18th Brazilian Congress of Thermal Sciences and Engineering
November 16-20, 2020 (Online)

ENC-2020-0275
STABILITY AND INJECTIVITY OF OIL-IN-WATER EMULSIONS STABILIZED BY STEARIC ACID AS NATURAL LIPOPHILIC SURFACTANT

Alandmara Rosa Dionizio Leôncio[1]
Rafael Valladares de Almeida[2]
Ranena Verónica Ponce Flores[1]
Márcio da Silveira Carvalho[1]
Mechanical Engineering Department, Pontifícia Universidade Católica do Rio de Janeiro, RJ 22451-900, Brazil[1]
Repsol - Sinopec of Brazil[2]
e-mails: alandmaradionizio@gmail.com; rafael.valladares@repsolsinopec.com; poncerv@puc-rio.br; msc@puc-rio.br

Abstract. *Stable emulsions are often formed in almost all phases of crude-oil production due to the presence of natural crude oil surfactants, such as asphaltenes, resins, oil-soluble organic acids, solids, and waxes. These molecules stabilize the oil-water interface through chemical interaction between them and other species in the water phase forming a resistant interfacial film. This work aims to study the formation and stability of emulsions stabilized by a fatty acid as natural surfactants in an oil-water model system, under ambient and high-pressure conditions, and their flow behavior through injectivity tests in sandstones. To this end, the study of emulsion stability and interfacial rheology analysis was performed by evaluating the droplet size distribution (DSD) and interfacial viscoelastic modulus as a function of the surfactant concentration, aqueous composition, and flow conditions. In the rheological tests, results showed that the presence of the fatty acid in the oil phase promoted a reduction in the oil-water interfacial tension (IFT) and elastic modulus larger than the viscous modulus, evidencing important surface activity. All emulsions formed with a buffer solution without salts were stable under ambient conditions. During emulsion injection in single-phase flow, water mobility control was observed through the reduction of the absolute permeability as a strong function of emulsion DSD and capillary number (Ca).*

Keywords: *Natural surfactants, Oil-in-water emulsions, Emulsion stability, Interfacial rheology, Injectivity tests.*

1. INTRODUCTION

Emulsions can be encountered in almost all stages of oil production, transportation, and processing, due to the presence of natural surfactants that occur in crude oil containing higher boiling fractions, such as asphaltenes, resins, organic acids, and bases (Kokal *et al.*, 2005; Goual, 2012). Oil is present as a dispersed phase in a large amount of produced water, and this water containing oil droplets can be re-injected into the reservoir as an Enhanced Oil Recovery (EOR) method. The increase in produced water affects oil production in Brazilian fields, resulting in technological investments to reduce related problems, such as in the Pampo Field in the southern Campos Basin (Ueta *et al.*, 2008), and the Pré-Sal in Santos Basin. Since produced water contains hazardous pollutants, it needs to be handled and fulfill high-quality standards before being discharged to the environment. Treatment before the disposal of such huge volumes is mandatory and costs the oil industry billions of dollars annually, otherwise, penalties might be charged, as occurred in 2018 on the Campos Basin platforms (SPE, 2011; G1, 2018).

Laboratory and pilot tests have shown the potential of emulsion injection as one of the most promising EOR methods. Sandpack flooding tests have shown that more than 15% of the remaining oil can be recovered by emulsion flooding in comparison to the water flooding (Mandal *et al.*, 2010). McAuliffe *et al.* (1973b) observed a reduction in core permeability during injection of crude oil-in-water (O/W) emulsions prepared with dilute solutions of sodium hydroxide. Experimental results in different outcrop sandstone cores showed that this reduction strongly depends on the drop-to-pore size ratio. When this ratio is lower than 1, very small droplets may pass through the pore throat without blockage and, if this ratio is higher than one, the droplets need to warp, thus occurring the Jamin effect and may or may not block the pores. A field test was reported by the same author (McAuliffe *et al.*, 1973a) at Midway Sunset Oilfield, California. A total of 33,000 bbl emulsion bank (14 % oil content) was injected in this area and, among the results, a decreased fingering and improved volumetric sweep efficiency were observed, supported by a reduction of the water production and salinity, as well as reduction of the rock permeability. Additional oil recovery was estimated in 55,000 bbl indicating positive responses to emulsion flooding which was attributed to the improvement of the reservoir heterogeneity by the oil droplets that blocked high reservoir permeability zones. Emulsion flooding results in an enhancement in oil recovery factor (RF) due to many reasons such as reduced interfacial tension (IFT), modification of rock wettability (Alvarado *et al.*, 2014), modification of oil and water mobility, and flow diversion of the wetting phase to low permeability paths due to the blocking of previously swept areas (Zhou *et al.*, 2019).

Capillary forces are an important factor responsible for oil trapped and the Capillary number (Ca), representing the ratio between viscous forces and capillary forces, determines how strongly the trapped oil stays in a porous medium. At high Ca, viscous forces are stronger and the extra pressure needed to deform the drop as it flows through the constriction is negligible. At small Ca, the capillary forces are more important and, consequently, it is more difficult to deform the droplet, leading to a strong mobility reduction. Cobos *et al.* (2009) and Guillen *et al.* (2012) proposed a model to describe this behavior at pore scale through a mobility reduction factor f, defined as the ratio of the average pressure measured during continuous phase flow, Δp_c, to that of the emulsion flow, Δp_e. For emulsion with drops smaller than the constriction, $f \sim 1$ and it is not a function of the Ca. On the other hand, when the size of the drops has the same order as the throat size or higher, f strongly depended on the Ca. At high Ca, $f \to 1$.

Emulsion stability influences the emulsion performance in porous media since drop breakup or coalescence leads to changes in the drop size distribution. It is closely related to the molecular structure of the surfactant and the aggregation and coalescence of the emulsion drop must be avoided. Several experimental works in the literature, such as the one presented by Engelke *et al.* (2013), have been performed by adding water-soluble synthetic surfactants in water to decrease IFT and stabilize the injected emulsion. Exploring the presence and behavior of naturally occurring surfactants is key for using produced water containing crude oil emulsions as an EOR method, without the need to add other chemicals or minimize the cost of necessary chemicals.

Emulsion stabilization by crude-oil natural surfactants occurs by the migration of the surface active molecules from the bulk to the oil-water interface, creating a film that reduces IFT and avoids or delay droplet coalescence. This can lead to stabilized interfaces and emulsion stability. Among these crude oil natural surfactants, there are acidic molecules, including naphthenic acids, that can ionize at the oil-water interface to form the acid anion and dramatically reduce IFT. Asphaltenes are the heaviest compounds in the crude oil account for a variety of polar groups and contribute to stabilizing water in crude oil emulsions by forming a high mechanical rigid film at the oil/water interfaces (Abdel-Raouf, 2012; Perles *et al.*, 2018). Together with resins, asphaltenes form an interfacial film and delay the droplets coalescence (Perles *et al.*, 2018), and asphaltene and stearic acid molecules compete for the adsorption sites at the interface (Sauerer *et al.*, 2018).

Brandal *et al.* (2005) have reported that the pH and composition of the injected water, such as salinity, have a major influence on emulsion stability. Soares (2017) studied the interfacial rheology of emulsions prepared with organic acids as a natural surfactant (stearic acid and a commercially available mixture of naphthenic acid, both with carboxylic nature), representing the naphthenic acid present in crude oil. A mixture of hexadecane and toluene was used as an oil phase for different models of aqueous phases, such as deionized water, as well as a THAM (Tris(hydroxymethyl)aminomethane) buffer solution, both with and without monovalent and divalent salts. As result, the presence of salts and high pH in the aqueous phase increase the elastic interfacial modulus and its components.

The purpose of this work was to experimentally form O/W emulsions by intentionally choosing the oil and aqueous phases, in order to study ideal O/W emulsion systems stabilized by one of the natural oleic surfactants found in oil production processes. To stabilize the emulsions, stearic acid was selected as a lipophilic surfactant with characteristics similar to natural crude oil surfactants to simulate produced water with oil droplets. Stability of the emulsions was analyzed through the evolution of DSD and bottle tests. Properties of the drops interfacial film considering the effect of salinity, pH variation, temperature, and other parameters that influence the interface rheology were evaluated. Analyzes of the viscoelastic modulus as a function of surfactant concentration were investigated to understand the emulsion characteristics. Flow behavior of stable emulsions was studied through sandstone injectivity tests.

2. MATERIAL AND METHODS

2.1 Emulsion formation and stability

Stearic acid ($C_{18}H_{36}O_2$), a saturated carbon carboxylic acid, derived from animal and vegetable fats and oils, was chosen for this study as the acidic lipophilic surfactant model, due to its simple molecular structure and the fact that linear carboxylic fatty acids are preferably adsorbed on O/W interface than other naphthenic acids containing cyclic components (Wang *et al.*, 2017). It is a weak acid that dissociates little in an aqueous medium, therefore, there is more acid in the non-ionized form and it acts as a non-ionic surfactant. It was added to reduce IFT and maintain the emulsion stability, and studies were performed at 45°C (the temperature at which the stearic acid is fully dissolved in the oil phase) and ambient conditions.

Emulsions were prepared with 95% of aqueous phase and 5% of oil phase doped with different stearic acid concentrations. Two model oils were used as the oil phase. The first model oil was hexadecane ($C_{16}H_{34}$), with density and viscosity equal to ρ = 0.7699 g/cm^3, and μ = 3.0892 cP at 25°C, and ρ = 0.7563 g/cm^3, and μ = 1.7129 cP at 45°C, respectively. The second model oil was a 9:1 mixture of hexadecane and toluene (C_7H_8), with density and viscosity equal to ρ = 0.7768 g/cm^3, and μ = 3.0943 cP at 25°C, and ρ = 0.7651 g/cm^3, and μ = 1.8812 cP at 45°C, respectively. Different aqueous phase were used in the experiments: synthetic seawater prepared following ASTM standard (D1141-98 - Standard Practice for the Preparation of Substitute Ocean Water); Milli-Q water; a buffer to maintain a basic pH of the aqueous solution; and a mixture of the buffer and NaCl (24530 ppm). The buffer solution was prepared with THAM base and HCl (hydrochloric acid) to adjust the pH value. THAM is considered a weak base ($R-NH_2$), and in the presence of acid (HCl) reacts as $(CH_2OH)_3C-NH_2+HCl \rightleftharpoons (CH_2OH)_3C-NH_3^{+}+Cl^{-}$, with a buffering capacity between 7 and 9 at 25°C.

At each test, 100 ml of emulsion was prepared by homogenizing the fluids with an Ultra Turrax T-25. Agitation time and speed were chosen to form emulsions with uniform appearance and without the presence of free water or oil at the end of agitation. Dilution tests were realized in order to identify the type of emulsion and emulsion stability was studied by monitoring oil film formation over a certain period of aging through bottle tests and by analyzing the evolution over time of the DSD, obtained using the drop size analyzer MASTERSIZER 2000 (Malvern). This equipment provides some statistical parameters of the diameter measurements (D-values), among them the median d(0.5) and d(0.9) representing the diameters of which 50% and 90% of the drop population (total volume) has a diameter smaller than this value, respectively.

2.2 Interfacial properties

To investigate the performance of the stearic acid as a surfactant, as well as the resulting interfacial viscoelastic properties, interfacial properties were studied by using a TRACKER (Teclis) and a DCAT 25 (DataPhysics) tensiometers. Dynamic oscillatory tests to estimate the total dilatation modulus (ϵ), the elastic dilatation modulus (ϵ') and the viscous dilatation module (ϵ"), were performed using the TRACKER (Teclis). IFT between both phases (oil and water) was measured by the DCAT 25 tensiometer using a Wilhelmy plate.

2.3 Core Flooding tests

The cores used in the Core Flooding tests were sedimentary outcrops belonging to the Bentheimer formation, composed predominantly of quartz, with approximately 3.8 cm in diameter, 10 cm in length, 0.23 of porosity, 26.5 ml of rock pore volume, 2500 mili-Darcy (mD) of permeability to N_2 injection, and an average pore diameter of 3.5 μm, estimated by mercury intrusion porosimetry (Palombo, 2017). The device used in the experiments is a Core Flooding System (CFS) available at the Laboratory of Microhydrodynamics and Flow in Porous Media (LMMP) at PUC-Rio, and its simplified scheme is illustrated in Fig. 1.

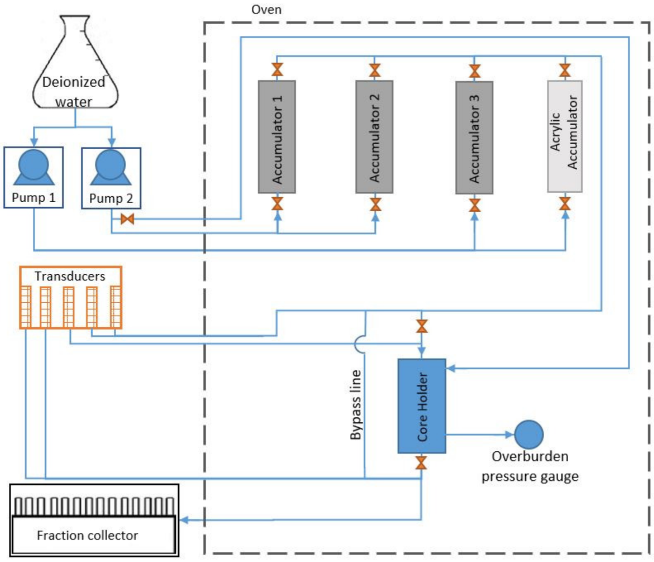


Figure 1. Core Flooding Experimental Apparatus Scheme.

The rock sample was inserted into the core holder and 3600 psi was applied as overburden pressure at room temperature (≈24°C). The systems have accumulators for work fluid and emulsion injection, a Gilson - FC 204 fraction collector used to collect volumes of fluids produced as a function of time, two pumps responsible for injecting fluids into accumulators and overburden pressure, pressure transducers to measure pressure differentials (dP), and a computer for acquisition and storage of data. For each core used, the dP was recorded during aqueous phase injection at different flow rates (q), and the absolute permeability (k) was determined according to

Darcy's law, from the slope of the linear correlation of q versus dP experimental data. The injectivity test consisted of injecting the continuous emulsion phase, followed by the emulsion, to compares the differential pressure response of both fluids for selected flow rates and, subsequently evaluate the flow behavior of emulsion injection. The flow rates adopted varied from 0.2 to 3 ml/min, and a total of $\approx$2 porous volume (V_p) of the fluid were injected for each flow rate. Permeability lost due to emulsion blockage was evaluated by re-injection of the emulsion continuous phase after emulsion injection.

3. RESULTS

3.1 Emulsion stability and interfacial properties

Table 1 presents the stability results from bottle and dilution tests obtained for the model systems studied by varying emulsification parameters such as aqueous phase, oil phase, stearic acid (SA) concentration, temperature (T), rotation speed (Speed), and mixing time (t).

Emulsions	Oil phase	Water phase	SA (% wt/v)	T [°C]	Speed [rpm]	t [min]	Emulsion formed	Stability study	Emulsion type
EM_01	HD	SSW	-	45	6500	2	No	-	-
EM_02	HD	SSW	0.5	45	6500	2	No	-	-
EM_03	HD	SSW	0.5	45	9000	5	No	-	-
EM_04	HD	SSW	0.5	45	24000	2	No	-	-
EM_05	HD	Milli-Q	0.5	45	10000	5	No	-	-
EM_06	HD	Milli-Q	0.5	45	8000	10	No	-	-
EM_07	HD	Milli-Q	0.5	45	10000	10	No	-	-
EM_08	HD + TL (9:1)	SSW	0.5	45	10000	10	Yes	1 hour	W/O
EM_09	HD + TL (9:1)	Buffer	0.5	≈24	10000	4	Yes	15 days	O/W
EM_10	HD + TL (9:1)	Buffer	1	≈24	10000	4	Yes	15 days	O/W
EM_11	HD + TL (9:1)	Buffer + NaCl	1	≈24	10000	4	No	-	-
EM_12	HD + TL (9:1)	Buffer + NaCl	1	45	10000	4	No	-	-
EM_13	HD + TL (9:1)	Buffer	1	≈24	20000	15	Yes	96 days	O/W

Table 1. Evaluation of emulsion formation and stability by varying model oil, water phase, stearic acid (SA) concentration, temperature (T), rotation speed (Speed), and mixing times (t). Hexadecane (HD); Toluene (TL); Synthetic seawater (SSW)

Dilatational interfacial rheology between synthetic seawater and hexadecane, and between Milli-Q water and hexadecane by varying stearic acid concentration at 45°C are present in Fig. 2 and 4, respectively. For both systems, an important decrease in IFT with the addition of the stearic acid was observed, and the water-oil interface in the surfactant presence developed a predominant elastic behavior. For the system with synthetic seawater, as the test goes forward, the droplet lost the Laplacian shape, as shown in Fig. 3. The IFT value was $\approx$10 mN/m (Fig. 2b) in the first 25 seconds of the test, suggesting rapid aging of the interface. After that, elastic and viscous modulus curves had irregular behavior, showing values of dilatational elasticity up to $\approx$400 mN/m and negative values of dilatational viscous modulus, as shown in Fig. 2d and 2f. The IFT reduction with synthetic seawater with 0 and 0.5% of stearic acid, was from 30 to $\approx$10 mN/m (considering the first point before the loss of the Laplacian shape) (Fig. 2a and 2b), stronger than that for Milli-Q water, from 34 to 28 mN/m (Fig. 4a), for the same stearic acid concentration. Both systems were unable to form emulsions. Salt addition decreases electrostatic repulsion between the head groups of the surfactant, interfering with interfacial behavior due to the competition of salt ions present in water with the polar part of the surfactant. In systems using salts, electrostatic forces keep the droplets stable and salts interfere with these mechanisms, leading to non-emulsion formation.

Results of the prepared emulsions (Tab. 1) showed that stearic acid form long-term stable emulsions of hexadecane and toluene (HD + TL) in salt-free buffer solution at $\approx$24°C. Dilatational interfacial measurements between buffer solution and 9:1 ratio of hexadecane and toluene doped with stearic acid at $\approx$24°C were not possible due to the droplet detached from the needle almost immediately after contact with the buffer solution, indicating that the IFT was too low. For this system, IFT was measured using the DCAT 25 tensiometer with different stearic acid concentrations, and a decrease in IFT with increasing stearic acid concentration was observed. The critical micellar concentration (CMC) for this model system was 0.30% (wt/v) of stearic acid corresponding to 3.2 mN/m IFT.

Stearic acid in an aqueous medium has a pH below 7. With the buffer presence, the pH goes to 8 and the weak acid equilibrium favors acid dissociation. Thus stearic acid behaves as an anionic surfactant. In addition, the dissociated stearic acid plus the ammonic compound THAM acts as a counter-ion. Accordingly, the buffer presence joining the polar part of the stearic acid enhances its solubility in the aqueous phase. This increases the stearic acid polar part in the aqueous phase, increasing its adsorption at the interface and favoring emulsions formation.

Figure 5 presents the microscopic analysis of EM_10 and EM_13 emulsions. Both emulsions were prepared with the same composition, however, due to the longer mixing time and speed, EM_13 was more mono-disperse with smaller

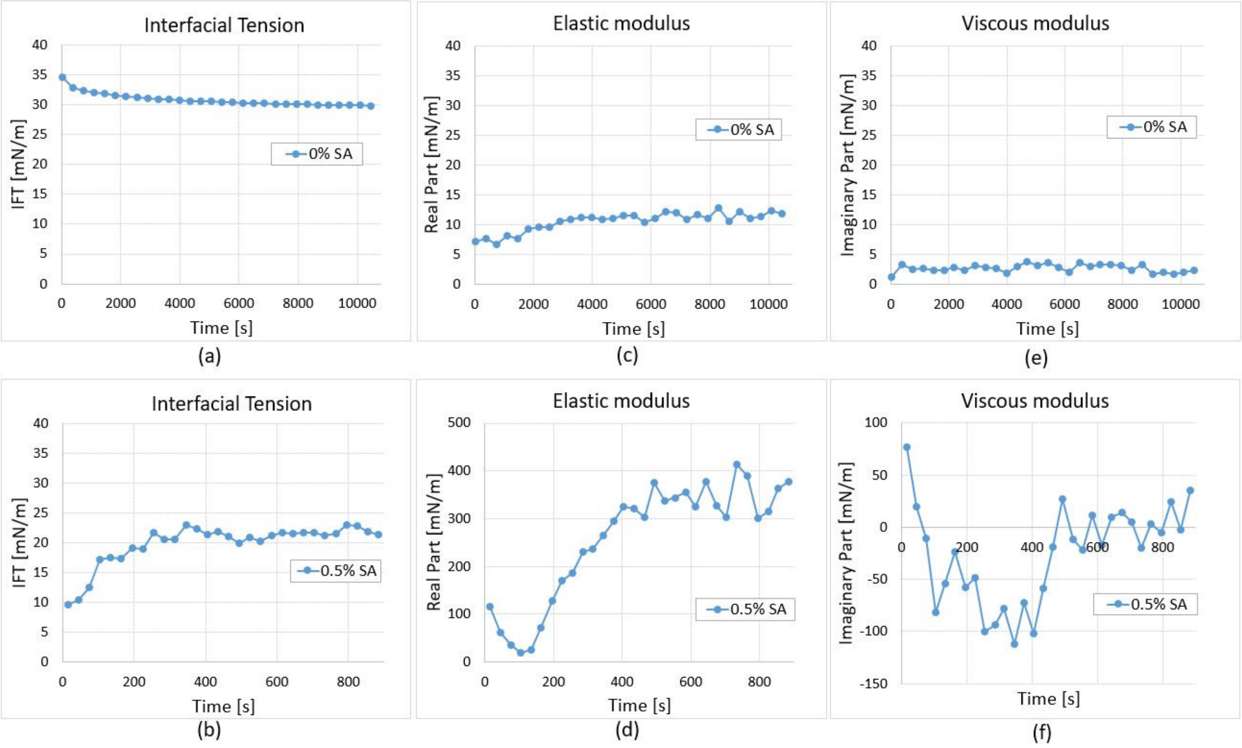


Figure 2. Dilatational interfacial rheology results at different stearic acid (SA) concentrations for the model system with hexadecane as the oil phase and synthetic seawater water as the water phase at 45°C: Interfacial tension (a) 0 %SA (b) 0.5 %SA; Elastic modulus (c) 0 %SA (d) 0.5 %SA; Viscous modulus (e) 0 %SA (f) 0.5 %SA.

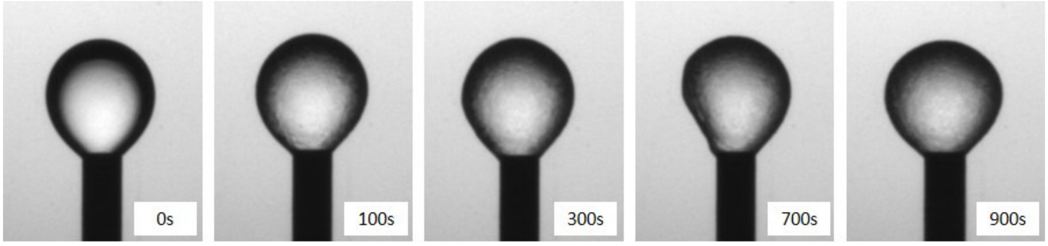


Figure 3. Drop shape per second (s) during dilatational interfacial rheology test on a drop of hexadecane doped with 0.5% (wt/v) of stearic acid and synthetic seawater as the bulk phase at 45°C.

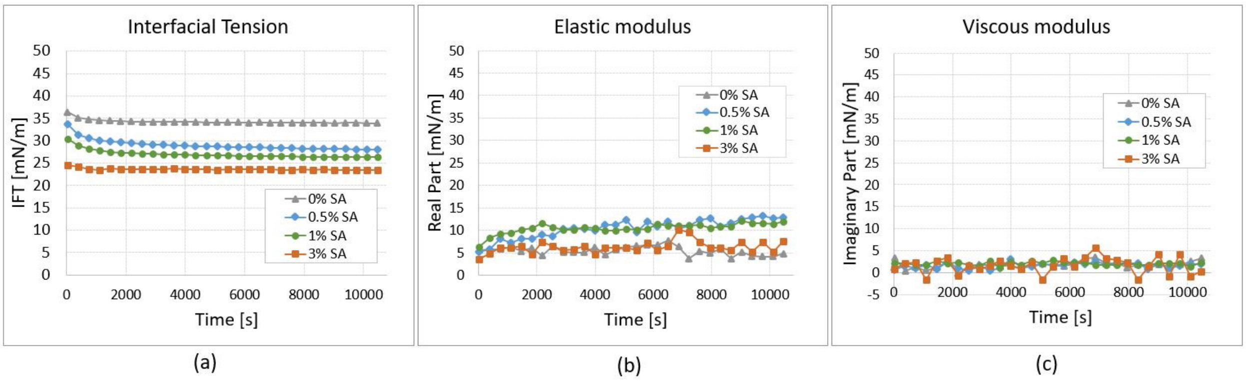
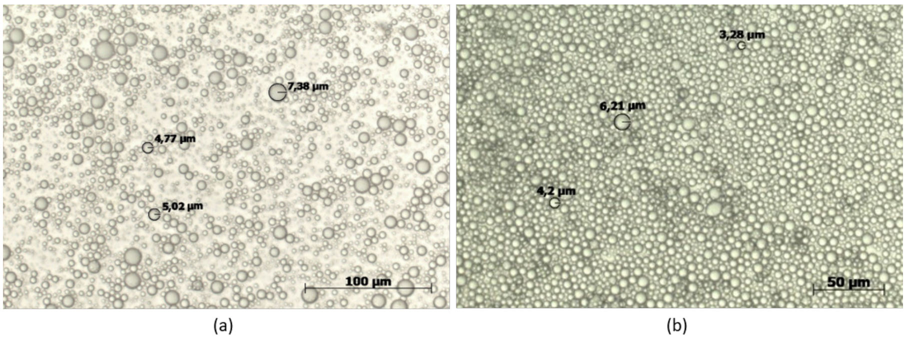


Figure 4. Dilatational interfacial rheology results at different stearic acid (SA) concentrations for the model system with hexadecane as the oil phase and Milli-Q as the water phase at 45°C: (a) Interfacial tension (b) Elastic modulus (c) Viscous modulus.

droplets than EM_10. Figures 6 and 7 show the DSD of EM_10 and EM_13 emulsions, respectively. The EM_10 emulsion DSD shows small variation over time, therefore, this emulsion was considered stable for the 15 days analyzed. The d(0.5) and d(0.9) values for EM_10 emulsion were 4.3 and 10.4 μm, respectively. According to the EM_13 emulsion

DSD, it was stable for the 96 days analyzed, in which the d(0.5) and d(0.9) values were 2.3 and 3.7 μm, respectively. None of the emulsions showed oil film formation over time through bottle test results. In addition, by the drop dilution method, both emulsions were O/W. Due to the stability of EM_10 and EM_13 emulsions, the model system and protocol for formulating them were selected to recreate these emulsions and use them in the injectivity tests.



(a)

(b)

Figure 5. Microscopic analysis of (a) EM_10 and (b) EM_13 emulsions - Model system: hexadecane + toluene (9:1) doped with 1% (wt/v) of stearic acid concentration and buffer solution.

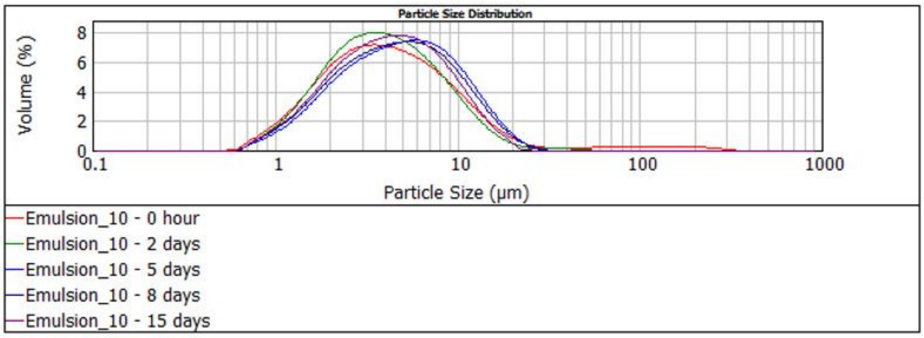


Figure 6. EM_10 emulsion DSD - Model system: hexadecane + toluene (9:1) doped with 1% (wt/v) of stearic acid concentration and buffer solution.

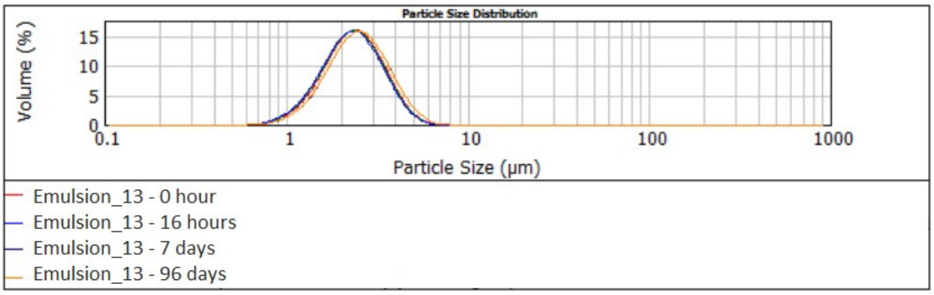
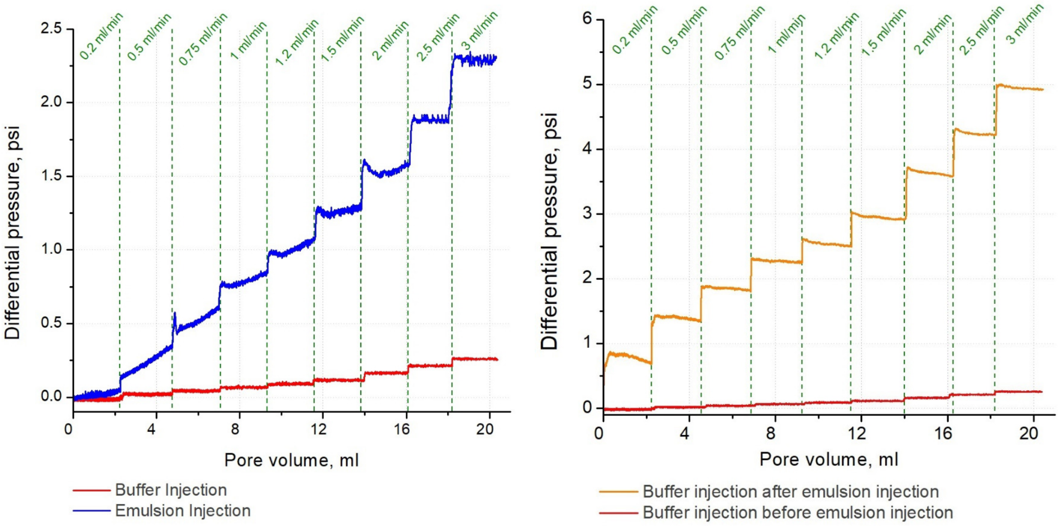


Figure 7. EM_13 emulsion DSD - Model system: hexadecane + toluene (9:1) doped with 1% (wt/v) of stearic acid concentration and buffer solution.

The system with a buffered saline solution as an aqueous phase (buffer + $NaCl$) was unable to form emulsions. Interactions between the ionized buffer and NaCl ions cause a decrease in the electric double layer at the droplet interface, leading to less repulsion between the surfactant heads at the interface, which means, more surfactant molecules will migrate from oil to the interface. So, the interfacial film will have more molecules compacted and there may be a very large reduction in surface area per molecule, decreasing the IFT. The coalescence process is accelerated and the interfacial film resistance falls, which may explain the non-formation of emulsions in the presence of salt.

3.2 1st Injectivity test

In the first injectivity test, EM_10 (EM_10a) emulsion was injected, which d(0.5) and d(0.9) values were 4.087 and 10.308 μm, respectively. Figure 8a compares the differential pressure response of buffer and emulsion injection for the selected flow rates. Unlike the behavior observed for buffer injection, it is possible to see an important increase in differential pressure during emulsion injection. At low flow rates, the pressure did not stabilize, which evidences drop filtration during emulsion injection. Figure 8b compares the differential pressure response during buffer injection before and after emulsion injection. The permeability to the aqueous phase injection (buffer) was recalculated by using Darcy's law after the emulsion injection and compared with the initial value to analyze the rock damage caused by emulsion injection. It changed from 2505.522 to 166.425 mD. The permeability reduction, in more than 93%, showed severe rock damage as a result of the clogging of the porous media by the emulsion drops.



(a) (b)

Figure 8. (a) Comparison of the differential pressure response during buffer and EM_10a emulsion injection (b) Comparison of the differential pressure response during buffer injection before and after EM_10a emulsion injection - 1st Injectivity test.

In order to check the drop break-up, retention, and percolation in the porous medium, the DSD of the emulsion effluent was compared with the original one, as showed in Fig. 9. For all flow rates, the DSD showed a multimodal distribution over time, which means that the curves begin to show a second distinct distribution and shift to the right compared to the emulsion before being injected, evidencing a coalescence process.

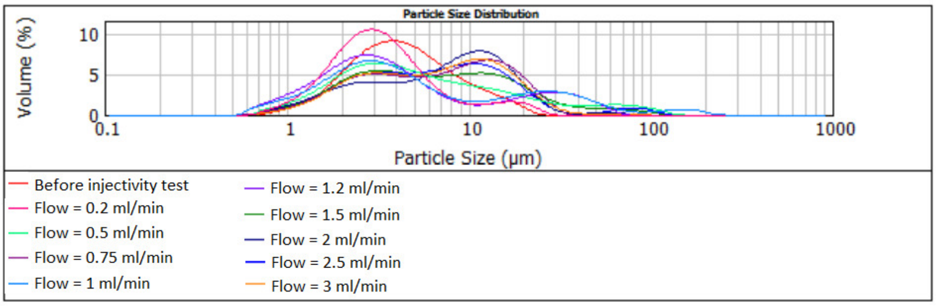


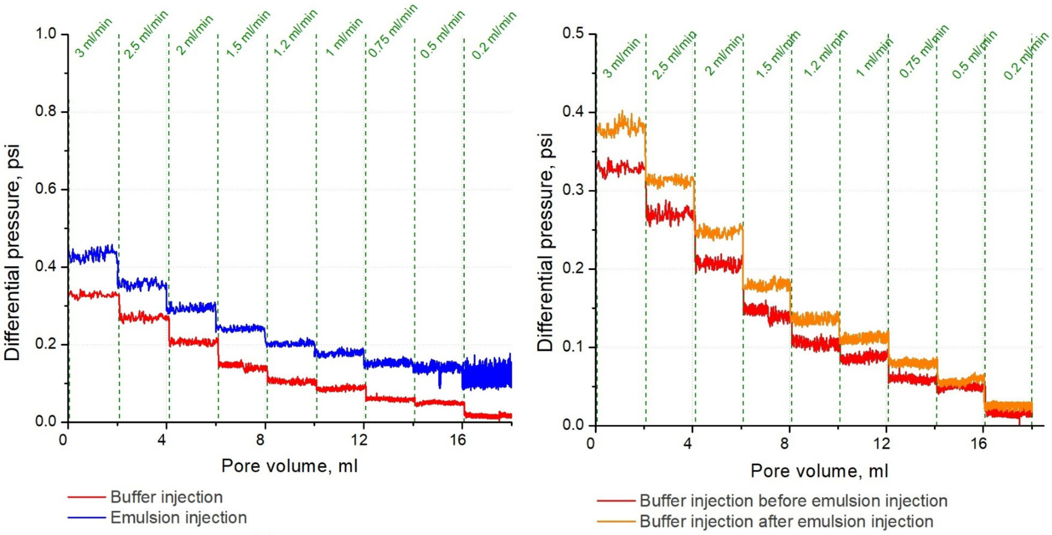
Figure 9. DSD of the EM_10a emulsion effluent - 1st Injectivity test.

To confirm the pressure response and the blocking behavior of the emulsion as function of the flow rate, this test was reproduced by varying the flow rates from highest to lowest values. It was noted that at the highest flow rate (3 ml/min) the pressure did not stabilize even after the injection of more than 40 V_p of emulsion, and similarly to the first test, there was more than 93% of permeability reduction after emulsion injection. Besides, at the end of the test, some residue was observed on the inlet end plug (flow distributor) and at the inlet face of the rock sample, containing emulsion drops and stearic acid crystals, indicating that the emulsion destabilized during the injection in the porous medium, and the interfacial film ruptured and the oil and water phases passed through the rock, leaving behind the surfactant. Since the injected emulsion is approximately three times larger than the pore throat diameter, at the operating conditions the interfacial film would not have sufficient elasticity to deform and cross the pore throat. In order, to study the pressure effect on the stability of the emulsion, the EM_10 (EM_10c) emulsion was recreated and subjected for 12 hours to $\approx$10 psi of pressure, and a reduction of the smaller droplet volume and increased population of larger drops were observed indicating the emulsion coalescence when submitted at higher pressures.

3.3 2nd Injectivity test

In the second injectivity test, EM_13 (EM_13a) emulsion was injected to evaluate the behavior of an emulsion with drop diameter in the same range as the average pore diameter of the rock. The d(0.5) was 2.367, and the d(0.9) was 3.768 μm, a little higher than the average pore diameter of the rock (3.5 μm). Figure 10a shows the evolution of differential pressure as function of the flow rate for buffer and emulsion injection. As expected, the emulsion pressure response was higher than that for the buffer injection. It can be noted that the pressure fluctuations for the emulsion increases with the reduction of the flow rate. As Ca decreases, capillary forces predominate and the droplets that formerly percolate the porous medium remain trapped. The differential pressure behavior during emulsion injection evidences this blockage. The large pressure oscillation shows that the drops block the pores and deform until they can proceed. According to Fig. 11, the experimental results were used to calculate the mobility reduction factor f as a function of Ca for emulsion injection, and for Ca above 1.5 x 10^{-8}, f stabilizes. This value corresponds to the critical Ca, and the dispersed phase of the emulsion blocks the porous medium only for Ca below this value.

Figure 10b shows the evolution of differential pressure as flow rate varies for buffer injection before and after EM_13a emulsion injection. Comparing the permeability before and after emulsion injection, a decrease from 2495.173 to 2156.208 mD ($\approx$16% of permeability reduction) was observed, a very low damage in comparison with the previous injectivity tests.



(a) (b)

Figure 10. (a) Comparison of the differential pressure response during buffer and EM_13a emulsion injection (b) Comparison of the differential pressure response during buffer injection before and after EM_13a emulsion injection - 2nd Injectivity test.

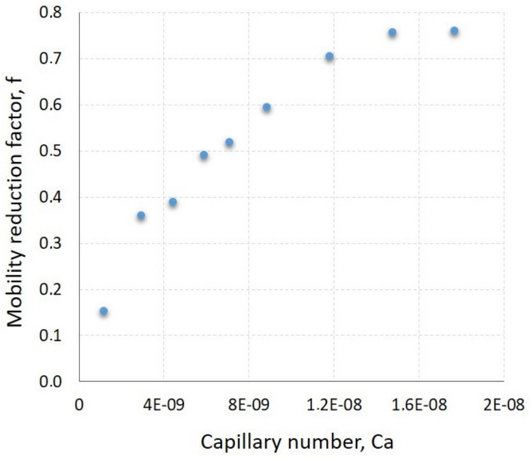


Figure 11. Mobility reduction factor f of EM_13a emulsion as a function of the capillary number.

Figure 12 presents the emulsion effluent DSD, and shows that no significant variation in the DSD curves was noted. At the end of the injectivity test, no residue was found in the inlet-end-plug and the inlet face of the rock sample. The EM_13 emulsion was recreated (EM_13b) and subjected to ≈10 psi of pressure during 12 hours, and no significant variation was observed, indicating that the emulsion remained stable during the test.

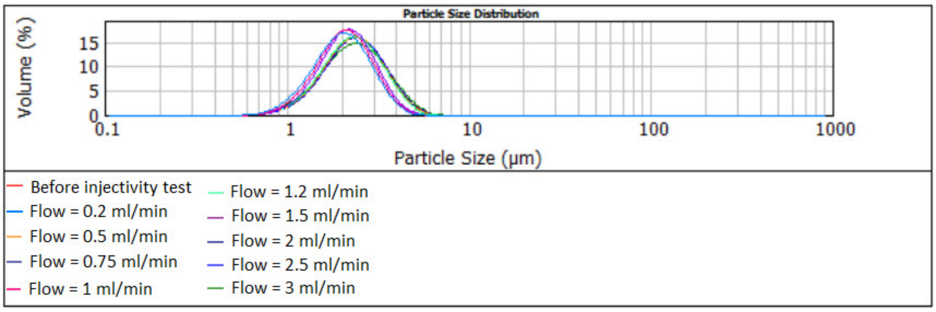


Figure 12. DSD of the EM_13a emulsion effluent - 2nd Injectivity test.

4. CONCLUSIONS

This work aimed to experimentally investigate the flow and stability of O/W emulsions stabilized by a fatty acid that mimics a lipophilic natural surfactant occurring in crude oils. Stearic acid was used to represent a natural surfactant. Stability of emulsions was analyzed through the evolution of drop size distribution (DSD), bottle tests, and interfacial rheology measurements for different model oil, water systems, surfactant concentration, and temperature.

In a system that contained hexadecane as the oil phase, stearic acid as the surfactant, synthetic seawater as the aqueous phase, and performed at 45°C, the stearic acid adsorbed on the interface and in presence of salts, a rigid and rough film with increasing aging time was formed. According to the dilatational interfacial rheology, stearic acid was able to reduce the IFT, and the dilatational visco-elastic modulus curves showed irregular behavior, with very high values of elastic modulus and very low values of viscous modulus. In the same system without salinity, the dilatational interfacial rheology results showed higher values of elastic modulus compared to the viscous modulus. Comparing both systems, the IFT reduction with synthetic seawater was larger than that for Milli-Q water for the same stearic acid concentration, hence the presence of salt leads to a stronger interfacial activity that destabilizes emulsions. In neither of both systems, stable emulsions were formed, which implies that the formation of an interfacial film does not necessarily promotes emulsion stabilization. In a buffer solution without salts as aqueous phase, and with a 9:1 ratio of hexadecane and toluene as the oil phase, the IFT decreased with stearic acid concentration, being the critical concentration CMC = 0.3% (wt/v). All emulsions formed with this system were very stable at room temperature (≈24°C). The presence of a monovalent salt in the buffer solution at room temperature (≈24°C) and 45°C did not form emulsions, so emulsion formation and stability are strongly related to the pH and salts presence in the water phase.

The flow behavior of stable emulsions was studied through emulsion flooding in sandstones through injectivity tests at room temperature (≈24°C). During emulsion injection in single-phase flow, water mobility control was observed through the reduction of the permeability to aqueous phase (buffer solution) injection as a strong function of emulsion drop size distribution (DSD) and Capillary number (Ca). The injectivity results of emulsions with particle size distribution (d(0.9)) larger than the average pore diameter of the porous media, showed permeability reduction, more than 93%, resulting in severe rock damage by the clogging of the porous media by the emulsion drops. The dispersed phase with a diameter larger than the average rock pore diameter was filtered through the porous medium, and differential pressure during emulsion injection did not stabilize and was higher compared to continuous phase injection. In addition, effluent analysis evidenced emulsion coalescence. In order to study the pressure effect on the emulsion stability, it was subjected to a pressure higher than the highest pressure recorded during the injectivity test, and coalescence was noted indicating that large drops do not resist the injection pressure.

The injection of an emulsion with particle size distribution (d(0.9)) in the same order as the average pore diameter of the porous media showed moderate rock damage (≈16% of permeability reduction), and during the test, the pressure fluctuations for the emulsion injection increases with the reduction of the flow rate. Large pressure oscillation indicates that the emulsion drops were blocking the pores and deforming until they can proceed toward the throats, evidencing emulsion mobility control effect. The mobility reduction factor f was calculated, and the results show that the emulsion blocks the porous medium for Ca below 1.5×10^{-8}.

The results obtained with the lipophilic natural surfactant had similar effects already observed in the literature for emulsions stabilized by water-soluble surfactants, showing big potential for the use of produced water containing crude oil emulsions as an Enhanced Oil Recovery (EOR), without the need for the addition of other chemicals.

5. ACKNOWLEDGEMENTS

The authors acknowledge the Coordination for the Improvement of Higher Education Personnel (CAPES), Repsol Sinopec of Brazil, and National Agency for Petroleum, Natural Gas and Biofuels (ANP) for financial support.

6. REFERENCES

Abdel-Raouf, M.E.S., 2012. “Factors affecting the stability of crude oil emulsions”. In *Crude oil emulsions-Composition stability and characterization*, IntechOpen.

Alvarado, V., Garcia-Olvera, G., Hoyer, P., Lehmann, T.E. *et al.*, 2014. “Impact of polar components on crude oil-water interfacial film formation: A mechanisms for low-salinity waterflooding”. In *SPE Annual Technical Conference and Exhibition*. Society of Petroleum Engineers.

Brandal, Ø., Hanneseth, A.M.D. and Sjöblom, J., 2005. “Interactions between synthetic and indigenous naphthenic acids and divalent cations across oil–water interfaces: effects of addition of oil-soluble non-ionic surfactants”. *Colloid and Polymer Science*, Vol. 284, No. 2, pp. 124–133.

Cobos, S., Carvalho, M. and Alvarado, V., 2009. “Flow of oil–water emulsions through a constricted capillary”. *International Journal of Multiphase Flow*, Vol. 35, No. 6, pp. 507–515.

Engelke, B., Carvalho, M.S. and Alvarado, V., 2013. “Conceptual darcy-scale model of oil displacement with macroemulsion”. *Energy & Fuels*, Vol. 27, No. 4, pp. 1967–1973. doi:10.1021/ef301429v. URL `https://doi.org/10.1021/ef301429v`.

G1, 2018. “Petrobras firma acordo com ibama para mudança no descarte de água das plataformas e pagará r$ 100 milhões para reparar danos”. URL `https://g1.globo.com/economia/noticia/petrobras-firma-acordo-com-ibama-para-mudanca-no-descarte-de-agua-das-plataformas-e-pagara-r-100-milhoes-para-reparar-danos.ghtml`.

Goual, L., 2012. “Petroleum asphaltenes”. In *Crude Oil Emulsions-Composition Stability and Characterization*, IntechOpen.

Guillen, V.R., Romero, M.I., da Silveira Carvalho, M. and Alvarado, V., 2012. “Capillary-driven mobility control in macro emulsion flow in porous media”. *International Journal of multiphase flow*, Vol. 43, pp. 62–65.

Kokal, S.L. *et al.*, 2005. “Crude oil emulsions: A state-of-the-art review”. *SPE Production & facilities*, Vol. 20, No. 01, pp. 5–13.

Mandal, A., Samanta, A., Bera, A. and Ojha, K., 2010. “Characterization of oil- water emulsion and its use in enhanced oil recovery”. *Industrial & engineering chemistry research*, Vol. 49, No. 24, pp. 12756–12761.

McAuliffe, C.D. *et al.*, 1973a. “Crude-oil-water emulsions to improve fluid flow in an oil reservoir”. *Journal of Petroleum Technology*, Vol. 25, No. 06, pp. 721–726.

McAuliffe, C.D. *et al.*, 1973b. “Oil-in-water emulsions and their flow properties in porous media”. *Journal of petroleum technology*, Vol. 25, No. 06, pp. 727–733.

Palombo, L., 2017. *A microtomografia de raios X e a porosimetria por intrusão de mercúrio na determinação de porosidade e densidade de rochas reservatório.* Ph.D. thesis, Universidade de São Paulo.

Perles, C., Guersoni, V. and Bannwart, A., 2018. “Rheological study of crude oil/water interface–the effect of temperature and brine on interfacial film”. *Journal of Petroleum Science and Engineering*, Vol. 162, pp. 835–843.

Sauerer, B., Stukan, M., Buiting, J., Abdallah, W. and Andersen, S., 2018. “Dynamic asphaltene-stearic acid competition at the oil–water interface”. *Langmuir*, Vol. 34, No. 19, pp. 5558–5573.

Soares, I.F., 2017. *REOLOGIA DE ÁCIDOS ORGÂNICOS NA INTERFACE ÁGUA/ÓLEO.* Master’s thesis, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil.

SPE, 2011. “Challenges in reusing produced water”. URL `https://www.spe.org/en/industry/challenges-in-reusing-produced-water/`.

Ueta, E.M., NETO, J.A.D.S., NUNES, M.S., BARRIOS, O. and BARRETO, E., 2008. “Swellable packer technology resolves water production problem–case history in campos basin, brazil”. *Documento Técnico Halliburton OTC*, Vol. 19612.

Wang, X., Pensini, E., Liang, Y., Xu, Z., Chandra, M.S., Andersen, S.I., Abdallah, W. and Buiting, J.J., 2017. “Fatty acid-asphaltene interactions at oil/water interface”. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Vol. 513, pp. 168–177.

Zhou, Y., Yin, D., Chen, W., Liu, B. and Zhang, X., 2019. “A comprehensive review of emulsion and its field application for enhanced oil recovery”. *Energy Science & Engineering*.

7. RESPONSIBILITY NOTICE

The authors are solely responsible for the printed material included in this paper.