. Emulsions without the demulsifier present quite small droplets, indicating good stability. As soon as the concentration of the demulsifier is augmented, the droplets start to increase in size and also the separation between them is considerable. This instability is reflected in an increase in the level of water separation observed in Figure 7.

3.3. Effect of Demulsifier on Nanoparticle Emulsions.

Emulsions with MCO were also tested with DIW and low-salinity emulsions with the addition of positively charged (SiO₂) and negatively charged (Fe₃O₄) nanoparticles. Nanoparticle-containing emulsions present a different interaction with the surfactant; adsorption will occur between the surfactant and the liquid–liquid interface and the solid–liquid interface, obtaining a reduction in surface tension and solid–liquid interfacial energy, respectively.^{32,33} This interaction will be determined by the surface charge of the nanoparticle and the head charge of the surfactant. Only two of the surfactants were tested as salinity was involved, and GZ emulsions are not considerably stable.

3.3.1. Silica Nanoparticles. **3.3.1.1. AOS.** The demulsifier was tried with emulsions that combined SiO₂ nanoparticles and surfactant (Figure 12). The water demulsification for the control sample was the same as that without SiO₂ nanoparticles in the emulsion. However, the addition of demulsifier had just a slight increase reaching 73% with 500 ppm, which is double the concentration required for nonparticle emulsions to present a slim increase in separation. The addition of the nanoparticles had a slight impact on demulsification, doubling the concentration required to achieve an increase in water separation.

As can be observed in Figure 13, there is not much difference between the micrograph for the control sample and the one for the demulsifier at the highest concentration, confirming what was measured macroscopically. Both of them presented small droplet sizes with peaks at 10 and 40 μm as the analysis shows (Supporting Information), suggesting a very stable emulsion phase.

Silica nanoparticle emulsion samples were also tested with a small salinity increase (Figure 12). 1PF and 1NaCl control samples had a 15 and 10% reduction for water separation, respectively. 1SF had a 18% increase in water separation, when compared to the nonparticle emulsion sample. For the former, increasing the demulsifier concentration had a considerable effect only with the 1000 ppm concentration, which achieved a 91% water separation. Droplet occurrence decreased considerably with the highest demulsifier concentration, as observed in Figure 13. There is also a clear increase in droplet size, which doubled from 10 to 20 μm as shown in the droplet analysis (Supporting Information).

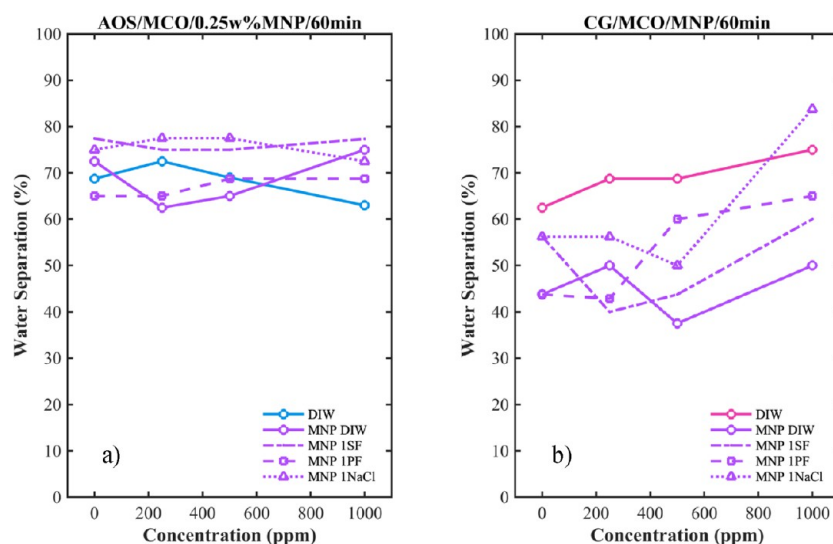


Figure 15. Demulsification of emulsions with medium crude oil and 0.25 wt % of Fe_3O_4 nanoparticles with DIW and low-salinity brines: (a) AOS and (b) CG.

For the 1PF emulsion, the demulsification is just minor with the addition of the demulsifying chemical, increasing it only by 5%.

The electrostatic attraction for the interactions between the SiO_2 nanoparticles and the surfactant can be considered unfavorable in this case as AOS is anionic (negatively charged) and the SiO_2 particles are also negative. Just as the charge dictates, they might not be attracted to each other; thus, the surfactant might not be fully adsorbed onto the nanoparticle surface, presenting just a minimum removal from the medium of the emulsion phase.³⁴ Overall, a slight decrease in the level of demulsification was observed for most of the emulsions tested. This response could be attributed to several reasons. The first thing to consider is the repulsion-assisted diffusion mechanism. Repulsive Coulomb interactions among surfactants and nanoparticles with the same charge will encourage surfactant diffusion to the liquid–liquid interface.³³ This might have as a result an increase in emulsion stability, as there would be more surfactant molecules at the interface, making the emulsion more difficult to separate. The second mechanism to consider is the NPs' ability to be adsorbed onto the droplet; this does not reduce the interfacial tension as with the surface active agents but creates a network on the droplets and therefore control coagulation, reducing the demulsification.³⁵

3.3.1.2. Coco Glucoside. Demulsification ability of the chemical demulsifier was also tested for the environmentally friendly surfactant, as recorded in Figure 12. Emulsion separation with DIW and MCO presented a separation very similar to that of the emulsions without SiO_2 NPs, with just a decrease of 6% overall in water separation. Micrographs from the DIW control sample and the highest demulsifier concentration can be observed in Figure 14a,b, and there is not a considerable difference between them. There is just a double on the size of droplets from 50 to 100 μm with a volume frequency of 50% (Supporting Information).

A minor increase in salt content still presented separation in emulsions even when there were nanoparticles present (Figure 12b). 1SF and 1NaCl emulsion control samples presented comparable water separation results between each other and between nonparticle emulsions. 1PF emulsions had a water release of around 20% less than the other two that registered

between 81 and 85%. The most unstable emulsion was 1NaCl, which obtained full separation at 15 min with the highest demulsifier concentration of 1000 ppm. Droplet sizes for the control sample were noticeably small with 10 μm at a 30% volume (Supporting Information). The addition of SiO_2 NPs therefore resulted in a time increase of 14 min to achieve the same separation with the same high concentration of the demulsifier compared to the emulsion without the presence of NPs. This time delay for demulsification effect also cascaded to the other two emulsions (Supporting Information). Performance for 500 and 1000 ppm does not present many differences, in which the optimal concentration for this brine would be 500 ppm. 1PF emulsion observed a better performance in water separation for the 1000 ppm, which aided in the release of 90% of the water content, having the same amount of oil demulsified. The biggest impact for these emulsions was observed for potassium formate, which had an increase of 27% for the water released and an increase of 90% for the oil separation. Overall, even when the demulsification followed the same trend as with the emulsions without NPs, the separation was to a lesser extent and the effect was more gradual. This slower reaction indicates that although a similar response was obtained, the presence of more surface-active species (nanoparticles added to the emulsion) at the interface made their displacement more difficult, hence the slower reaction of the demulsifier. When particles attach themselves to fluid interfaces, the interfacial dynamic resistance to changes in area increases and so does the emulsion stability.³⁶

The interaction is somewhat different when compared to AOS; this is due to the surface charges of the particle and the surfactant, which in this case is nonionic. Nonionic surfactants can be adsorbed onto SiO_2 NPs through the silanol groups present in the particle with hydrogen bonding.³⁶ With the demulsifier being a nonionic surfactant as well, it can also be attached to the particle by the same means as the emulsifier (Figure 18d). Emulsion stability might be increased by the presence of nanoparticle flocs that were induced by the nonionic surfactant, affecting the demulsification by slowing down creaming.

3.3.2. Magnetite Nanoparticle Emulsion. **3.3.2.1. AOS.** Emulsions in the presence of surfactant and magnetite

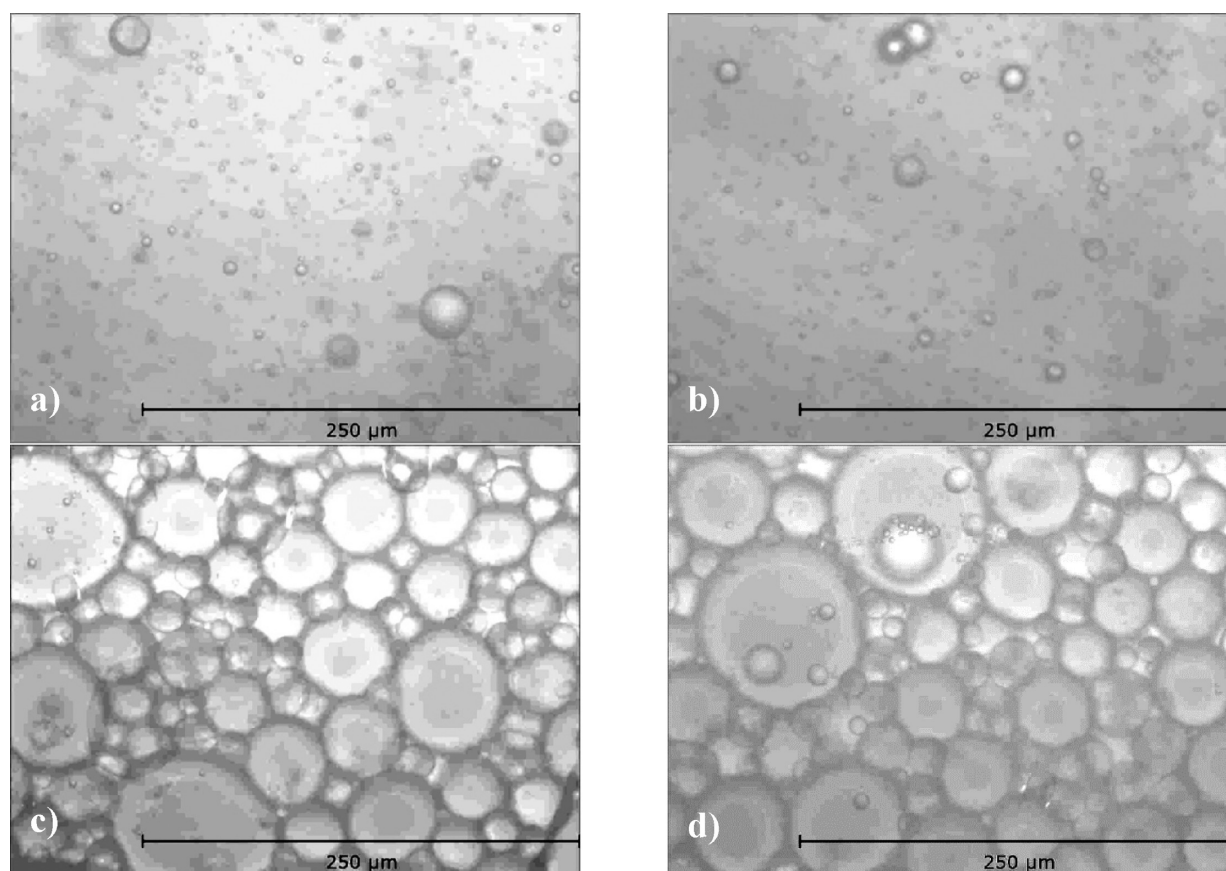


Figure 16. Micrographs of AOS emulsions with MCO and 0.25 wt % of Fe_3O_4 nanoparticles: (a) DIW/control, (b) DIW/1000 ppm, (c) 1NaCl/control, and (d) 1NaCl/1000 ppm. Scale 250 μm .

nanoparticles were tested with the same demulsifier. In the case of DIW (Figure 15), the blank sample presented a slight increase of 4% of water separation when compared to the blank sample without particles. The addition of the demulsifier between 250 and 500 ppm appears to be unfavorable, as there is a minor reduction in the water separation of about 10% until when the maximum concentration is tested that presents an oil separation of 12.5%. The addition of MNPs doubled the concentration for which the most water separation was observed in comparison to SiO_2 NP emulsions and quadrupled it when compared to the nonparticle emulsions. Yet, no full separation was achieved. If the control sample and the highest demulsifier concentration samples are compared on Figure 16, there is not that much difference in droplet size (Supporting Information).

Low salt concentration brines were tested, and water separation is alike when compared with the control samples without particle presence. Between all the brines tested, the water separation between the blank samples and the demulsifier containing samples has no significant difference. However, it is lower than the original samples with no particles and marginally lower when compared with the emulsions with SiO_2 NPs. As an example, 1NaCl emulsions presented droplet sizes that were slightly bigger than those observed for DIW as observed in Figure 16c and d with size ranging between 20 and 70 μm (Supporting Information) for the control and the highest demulsifier concentration, respectively. It could be assumed that the rest of the brines presented a similar response, as they had comparable water demulsification (Figure 17).

In contrast with the SiO_2 NPs, the MNPs present an electrostatic attraction to the surfactant present in the emulsion phase, as the MNPs are slightly positive and the surfactant is negatively charged (18c). This interfacial activity can redistribute the surfactant present at the interface through desorption and move the molecules onto the MNP surface. If the MNPs can stay at the interface, the diminishment of the interfacial area will support interfacial tension reduction.³³ The positioning of the MNPs at the interface would tend to stabilize the emulsion. The very small separation that was achieved with the demulsifier might be due to the fact that it was not only a surfactant at the interface but also MNPs, in which the combination appears to be more difficult to demulsify. With the demulsifier being a nonionic surfactant, it represents a more challenging substitution of the AOS surfactant from the surface of the nanoparticle.

3.3.2.2. Coco Glucoside. MCO emulsions with DIW and CG in the presence of Fe_3O_4 nanoparticles presented a considerable water and oil separation reduction (Figure 15), in comparison with emulsions without NPs and with emulsions containing SiO_2 NPs.

The water demulsification for the blank sample was reduced in about 20% when compared with the nonparticle-carrying and the SiO_2 particle emulsions. Oil separation was the same with 0%. The demulsification for these emulsion systems was nonparticle systems > SiO_2 NPs > MNP emulsions. Water removal for the samples with the demulsifier was also reduced between 25 and 38% depending on the demulsifier concentration related to the nonparticle emulsions. When contrasted to the SiO_2 emulsions, the reduction was fairly less,

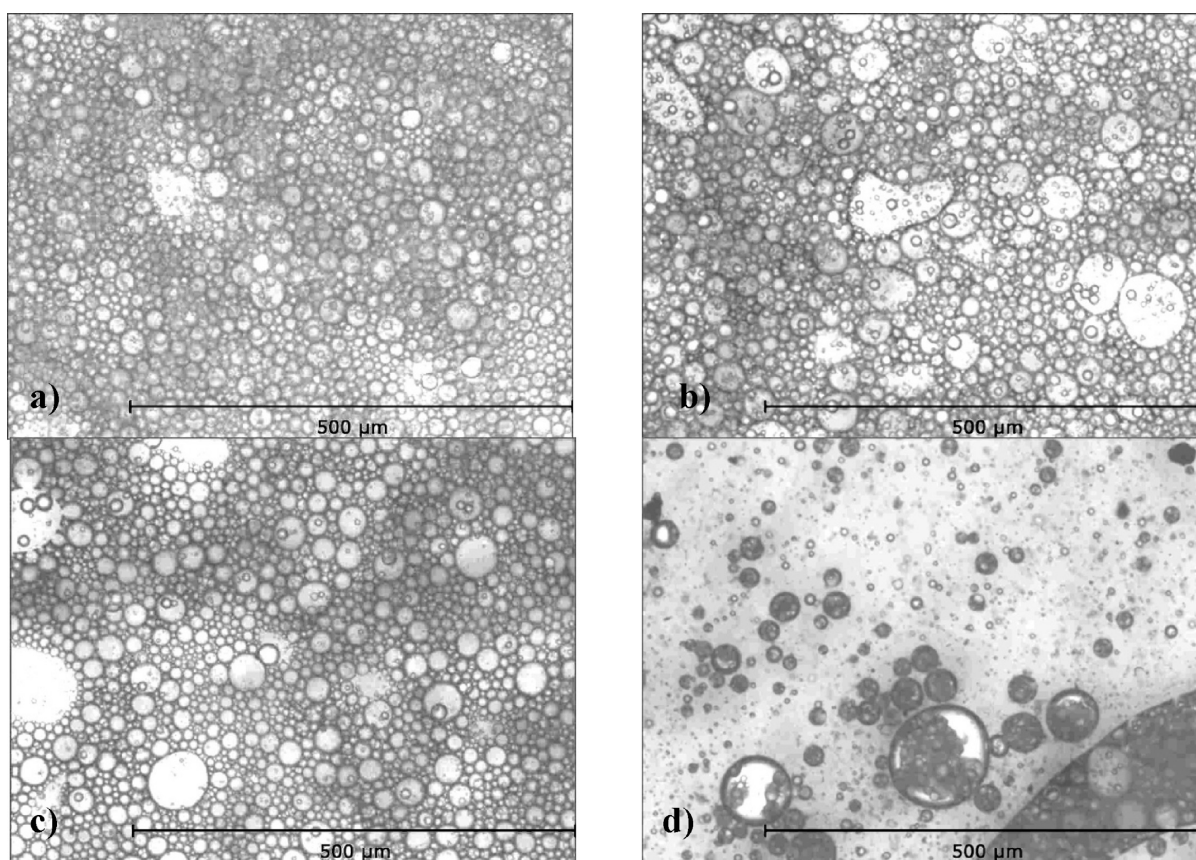


Figure 17. Micrographs of CG emulsions with MCO and 0.25 wt % of Fe_3O_4 nanoparticles: (a) DIW/control, (b) DIW/1000 ppm, (c) 1NaCl/control, and (d) 1NaCl/1000 ppm. Scale 500 μm .

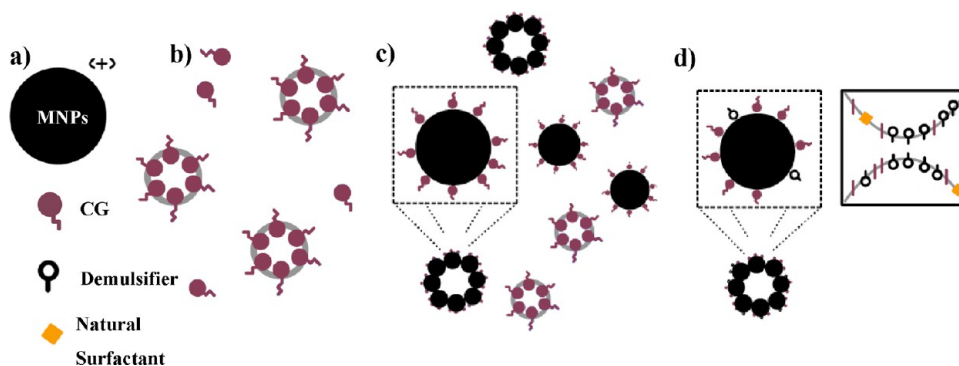


Figure 18. Magnetite nanoparticle interactions. (a) Interfacial active species, magnetite nanoparticles, CG, demulsifier, and natural surfactants. (b) Surfactant-based emulsion. (c) Addition of MNPs to the surfactant-based emulsion system, the surfactant adsorbed onto the surface, and presence of nanoparticle-adsorbed droplets. (d) Interaction of demulsifier in the presence of the rest of the surface-active species.

between 19 and 31%. From the micrographs in Figure 17, it can be determined that the demulsifier did not have a considerable impact on the DIW samples, which correlates with what was obtained for the water separation process. These emulsions presented droplet sizes of 20 μm (Supporting Information), lowering the incidence of 8% for the demulsifier sample when compared.

This type of emulsion was also tested with a minor increase in salt content, and the results are observed in Figure 15. The demulsification obtained for 1PF control was reduced by 6% just by the presence of MNPs. Overall demulsification with polysorbate polyester at the maximum concentration was considerably reduced in about 30%. 1SF had an equal response

as the emulsion with SiO_2 , with a decrease of 30% in comparison with the nonparticle control. Blank samples with 1SF and 1NaCl presented the same water separation, and just 1PF showed a lower separation. In contrast with the nonparticle emulsion and SiO_2 NPs, 1NaCl did not present a full phase demulsification for MNP emulsion. However, it was still the highest level of demulsification achieved. These samples presented droplet size and arrangement similar to the ones observed in DIW; however, there is a drastic change present for the demulsifier sample. Droplets are more spaced out, and they also reached bigger sizes of 120 μm (Supporting Information). For the sample with the highest demulsifier concentration, the droplets appear to have nanoparticles inside

and also surrounding the droplet, indicating that the particles are more reactive to this surfactant as this was not observed for AOS. The reaction time for water separation was definitely slower for all of the brines tested as maximum separation was observed between 35 and 55 min. Generally, the demulsification seen was in smaller quantities than that for the other two emulsion samples.

Considerably more stable emulsions are obtained in the presence of MNPs. The interaction between the MNPs that are positive and the nonionic surfactant appears to be stronger than that obtained for SiO₂ NPs; this might facilitate the creation of nanoparticle aggregation stabilizing the emulsion via particles as well as surfactant (Figure 18). The nonionic polysorbate is able to destabilize the emulsion while it partially substitutes the surfactant from the interface and on the particle surface. Hence, separating water and oil from the emulsion phase is not to a high extent.

4. CONCLUSIONS

The effectiveness of demulsifiers is influenced by a range of variables explored within this study, including oil type, surfactant type, salt concentration, and particle presence. Overall, superior separation efficiency was observed for LCO emulsions when compared to that of MCO. This difference could be attributed to temperature effects on viscosity, promoting an enhanced coalescence rate due to increased mobility and vibration within the phases. The stability of LCO emulsions with AOS and GZ was comparable, whereas CG exhibited slightly lower stability. Therefore, the displacement of AOS and GZ from the interface appears to be more difficult for the polysorbate polyester. It becomes evident that there is affinity between similar agents, where like removes like. LCO emulsions with the surfactants tested will tend to separate completely after a few minutes with a high salt content in the water phase and the application of temperature; therefore, the use of demulsifiers for these compositions is not recommended. Yet, more salt would be needed to obtain this effect for the ionic surfactant. It is evident that the stability or instability of the emulsion depends highly on the composition of the oil phase. The use of environmentally friendly surfactants is recommended. They exhibit an inclination to produce emulsions if it is required, but also a lesser amount of demulsifier would be needed if separation is necessary for further operations. For AOS/MCO SiO₂, the addition of nanoparticles doubles the demulsifier concentration to achieve an excess of water separation further than the control sample. The addition of MNPs to the same emulsion quadrupled the demulsifier concentration to attain water removal. Generally, nanoparticle addition slightly diminished the separation efficiency by around 10%. Emulsions with CG and SiO₂ NPs displayed comparable demulsification to nonparticle emulsions, although at a slightly slower rate. Meanwhile, MNPs lead to a stronger emulsification effect, reducing water removal by 20% when compared with nonparticle and SiO₂ NP emulsions. Electrostatic attraction or hydrogen bonding tends to govern the interactions between particles and surfactants and significantly depend on their respective charges. Fe₃O₄ had more impact on the emulsification ability than SiO₂ nanoparticles, which had a better affinity to the surfactants tested. Hence, when using these combinations in the industry, one should look for the charges of every component/chemical used in the mixture. The effectiveness of the demulsifier would largely rely on its capacity to compete with pre-existing surface

active species attached to the interface, as in these cases there are some compositions, surfactants, and nanoparticles, which interact with each other and could increase the emulsion stability and therefore make the demulsifier application.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.3c01677>.

Calibration curves on the GC-FID and the refractometer; specific graphs detailing the droplet size analysis of the emulsions tested; plots showing the demulsification against time; and the specifics on the emulsions tested (PDF)

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Notes

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