

The effect of formate brines on the emulsification of ionic, non-ionic, and enzymatic surfactants



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HIGHLIGHTS

- Surface and Interfacial properties of environmental-friendly surfactants were compared with a commercial surfactant for sodium and potassium formate and sodium chloride.
- Emulsification ability of environmental-friendly and commercial surfactant was evaluated for heptane, light and medium crude oil.
- Surface tension reduction in brine presence depends on the type of surfactant used.
- Ionic surfactants reduce its repulsion between head groups in salt presence.
- Polyglucosides have a similar effect as with ionic, the molecules are slightly more negatively charged linked to the OH groups in the molecule.
- Coco glucoside has similar thermodynamical properties as AOS which would indicate that it could be used to replace sulfonates, when environmental restrictions are in place.
- Emulsification for Sodium Formate and Sodium Chloride behave similarly, however, for those made with Potassium Formate pH needs to be considered since it can affect the behaviour of asphaltenes, or resins present in the crude oil.
- For most emulsions, the result of the rheology behaviour was shear thinning.
- Coco Glucoside presented a Newtonian behaviour for crude oil which could indicate that these emulsions would remain stable even at high shear rates that can be achieved in the production stage.

ARTICLE INFO

Article history:

Received 4 May 2022

Received in revised form 11 August 2022

Accepted 13 August 2022

Available online 14 September 2022

Keywords:

Emulsification

Alpha Olefin Sulfonate

Coco Glucoside

Critical Micelle Concentration

Gibbs Energy

Formate Brine

ABSTRACT

Environmental concerns on contamination of subsurface porous media by toxic chemicals have motivated the petroleum industry to replace them with environmentally sustainable (green) and biodegradable alternatives. Green surfactants have emerged such as sugar, enzymatic, and microbial based surfactants. However, their emulsification with different oils and salinity conditions is unknown. In this study, different oil and brine systems are tested to measure interfacial properties, rheology and emulsification of Coco Glucoside (CG), a sugar-derived surfactant; and Greenzyme (GZ), an enzymatic-environmentally friendly surfactant. Emulsification with light and medium crude oil in the presence of sodium chloride and sodium formate brines gave similar results with 10–20 μm average droplet size. However, medium-heavy crude oil with potassium formate produced 98 vol% emulsion with 3–6 μm average droplet size. Most of the emulsions demonstrated a shear thinning behaviour apart from emulsions resulting from Coco Glucoside and medium-heavy crude oil in which a clear Newtonian behaviour was observed.

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1. Introduction

Surfactants have vast applications in the petroleum industry in all production stages of an oil field (Schramm, 2000). They are commonly utilised during flooding to aid additional oil recovery by reducing surface tension (Felix et al., 2015; Bashir et al.,

2022). Surfactants are also a usual component of stimulation and completion fluids to prevent formation damage or corrosion in the pipelines (Renpu, 2011; Santanna et al., 2012). Petroleum sulfonates have been used and studied for several applications in this industry (Barakat et al., 1983) due to their availability, low cost and ease of manufacture. For this reason, alpha olefin sulfonates are the only commercial surfactants tested in this study.

Since the concern of the impact on the environment has risen there has been an upsurge in popularity of environmentally

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friendly surfactants made from sugar, enzymes, fatty acids, biomass or microbially produced (Kjellin and Johansson, 2010). In this paper, sugar and enzyme-based surfactants are used to compare their performances with a commercial surfactant such as Alpha Olefin Sulfonate (AOS). For the sugar-based surfactant, Coco Glucoside (CG) is used except in the case of the enzymatic when Greenzyme was chosen. Coco Glucoside is a non-ionic fatty alcohol glucoside with carbon chains that comprise from C8 to C16 (Pantelic and Cuckovic, 2014) and is classified as an Alkyl Polyglucoside (APG). The molecular composition is shown in Fig. 1. It is derived from the coconut fatty alcohols which react with glucose from either wheat, corn or potato (Pantelic and Cuckovic, 2014). These can be obtained from natural renewable sources and is entirely biodegradable.

Greenzyme is an enzyme protein which is produced by oil-seeking microbes in batch fermentation and can be considered as a zwitterionic surfactant (Rahayyem et al., 2019). It has been used mostly in enhanced oil recovery processes to change the wettability of the rock to increase recovery (Khusainova et al., 2015).

Sodium Alpha Olefin Sulfonate (AOS) is an anionic surfactant comprised of a carbon chain of C₁₄-C₁₆. It has high surface activity and low sensitivity to water hardness in addition to being fairly simple to produce at a moderate cost (Baviere et al., 1988). AOS is a popular commercial surfactant used throughout the oil industry along with other anionic surfactants such as sulphates (Wang et al., 2017).

All of these surfactants produce two-phase dispersions in which two immiscible fluids are mixed (Schramm, 2000). To create these dispersions requires the presence of oil and water phases in addition to a surface agent. In the petroleum industry these components are; oil which is contained in drilling mud or crude oil, brines which can be either formation or operational brines, and the surfactant that is an element in numerous well operations as mentioned previously.

There are several types of brines that can be found in an oil well, which can be classified as organic or inorganic (Caenn et al., 2016). One of the most commonly used salts is sodium chloride. However, the disposal for these brines is quite costly. The use of formate brines is preferable since they can degrade into water and therefore decrease disposal costs. Formate brines are divided in sodium, potassium and caesium formate and were initially developed to overcome off-shore drilling and completion challenges (Downs, 1993). These types of salts present a very high water solubility which increases as the alkali metal moiety in the Periodic Table rises. It is possible to combine formate salts to target a wide range of densities. These brines are also comparable with halides regarding their true crystallization point and are considered to be

having the best characteristics for deep and low-solids drilling as well as slim hole drilling (Byrne, et al., 2002).

These brines are commonly used as a base fluid in drilling and completion operations and generally applied in high pressure and high temperature environments. Sodium formate has been proved to be the most stable when compared to potassium and sodium chloride, even when aged at 315°F (Bybee, Nov. 2006). This formate salt provided enough thermal stabilization for a water base fluid in combination with xanthan gum to drill long open-hole sections of horizontal wells without the use of synthetic polymers. It has also been recorded that they can be rheologically stable at bottom hole temperatures of 400°F (Messler et al., 2007).

Formate salts can be applied in environmental sensitive regions since they produce non-hazardous brines and are readily biodegradable (Saasen, 2002). They are considered to be easy to maintain and recycle, therefore reducing the cost of discharge (Downs et al., 1994).

Formation damage is also improved when formate brines are used improving the performance of the production of the well (Byrne, et al., 2002). This is specifically important for high temperature wells as new-fluid technologies can increase the damage by the production of H₂S by microbial activity. Experimental tests have proved that the formate brines presented better return than oil-based mud of the same density despite the higher losses of fluid into the formation in high permeability rocks of an oil reservoir.

Polymers have shown to increase the stability of formate brines at higher temperatures (Howard, 1995). Some ions can be water structure breakers which tend to lower the transition temperature and affects the conformational change of the polymer. In the case of the formate ion, this tends to be a water structure maker and will raise the transition temperature of polymers. This results in them withstanding the increase in temperature without decreasing the viscosity by polymer degradation. Potassium formate has been proved to increase the transition temperature of Xanthan Gum significantly at high salt concentrations when compared with sodium and calcium chloride. Even other biopolymers can be influenced positively by the presence of formate brines.

Since the use of these brines is relatively new in comparison with halide brines, the amount of work that is related to formate salts is scarce when the emulsification ability of surfactants is the focus. Brine concentration and composition can directly affect the ability of the surfactant to create emulsions. Increasing salt concentration would incite a salting out effect in the surfactant, meaning the surfactant loses solubility. The aim of this study is to understand the emulsification ability of CG and GZ with Formate salts and compare them with the commercial standard (AOS) by measuring the water separation, evaluating their droplet size and rheology behaviour.

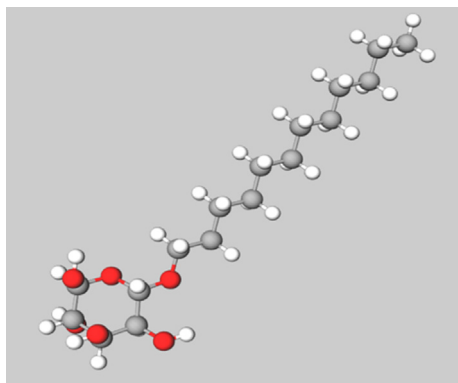


Fig. 1. Coco glucoside molecular structure. Grey: Carbon Red: Oxygen White: Hydrogen. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2. Theory

Surface tension or interfacial tension at the water–air interface/water–oil interface can be decreased by the addition of a surface agent which is adsorbed at the interface (Mukherjee et al., Mar. 2013). The surface tension is the direct result of the net attraction that the molecules in the liquid interface bear (Wang et al., 2018). These molecules at the interface contain a higher potential energy since they are not surrounded by additional molecules of identical nature (water–air, water–oil). Therefore, the energy of these molecules becomes greater than that present at the bulk phase. One square centimetre of surface formed requires surface energy to be spent for transporting the molecules to the surface (Chattoraj and Birdi, 2859). Surface tension can be used to determine the critical micelle concentration (CMC) of a surfactant (Savic et al., 2014). Below the CMC in the solution there would be only monomeric

surfactant molecules. These molecules assemble into aggregates that are defined as micelles when the surfactant concentration is equal to or greater than the CMC. At the CMC the surface tension is minimised and as surfactant concentration increases after this point the surface tension remains constant.

The extent of adsorbance of a solute, in this case being surfactants, at the liquid–vapor interface is determined by the use of the Gibbs adsorption equation through the surface tension (Bermúdez-Salguero and Gracia-Fadrique, 2015). The equation that relates the surface tension and the concentration of the surfactant can be defined as:

$$\Gamma_2^1 = -\frac{c_2 d\gamma}{RTdC} = -\frac{1}{2.303nRT} \left(\frac{d\gamma}{d\log C} \right) \quad (1)$$

where Γ_2^1 is the surfactant surface excess, C is the concentration of the surfactant in M/L, γ is the surface tension in N/m, and therefore $\frac{d\gamma}{d\log C}$ is the slope between the surface tension and the concentration, n refers to the number of species that are formed due to the dissociation of the surfactant. For non-ionic surfactants is $n = 1$ and for dissociated ionic surfactant $n = 2$. R is the gas constant ($8.314 \text{ Jmol}^{-1}\text{K}^{-1}$) and T is the temperature in °K.

With the surface excess it is possible to calculate the minimum area per molecule A_{\min} (Ananda et al., 1991); the maximum surface pressure at the CMC (π_{cmc}) (Jiang et al., 2011), the Gibbs Energy of Micellization (ΔG_{mic}^0), and the Gibbs Energy of Adsorption (ΔG_{ads}^0):

$$A_{\min} = \frac{1}{N_A \Gamma_2^1} \quad (2)$$

$$\pi_{\text{cmc}} = \gamma_o - \gamma_{\text{cmc}} \quad (3)$$

$$\Delta G_{\text{mic}}^0 = RT \ln \text{CMC} \quad (4)$$

$$\Delta G_{\text{ads}}^0 = \Delta G_{\text{mic}}^0 - \frac{\pi_{\text{cmc}}}{\Gamma_2^1} \quad (5)$$

Where N_A is Avogadro's number (6.023×10^{23} per mol), is the surface tension of water and γ_{cmc} is the surface tension of the respective surfactant at the CMC.

Rheological characterization of the emulsion flow is performed to determine its behaviour. The relationship between shear stress against shear rate can be used to fit the response to various rheological models (Tadros, 2005). The mixture of a dispersed phase into a continuous phase that is considered a Newtonian liquid could generate all sorts of non-Newtonian behaviour (Mueller et al., 2010). Emulsions can present both, Newtonian and non-Newtonian behaviours. For Newtonian behaviour the relationship between shear stress and shear rate is as follows:

$$\tau = \mu \dot{\gamma} \quad (6)$$

Where τ is the shear stress in Pa, μ is the viscosity in Pa.s and $\dot{\gamma}$ is strain rate in 1/s. For non-Newtonian emulsions two models were used in this investigation. These are the Herschel-Bulkley (Herschel and Bulkley, 1926) and Power Law models which are defined in Equation (7) and (8) respectively.

$$\tau = \sigma + K \dot{\gamma}^n \quad (7)$$

$$\tau = K \dot{\gamma}^n \quad (8)$$

Where σ represents the yield stress below where there is no flow, K is the consistency index (Pa.s) and n is the power law index (Herschel and Bulkley, 1926).

3. Experimental methodology

3.1. Materials

The oil phases investigated in this study are heptane 99 % extra pure and two types of crude oil. The crude oil mixtures are a condensate oil and a crude oil with a 20 % petroleum ether dilution to create an oil phase of 21–22 API. Three types of salts compounded the brines: extra pure sodium formate (NaCOOH, SF), potassium formate (KCOOH, PF) 99 % with less than 2 % water and extra pure sodium chloride (NaCl, SC). The salts were all purchased from Fischer Scientific. The anionic surfactant, Hansanyl OS with Alpha Olefin Sulfonate (AOS, $C_{14}\text{-}C_{16}$ 324 g/mol) as the active ingredient and Coco glucoside (CG, 320.42 g/mol) were purchased from Enaspol and Naturallythinking, respectively. The enzymatic surfactant Greenzyme™ (GZ, 85,000 g/mol) was kindly provided by Biotech Processing Supply Solutions. BARAZAN-D was used as the Xanthan Gum (XG) which was supplied by Halliburton. Deionized water (DIW) was obtained from the Barnstead Smart2Pure water system by Thermo Scientific. All the chemicals were used without further purification.

3.2. Brine preparation

Brine samples were prepared with a concentration ranging between 1 g/dL (10,000 ppm) to 7 g/dL (70,000 ppm) at a room temperature of 25 °C (+/-2 °C). The mMol/L equivalence is described in Table 1. The required amount of salt was placed in a beaker and measured on a precision balance. The beaker was then filled with deionized water up to the volume to prepare. Water was measured with a volumetric flask and beakers were used to have easier brine access to prepare the emulsions. The brines were mixed on a magnetic stirrer/ultrasonic bath until the salts were completely dissolved.

3.3. Polymer brine preparation

In order to create a polymeric brine, the same procedure of brine preparation was followed. However, when the salt was dissolved, a vortex was created to add the Xanthan Gum in small quantities until the desired weight was added. The polymer mixture was continuously stirred overnight to fully hydrate the polymer.

3.4. Emulsion preparation

The emulsion was prepared in 25 mL test tubes with a 1:1 ratio of water phase to oil phase with a total of 15 mL. Surfactant concentration was considered as vol% relating only to the water phase. The test tubes containing the emulsion base were mixed in a vortex mixer for 2 min at 3000 rpm until a homogeneous blend could be observed and left for equilibration until no changes in the emulsion phase were seen.

Table 1
Brine mMol/L equivalence to g/dL.

Concentration	NaCl (mM/L)	NaCOOH	KCOOH
1 g/dL	182.21	147.03	118.87
3 g/dL	546.64	441.11	356.63
5 g/dL	911.07	735.18	594.38
7 g/dL	1275.51	1029.26	832.14

3.5. Characterisation

The surface tension and interfacial tension of different brine solutions with a range of 50 to 20,000 ppm surfactant concentrations with air/heptane were tested in an Attention Du Nouÿ Ring Tensiometer model Sigma 703D for AOS, CG and Greenzyme. Each measurement was repeated at least 3 times to ensure reliability.

Rheological properties of the emulsion samples were obtained in the Discovery HR-3 from TA Instruments with a conical Peltier plate. A sample of around 1 mL was placed on top of the experimental base, then it was brought up to temperature to initiate the viscosity and shear stress measurements at a controlled shear rate.

The emulsion drop size distribution and type of emulsion was analysed by microscopy with an Olympus BX60M microscope with two lenses 50x and 100x depending on the emulsion specimen. Samples of the emulsions were taken with a pipette, after removal of the oil phase when applicable, and placed on a glass microscope slide in order to take the images with Clemex software. The analysis of the droplet size was performed on FIJI to convert the image to black and white and adjust the contrast. The process can be adapted to specific characteristics of the image (Schindelin et al., 2012) and MATLAB can be used to detect, determine and obtain an excel file of the diameter of the droplets. This was done for several images until a determined number of droplets were recorded for each emulsion.

4. Results and discussion

4.1. Surface tension and the Gibbs energy

Surfactants aid in the emulsion creation also known as emulsification. These occupy two important roles in the process; lowering the interfacial tension and to some extent preventing recoalescence (Walstra, 1993). During emulsification, droplets are deformed by the shear force and the surfactant is adsorbed into the interphase while these droplets continuously coalesce and may reduce their droplet size. The concentration of the surfactant in solution decreases due to its presence in the increased surface area of the droplets. A low interfacial tension represents less energy needed to decrease the droplet size. The lowering of the IFT depends on the type of surfactant used.

Surface tension of the emulsifiers with deionized water and the different types of brines was measured to identify the effect of the type of salt on this surfactant ability. All the surfactants were analysed in deionized water in addition to sodium formate, potassium formate and sodium chloride brines. The brine concentration was 7 g/dL for all cases. Values for the solutions and DIW were used to calculate the Gibbs Energy of Micellization and Adsorption. Measurements for the values of surface tension without the presence of surfactants were also recorded and can be observed in Fig. 2.

For AOS it was found that the critical micelle concentration for deionized water was 1.67 mMol/L with a surface tension of 32.45 mN/m as seen in Fig. 3. Similar values ranging from ~ 38 mN/m (Majeed et al., 2019) to 32 mN/m (Farajzadeh et al., 2008) were reported in other studies. However, when the surface tension was tested in the presence of brines it was considerably reduced with a surfactant concentration lower than that of deionized water. In this experiment the presence of NaCl showed that without surfactants, the surface tension decreased slightly, a value of 1.8 mN/m. Considering that the surface tension of water is 72 mN/m this is not a substantial change. It has been reported in the literature that the sole presence of salt can increase the surface tension (Jones and Ray, 1941). However, this statement is not accurate in all cases

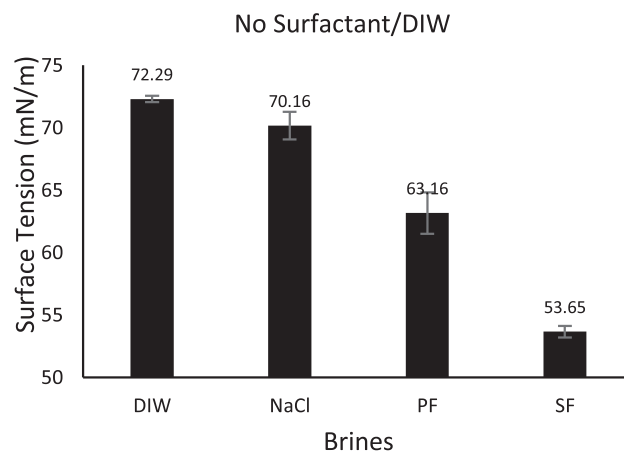


Fig. 2. Surface tension of Deionized Water, 7 g/dL Sodium Formate, 7 g/dL Potassium Formate and 7 g/dL Sodium Chloride and Air.

since a decrease of the interfacial tension has also been documented and therefore the type of salt is also important (Minofar et al., 2007; Weissenborn and Pugh, 1996). This increase in surface tension is related to the negative adsorption of these specific ions on the interface between the solution and the air phase.

A more noticeable alteration can be observed for potassium formate, in which the interfacial tension was reduced by almost 10 mN/m. Sodium formate has the highest variation with a value of 53 mN/m. Meaning that one of the ions is positively adsorbed onto the surface, therefore decreasing the interfacial tension. Since the presence of Na^+ is in sodium formate and sodium chloride and the decrease was not observed for chloride, this effect could be linked to the presence of the carboxylate ion (HCOO^-) which tends to collocate itself in the interface and act like a hydrotropic compound (Minofar et al., 2007). This effect could also be stronger in NaCOOH than in KCOOH due to the ionic strength is higher for Sodium Formate than for Potassium Formate. Even though the grammage concentration is the same they are molecularly different since it has more carboxylate ion available in solution.

As observed for NaCl brine the surface tension was reduced to 28 mN/m with an AOS concentration of 0.308 mMol/L (100 ppm), 5 times less than the CMC for deionized water. Comparable figures were measured for this type of brine at a concentration of 1 M/L and which is slightly lower than the one used in this study of 1.27 Mol/L (Majeed et al., 2019; Farajzadeh et al., 2008). Sodium and potassium formate behaved comparably, decreasing the surface tension to 27.1 mN/m and 26.6 mN/m respectively both at 300 ppm. However, the lowest values were achieved with Potassium Formate. From this concentration onwards the values are similar regardless of the salt type. Hence, it can be observed that ionic surfactants in the presence of electrolytes are still able to reduce the surface tension for all three types of salts (Para et al., 2003). The decrease of the surface tension can be attributed to the presence of electrolytes which diminish the repulsion that is present in ionic head groups that hold the same charge within micelles. This enables the surfactant monomers to pack more tightly throughout the surface and therefore reducing the surface tension as their presence increased on the surface (Staszak et al., 2015). From Fig. 3 (b, c, d) it can be observed that the effect that the salt ions create is more prevalent for the ionic surfactant which reached the lowest values of surface tension when compared to CG and Greenzyme.

The CMC value of CG was found to be at 0.936 mMol/L for deionized water (Fig. 3 a) with a surface tension of 28.81 mN/m. This is a considerably low concentration compared with the

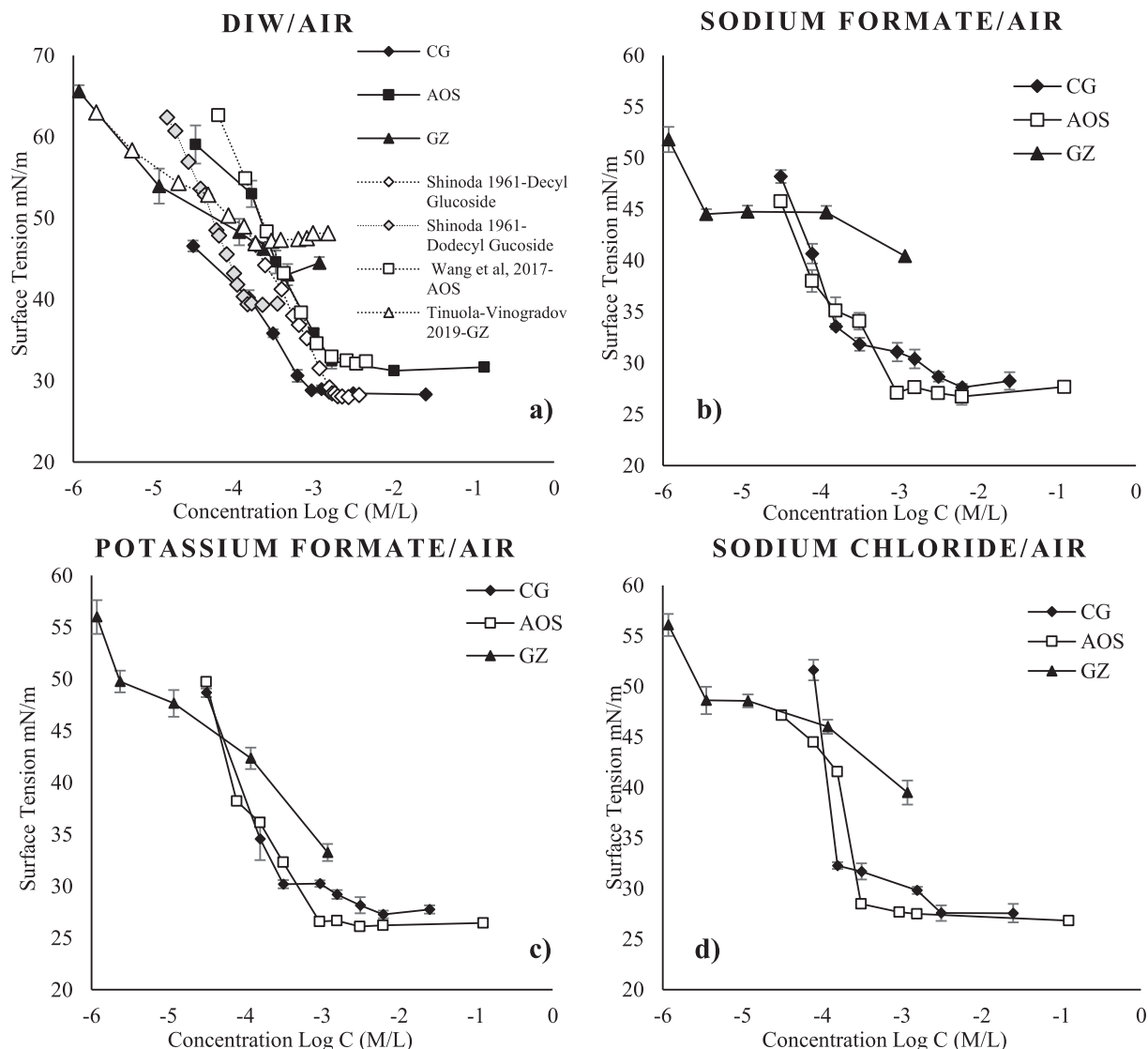


Fig. 3. Surface tension response of AOS, CG and GZ solutions with a) Deionized water, b) Sodium formate, c) Potassium formate and d) Sodium chloride brines. Comparison with data from Wang et al. (Wang et al., 2017); Shinoda (Shinoda et al., 1961) and Tinoola-Vinogradov (Udoh and Vinogradov, 2019).

obtained for AOS (Fig. 3 a). Non-ionic surfactants have a tendency of lower CMC values when compared with ionic and zwitterionic surfactants in the case of deionized water (Tadros, 2013; Balzer, 1993). Values of CMC for alkyl polyglucosides can vary. As the chain length increases the CMC value decreases and therefore it can fluctuate from 0.078 mM/L (25 ppm) for C_{14} to 1.56 mM/L (500 ppm) for C_8 . The CMC obtained for CG agrees to its mid-length chain of C_8 - C_{12} .

Close to the CMC values, the surface tension is similar for deionized water and all the brines tested for concentrations above the CMC. However, lower values of surface tension were reached at lower concentrations in the presence of salts. The lowering of the surface tension in the presence of electrolytes has been reported before for nonionic surfactants (Miyagishi et al., 2001). The repulsive interactions that domain the reduction of the surface tension in the ionic surfactants are not applicable to nonionic surfactants. Initial research for this topic indicated that the reduction was due to the salting out effect on ethylene oxide groups that was induced by the increase of electrolyte concentration. However, this conclusion cannot be applied to APGs (Schick et al., 1962). The outcome of the polyglucosides is more related to the micelle, for

which is assumed that its surface is more inclined to be negatively charged. Therefore, the similarities to ionic surfactants regarding the decrease in the CMC (Balzer, 1993). This negative charge could be linked to the OH groups interacting with the water phase.

It must be noted that at higher concentrations of CG, the overall surface tension is slightly increased to 30–31 mN/m for the solutions with salt presence from 28 mN/m with deionized water. This could indicate that the salt presence has a small negative effect on the surfactant performance producing a salting-out effect (Balzer, 1993). Increasing surfactant concentration can compensate this effect as it can be observed from 1000 ppm and further when all the points converge. There is no significant difference between the surface tension values obtained for any of the brines as surfactant concentration is increased further.

The gap between the data of deionized water and brines is larger for AOS, demonstrating that the presence of electrolytes has a stronger, positive adsorption effect on the ionic surfactants than non-ionic (Miyagishi et al., 2001). AOS reached the lowest surface tension values (26.11–28.47 mN/m) compared to CG (27.26–30.18 mN/m) which supports this behaviour although these figures are extremely close.

Greenzyme presented the highest surface tension values in comparison with the other two surfactants. The CMC was found to be at 0.176 mMol/L for deionized water (Fig. 3 a) with 47.2 mN/m. Surface tension values at CMC are 20 mN/m higher than those of AOS and CG at CMC values. Similar values of 47.1 mN/m for the surface tension and 0.174 mMol/L at CMC were reported in the literature just recently (Udoh and Vinogradov, 2019). They concluded it is considerably difficult to find this specific information for Greenzyme since it is a new surface agent. The lowest surface tension obtained corresponds to potassium formate brine, with 43.7 mN/m. There is only a difference of 2.3, 0.8 and 1.6 mN/m for sodium chloride, sodium formate and deionized water, respectively. Even when the surface tension values were higher when compared to the other two surfactants tested, at increased salt concentration there was a slight improvement of the surfactant performance. This effect was also reported in a previous study (Udoh and Vinogradov, 2019) in which Na^+ caused a decrease in the surface tension although it was the lowest surface activity registered in comparison with Ca^{+2} , Mg^{+2} , Na^+ & Ca^{+2} , Na^+ & Mg^{+2} , Na^+ & Ca^{+2} & Mg^{+2} . These brines showed a decrease in surface tension at low (0.0083 M) and medium (0.75 M) salt concentrations, yet at higher ionic strength (3 M) all these combinations had an increase.

This surfactant can be considered a good hydrotrope. As stated in the literature, enzymes have very little effect on the decrease of the interfacial tension and considering this influence almost irrelevant (Khusainova et al., 2015). Enzymes mostly modify solid to liquid interactions, therefore having more impact on the rock surface than in the oil–water interface. The de-adhesion of the crude oil from the rock is totally related to the catalytic effect of the enzymes that is dependant of the oil composition.

Thermodynamic processes of micellization were evaluated by surface tension measurements (Jiang et al., 2011) and the results of this assessment can be found on Table 2. The decrease of the Gibbs free energies in the system depends on the surfactants adsorption at the interface or their aggregation in the solution. The largest A_{min} was obtained for Greenzyme, indicating that the molecule of this surfactant is particularly large in comparison with the other two surfactants (Udoh and Vinogradov, 2019). Therefore, its packing in the surface is not as taut indicating a higher surface tension. The smallest area is that of CG (0.65 nm²) followed closely by AOS (0.86 nm²) which indicates that these molecules are closely packed at the interface (Jiang et al., 2011), hence lowering the interfacial tension. The smallest area of CG corresponds to the highest surface excess. This may be due to the lack of the ion-to-ion repulsion producing a better adsorption at the interface for this particular surfactant. This surfactant also presents the highest π_{cmc} confirming a better adsorption at the interface for CG which would cause an additional diminishment in the surface tension. This maximum surface pressure of 43.5 mN/m for CG was followed by AOS with 39.8 mN/m indicating that either the repulsion forces are slightly stronger for AOS or the molecule size prevents it to aggregate in a denser form. The minimum π_{cmc} was that of Greenzyme which overall does perform subpar when compared with the anionic and nonionic surfactants in the sample. This may be due to looser binding of the molecules as they are considerably bigger. The negative value of ΔG_{ads}^0 and ΔG_{mic}^0 indicates the instant micellization of the surfactants as they are in solution. The values for

ΔG_{ads}^0 are more negative than those found for ΔG_{mic}^0 which denotes that the Greenzyme molecules would perform better at adsorption than at the micellization process (Jiang et al., 2011). Therefore, the surfactant molecules would first adsorb at the surface before commencing the micellization process. The most negative values correspond to Greenzyme, for both, adsorption and micellization energies. This indicates that Greenzyme tends to adsorb to the interface better and the larger size of its molecules require less monomers to incite aggregation (Udoh and Vinogradov, 2019). CG has similar values for both energies, indicating that almost the same amount of work is needed to create a micelle or to adsorb at the surface. For AOS the adsorption energy is higher than micellization, suggesting that it adsorbs better at the interface achieving this before starting to create micelles.

4.2. Interfacial tension

The interfacial tension between the brines and a synthetic oil phase (heptane) was measured to investigate the effect of the increased salinity in the water–oil interface when these surfactants were used. It could be inferred that the response might be comparable to the air–aqueous solution interface since the oleic phase and the air phase have both nonpolar molecules (Rosen and Kunjappu, 2012). The IFT between deionized water and heptane has been reported with a value of 50.71 mN/m at 25 °C (Zeppieri et al., 2001). Interfacial tension registered for the used brines without the presence of surfactant was 27.95 mN/m for sodium formate, 27.44 with sodium chloride and the lowest values registered with potassium formate with and 24.64 mN/m as observed on Fig. 4.

A considerable decrease in the interfacial tension is observed when salt is added to the solution (Fig. 5). For AOS the lowest values reaching between 2.35 and 2.68 mN/m were attained with potassium formate and sodium chloride. A close cipher of 3.563 mN/m for IFT was allocated to Sodium Dodecyl Sulfate (SDS), a comparable anionic surfactant in the presence of NaCl brine at very low concentrations (Jha et al., 2018). Lower IFT's were reported for AOS and pentadecane, however, the measurements were taken at 45 °C which lowers the IFT (Wang et al., 2017).

CG performed better in the presence of oil than AOS, reaching values of less than 2 mN/m as observed in Fig. 5 a. The IFT for KCOOH brine was the lowest recorded when compared with the other brines, reaching values of 0.4 mN/m at concentrations of 50 ppm (0.15 mMol/L). For NaCOOH and NaCl values of 0.7 mN/m were attained at concentrations higher than 300 ppm (0.93 mMol/L). Decreasing of the interfacial tension with the presence of salt was reported as well for a commercial non-ionic surfactant known as Triton X-100 having similar CMC values of 125–140 ppm with CaCl_2 , MgCl_2 and NaCl at different concentrations (Akhlaghi et al., 2020). Similar IFT's were observed for several APG's that ranged between 8 and 16 in carbon chain (Iglauer et al., 2004). The alkyl chain length influences the IFT as longer chain length increases the reduction. The sugar rings also have a big influence. The higher count of rings increases the water solubilization of the molecule making it more hydro thereby increasing the IFT. The electrolytes present in the solution hydrates the sugar ring particularly depending on the type of ions coming from the salts

Table 2
Thermodynamic Characteristics of the Surfactants with Deionized Water.

Surfactant	CMC mmol/L	Γ mol/m ²	A_{min} nm ²	γ_{cmc} mN/m	π_{cmc} mN/m	ΔG_{-mic} kJ/mol	ΔG_{-ads} kJ/mol
Coco Glucoside	0.93	2.56x10 ⁻⁶	0.65	28.82	43.47	-17.29	-17.0
AOS	1.67	1.93x10 ⁻⁶	0.86	32.50	39.79	-15.84	-20.67
Greenzyme	0.1176	7.34x10 ⁻⁷	2.20	47.35	24.94	-22.43	-33.00

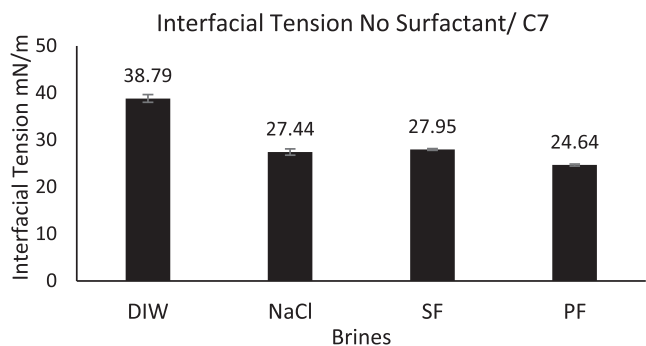


Fig. 4. Interfacial tension of Deionized Water, Sodium Formate, Potassium Formate and Sodium Chloride with Heptane (C7).

rendering the surfactant more hydrophilic, even though the IFT is reduced.

Greenzyme presents an interfacial tension with deionized water with a flat tendency of 6.8 mN/m at low and medium concentrations as seen in Fig. 5a. The CMC for DIW and heptane for Green-

zyme decreased considerably compared with the air interphase to a value of 100 ppm. They also showed a different activity than the other surfactants as the salt presence increases the interfacial tension from values of 7 mN/m to 12–13 mN/m regardless of the type. Greenzyme appears to have an inconsistent trend regarding electrolyte presence as presented in 2019 (Rahayem et al., 2019). There was a sinusoidal response on the IFT as the NaCl concentration was increased. However, the IFT values that were obtained for those experiments were considerably lower ranging between 0.7 and 3 mN/m compared to those obtained in this investigation. Even lower IFTs of a range between 0.01 and 3.95 mN/m have been described for Greenzyme (Wang et al., 2008). Yet, in these cases, the oils tested were *n*-decane and crude oil, respectively. Since the oil phase used in this study was *n*-heptane, it can be inferred that the performance of Greenzyme can improve as the complexity of the oil is increased. The composition of the oil plays an important role as the catalytic effect derived of the enzyme requires a particular bond type present in the oil phase (Khusainova et al., 2015).

It was noted that there is a clear effect of the brines on the interfacial tension for the three surfactants which could affect the emulsification ability of these surfactants as seen on Fig. 5 b, c and d. In

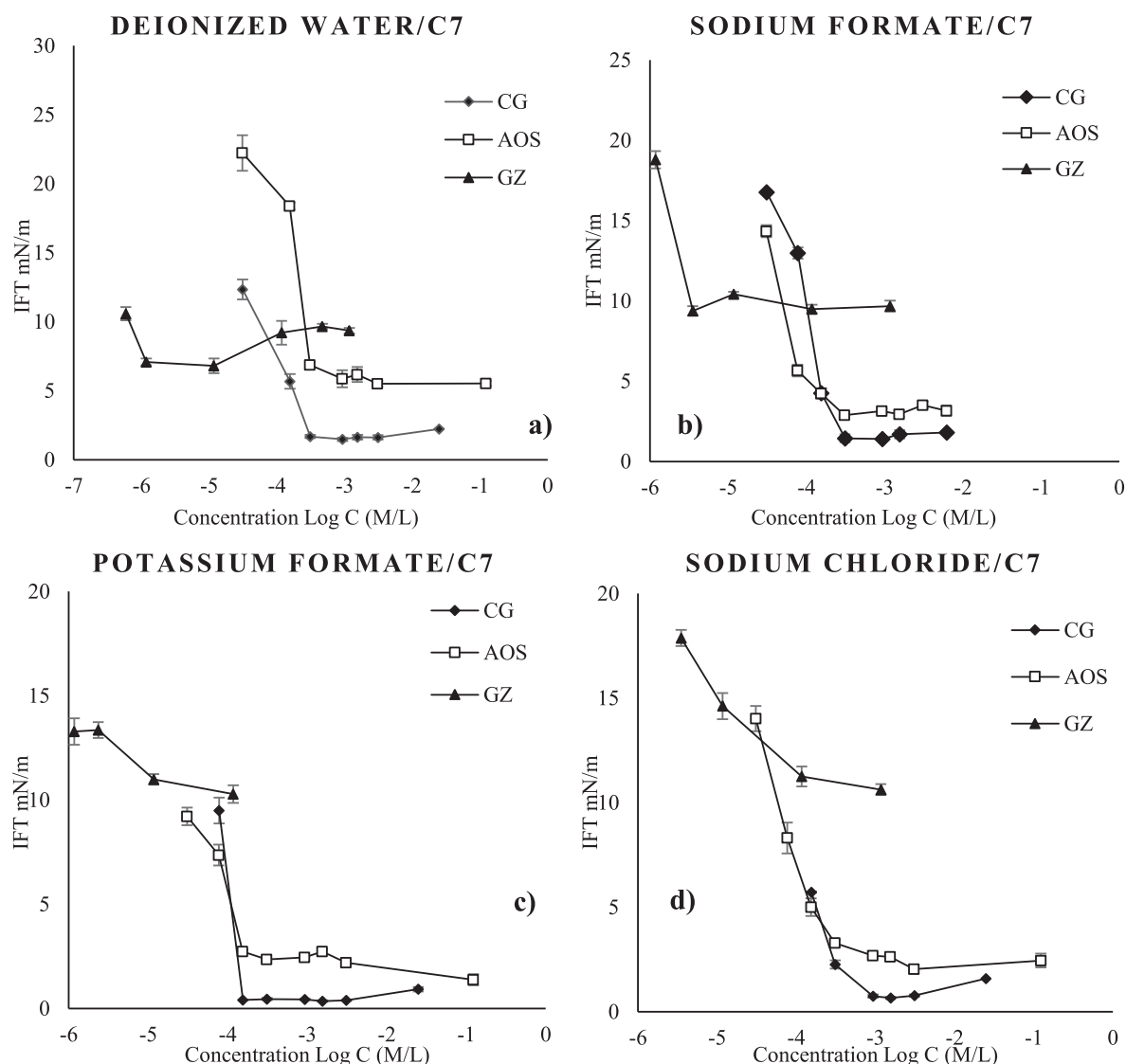


Fig. 5. Interfacial Tension of an AOS, CG and GZ solutions against heptane (C7) with a) Deionized Water, b) Sodium Formate, c) Potassium Formate and d) Sodium Chloride.

contrast with the surface tension in which AOS reached the lowest figures in the presence of heptane as the oleic phase, the best performance can be allocated to CG, followed closely by AOS as seen in Fig. 3. Lowest IFT values were observed in KCOOH brine, this was present in both surface and interfacial tension, and it was noted for both, AOS and CG. As mentioned, there was a considerable increase of 108 % in the IFT for Greenzyme when the solutions tested contained dissolved salts.

Thermodynamic characteristics of the interfacial tension of the surfactant solutions with deionized water and heptane are depicted in Table 3. A_{\min} displayed no change as the same surfactants were used. Greenzyme still attained the highest molecule size (0.37 nm^2) (Udoh and Vinogradov, 2019) with the uppermost IFT at CMC (7.08 mN/m) and the smallest remained with CG (0.11 nm^2) followed by AOS (0.19 nm^2). The highest surface excess for these cases befalls on AOS with 1.45×10^{-6} . Coco Glucoside still presents the highest surface pressure with 36.42 mN/m followed closely by AOS and Greenzyme. A better performance of Greenzyme can be observed indicating that the repulsive forces are slightly lower aiding to tighter molecule packing. As it is made from an oil-seeking enzyme, the presence of an oil phase might have caused the change in the behaviour of the surfactant. ΔG_{mic} and ΔG_{ads} still have more negative values for Greenzyme, performing better at adsorption than at micellization processes. AOS presents similar micellization and adsorption energies indicating that the amount of energy needed for either process is almost the same for this surfactant. For the presence of heptane, CG has a better adsorption than micellization indicating that it tends to go through adsorption before micellization.

4.3. Emulsification with alkane phase

Emulsions can be affected by the type of oil, salinity, surfactant characteristic, temperature, alcohol content, water to oil ratio and presence of solids (Kanicky et al., 2001). With correct composition at a specific salinity range an optimal formulation is achieved in which the interfacial tension can reach ultralow values (Bansal, 1978). Surfactant emulsion ability can be decreased by the presence of salts in the water depending on the surfactant which can change the volume of emulsion created.

The surfactant emulsification ability was tested by evaluating the amount of water segregated and the amount of water solubilized into the emulsion. This was reported after the equilibrium time was reached which in this case was between 2 and 5 days. At this point no emulsion change was registered. The more water that was dissolved into the emulsion phase, the better the emulsion ability for the surfactant (Ahmed et al., 1999). The salinity scan that was developed to test this involved sodium chloride, sodium and potassium formate at concentrations of 1, 3, 5, 7 g/dL.

In all cases, the water segregation increased as the salinity also increased. The salinity concentration decreased the ability of the surfactant to create and stabilize the emulsion phase due to the mobilization of the single surfactant molecules to the oil phase, also called salting out effect (Beunen and Ruckenstein, 1982). The IFT would tend to decrease due to the adsorption excess being positive. For emulsions with AOS and heptane, increasing the surfactant concentration from 2 to 4 % does not create a substantial

change in water segregation between these concentrations with deionized water (Fig. 6). The surfactant behaves similarly between all the brines. For NaCl lower salinities emulsify more water for both concentrations. However, higher concentrations of this salt destabilize the emulsion considerably. Potassium formate at higher salinities has less water segregation than the other two brines at 4 % AOS. This could be attributed to the lower interfacial tension presented with this type of salt, as discussed in the previous section. KCOOH was shadowed closely by NaCOOH.

AOS has low solubility and tends to aggregate when the salt concentration surpasses 5 g/dL at 24–25 °C (Baviere et al., 1988). Instead of diluting it is observed that the surfactant forms a precipitate just after adding it to the brine making it more difficult to mix, therefore decreasing its surface activity (Wang et al., 2017). Increasing the temperature above 30–35 °C will solve this issue as tested in the laboratory. In order to obtain the best performance of AOS a low salinity and low carbon chain is needed, as well as a high alcohol concentration which is very unrealistic for its application in the oil industry (Baviere et al., 1988).

Water solubility was low for all the emulsion samples at the highest salinity, which was not more than 5.4 %. This may be due to the fact that neither of these emulsions had the presence of a co-solvent in them. A co-surfactant aids with the solubilization of the phases into the emulsion and, alcohols are used for this purpose (Puerto and Gale, 1976). Propanol, butanol and pentanol have been proven effective to increase solubilization depending on the chain length of the surfactant. Alcohol was not considered for these emulsions because this research is more focused on the reaction of stimulation and completion fluids. Surfactant concentration with synthetic and crude oils and for these fluids the use of alcohol is for very specific circumstances like for water sensitive reservoirs when either surfactant or alcohol can be used (Zana, 1995). Addition of alcohol to the operation leans towards Enhanced Oil Recovery classification (Winsor, 1948).

For NaCl, heptane and intermediate-branched C_{16} AOS at 25 °C it was previously reported (Barakat et al., 1983) that the solubility is around $18 \text{ cm}^3/\text{cm}^3$ with an optimal salinity of 0.5 g/dL, being the optimal salinity substantially higher from 5 to 20 g/dL for straight-chain surfactants. Nevertheless, this study used sec-butanol and isopentanol alcohols in the system to create the emulsion phases. Theory suggests that the oil solubilization should decrease with the increase of salinity. However, this phenomenon cannot be observed either due to the lack of co-solvent or for the low temperature tested.

These emulsions can be classified as Type II, from the Winsor classification (Strassner, 1968). This is a reversed behaviour since they did not change phase normally; a standard behaviour compasses from Type I to type III to type II as the salt concentration is increased. However, this behaviour is also affected by the type of oil phase which for these cases have a low alkane carbon number (ACN) (Baviere et al., 1988). The presence of a low ACN can reverse the normal behaviour of the emulsion phase making the transition Type II > Type III > Type I. Type I and Type III was not able to be found for these samples' composition.

CG exhibits a better performance since it presents a lower water segregation than AOS even at high salinities having 89 % at 7 g/dL for Sodium Chloride, and 93 % for 7 g/dL Sodium and Potassium

Table 3
Interfacial Thermodynamic characteristics of CG, AOS and Greenzyme with deionized water.

Surfactant	CMC mmol/L	Γ mol/m ²	A_{\min} nm ²	γ_{cmc} mN/m	π_{cmc} mN/m	ΔG_{mic} kJ/mol	ΔG_{ads} kJ/mol
Coco Glucoside	0.31	1.009×10^{-6}	0.11	2.37	36.42	-20.01	-43.72
AOS	0.30	1.45×10^{-6}	0.19	6.87	31.92	-20.04	-21.98
Greenzyme	1.2×10^{-6}	4.42×10^{-7}	0.37	7.08	31.71	-33.84	-71.80

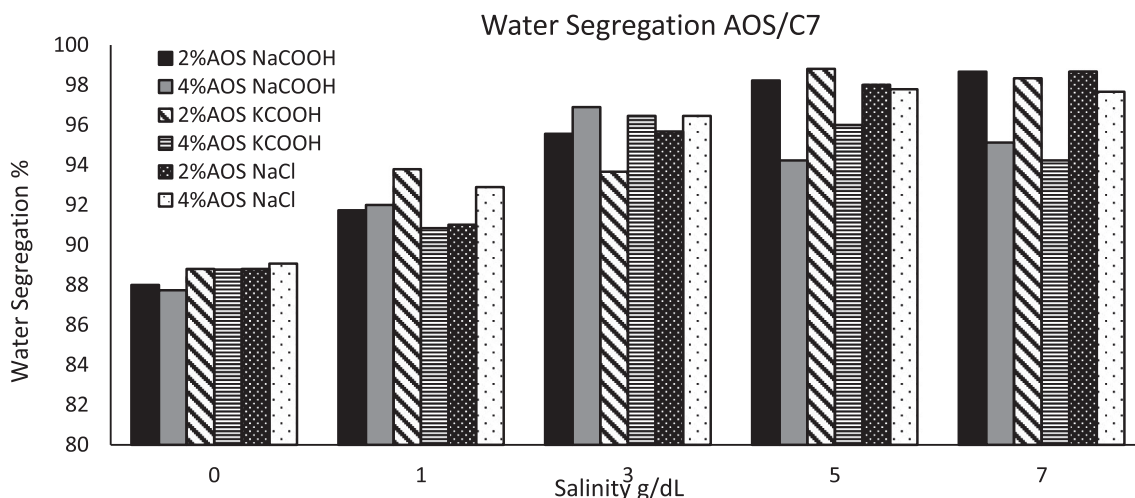


Fig. 6. Water segregation for AOS/C7 emulsions with different brine composition.

Formate considering that it also has less surfactant concentration (Fig. 7). Water separation is more evident at a lower CG concentration ranging between 90 % and 97 % for the range of salinities. And 89 % to 93 % for the highest concentration of the surfactant. For NaCl, the effect of the surfactant concentration is more evident, even when the concentration used was substantially low, it changed from a solubility of 3.3 % for 0.4 % to 10.3 % for 0.8 % which is greatly higher despite the elevated salt concentration. According to the surfactant concentration an increase would present a decrease of the water segregation. At higher surfactant concentrations the performance with NaCl brine appears to be considerably better despite the increase in salinity, followed by NaCOOH and KCOOH.

Greenzyme presents an emulsification comparable with the other two surfactants, with no salt addition and very low salinities. The high interfacial tensions achieved between brines solutions and heptane in contrast with the other two surfactants, could be considered as a strong reason why Greenzyme had a low emulsification ability with concentrated electrolyte. The behaviour of

Greenzyme is similar for sodium chloride and potassium formate at high concentration of the surfactant and low salinities of 0–1 g/dL, having water segregations of 82–86 %. Greenzyme at 8 % with KCOOH for both concentrations and in NaCOOH presents higher water segregations ranging between 88 and 96 %, changes with increasing salinity can be observed in Fig. 8. Best emulsification was found with low salinity water, going above 10 g/dL of any type of salt tested will result in a complete phase separation between minutes of mixing.

Greenzyme presented very unstable emulsions even at low salinities (Fig. 9). With time the oil phase starts to separate from the emulsion and in some cases complete phase separation is achieved.

The Table 4 shows a summary of the percentage of water dissolved into the emulsion phase of each surfactant with the corresponding brine and heptane as the oil phase. In every case the whole oil phase was solubilized into the emulsion just changing the water concentration.

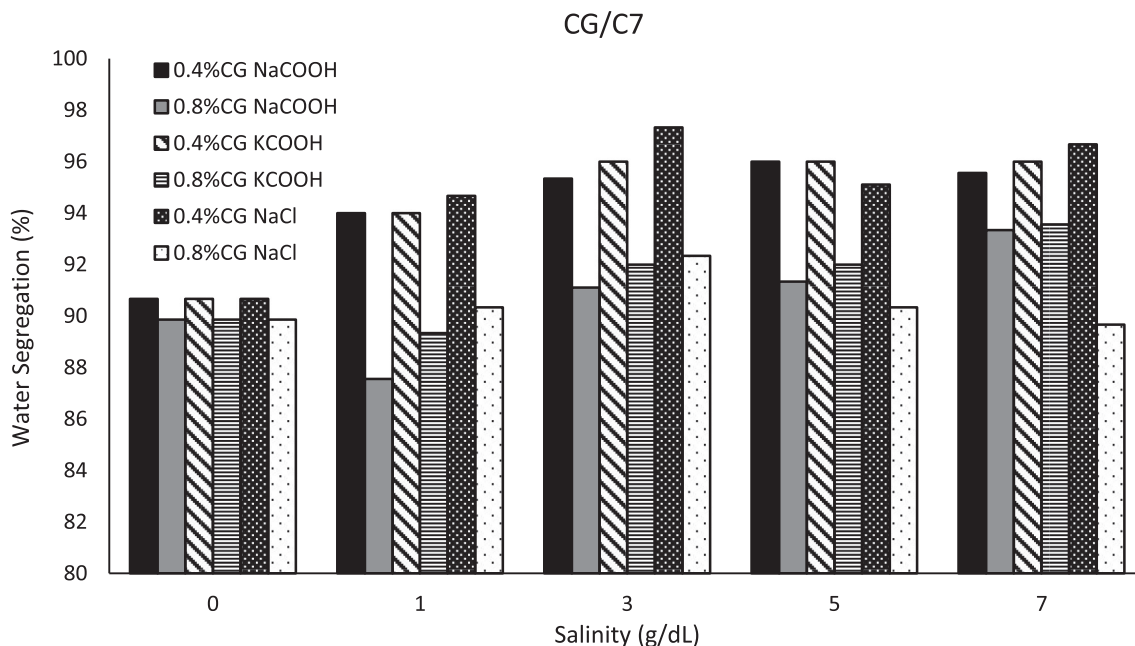


Fig. 7. Water segregation for Coco Glucoside/C7 emulsion with different brine compositions.

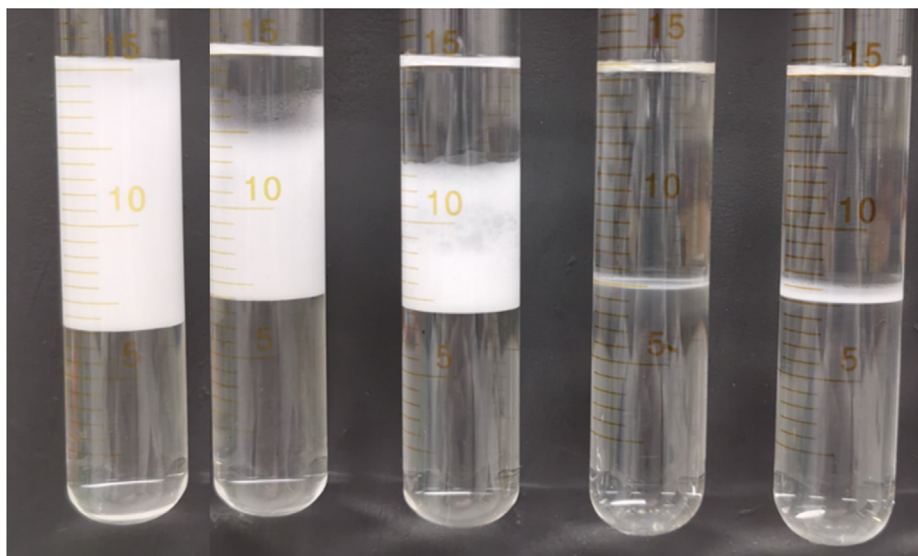


Fig. 8. Emulsion behaviour for Greenzyme and heptane with 0, 1, 3, 5 and 7 g/dL of Sodium Formate brine.

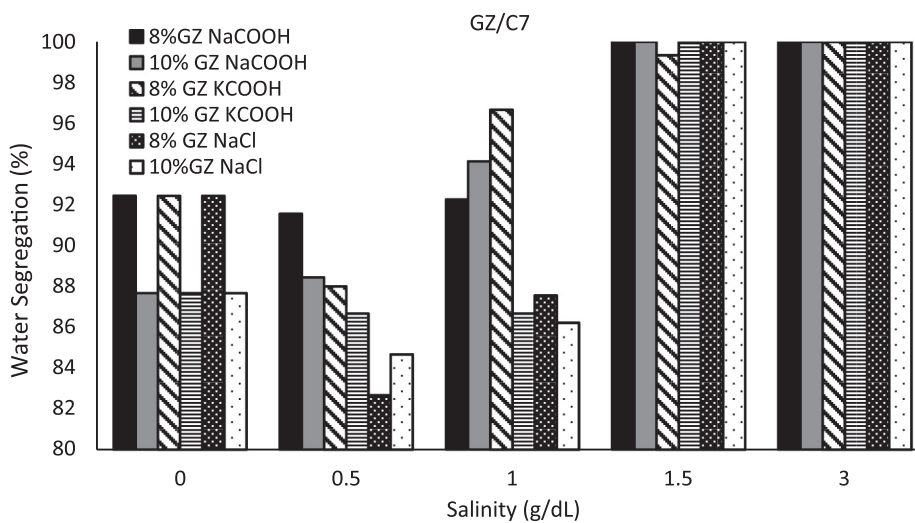


Fig. 9. Water segregation for GZ/C7 emulsions with different brine compositions.

Table 4

Water in emulsion phase according to surfactant and brine type in the presence of heptane.

% Surfactant		Sodium Formate g/dL				
		0	1	3	5	7
0.4 %-0.8 %	CG	10-11 %	6-13 %	4-9 %	4-9 %	4-5 %
2-4 %	AOS	11-12 %	6-13 %	4-5 %	2-3 %	2-5 %
8 %-10 %	GZ	8-13 %	6-8 %	0	0	0
		Potassium Formate Salt g/dL				
		0	1	3	5	7
0.4 %-0.8 %	CG	10-11 %	6-11 %	4-8 %	4-8 %	4-7 %
2-4 %	AOS	11-12 %	7-10 %	4-7 %	2-3 %	2-6 %
8 %-10 %	GZ	8-13 %	4-14 %	0	0	0
		Sodium Chloride g/dL				
		0	1	3	5	7
0.4 %-0.8 %	CG	10-11 %	6-10 %	3-8 %	5-10 %	4-11 %
2-4 %	AOS	11-12 %	8-9 %	5-6 %	2-3 %	2-3 %
8 %-10 %	GZ	8-13 %	13-14 %	0	0	0

Water % in emulsion

Loose emulsion separating in a few minutes

Emulsion formed but will retain a very small amount of water (1-3%)

Emulsion formed but will retain a small amount of water (4-12%)

Emulsion formed and will retain a considerable amount of water (13-20%)

4.4. Emulsification with Medium-Heavy crude oil

For emulsions with crude oil and AOS, when the salinity is increased the emulsion ability of the surfactant is decreased considerably. In the case of NaCl the emulsion ability is almost non-existent as can be seen in Fig. 10. Sodium formate and sodium chloride can emulsify a considerable amount of water up to 3 g/dL. Yet, in the presence of KCOOH, 60 % of water was solubilized into the emulsion for 2 % AOS and 80 % for 4 % of AOS. As seen in the surface and interfacial tension measurements, KCOOH by itself can decrease the tension that exists between interfaces. The addition of the surfactant to the solution and the presence of asphaltene in the crude oil appears to be aiding in the stabilization of the emulsion phase (Technologies, 2018).

Emulsions made with crude oil and CG produced less emulsion phase compared with heptane when sodium formate and chloride were used. These salts created a weak emulsion when the salinity is increased that along with long equilibration times can release most of the water added to the solution. Only for DIW and 1 g/dL the emulsion contained 14 % and 8 % of water solubilized. From 3 g/dL onwards it only solubilized 2 %. As seen in the emulsions made with heptane, there is also less water separation in the presence of NaCl brines at high surfactant-high salinity concentrations. Nevertheless, the same effect of KCOOH that was present for AOS emulsions is noticeable for CG as can be observed in Fig. 11.

There is a high emulsification ability at high salt concentrations. Results show 75 % of the water present in the solution was mixed into the emulsion phase for 0.4 % CG and almost 100 % was emulsified for 0.8 % CG. These emulsions were extremely stable and were not separated by segregation for more than 6 months. CG emulsion behaviour is shown in Fig. 12.

The response of AOS and CG with KCOOH salt was quite particular. In order to identify whether the cation or the anion of the salts were the reason of this outcome extra tests were completed with potassium chloride (KCl) at the same molar concentration as 7 g/dL KCOOH. These tests presented a complete phase separation at 9.5 g/dL for KCl as can be observed in Fig. 13.

These results indicated that the cation alone might not be the reason of the higher emulsification ability of this mixture. Therefore, anions were also compared in tests with sodium formate, in which formate is the alike anion. The concentration of KCOOH at

7 g/dL is 832.14 mMol/L and the concentration of NaCOOH at 7 g/dL is 1029.26 mMol/L. This reason was discarded as the concentration of NaCOOH is higher and is not behaving in the same manner as KCOOH. As discussed, the results obtained were very different as sodium formate did not create thick and stable emulsions at high salinities whereas potassium formate did for both surfactants, AOS and CG. Where CG displayed a stronger effect creating a more dense and viscous emulsion.

Since petroleum ether was added to the crude oil to increase its API grade, a scan with the same surfactant concentration, brine and oil content but increasing petroleum ether dilution for the crude oil was completed. This was done in order to discard whether the presence of petroleum ether was the motive of the variation on the results (Fig. 14).

As it can be observed in Fig. 14 increasing the amount of petroleum ether from 20 % to 50 % still produces a very strong emulsion phase, however, when 80 % is reached, the emulsion only has 0.5 mL of water solubilized. Therefore, the presence of petroleum ether in the crude oil was not the reason of the increased emulsion phase presented at high salinities. Two other tests were run with condensate crude oil and full phase separation was obtained, indicating that a very light crude oil does not present the characteristics required to produce a stable emulsion at high salt concentrations of KCOOH.

Hence, cation, anion and petroleum ether content were discarded as reasons for high emulsification for potassium formate. Another property that can have an impact on emulsification by adjusting it is pH (Technologies, 2018). Crude oil contains polar fractions, acidic and basic groups (asphaltenes and resins) which pH can influence. Basic medium creates the strongest interfacial films for resins, also making the weakest films for asphaltenes. The opposite is true in the case of acidic media. The emulsion type can also be determined by pH. Acid pH can produce stable water in oil emulsions. The response for a basic pH is a stable oil in water emulsions. Nonetheless, high salinity concentrations can produce instead water in oil emulsions and in these cases, W/O emulsions were obtained for both AOS and CG.

pH measurements for several points of salinity were tested for potassium and sodium formate and sodium chloride which can be observed in Fig. 15. Sodium chloride brine for salinities between 3 and 7 g/dL gave a pH range of 6.3 to 7.94 which rests on the neu-

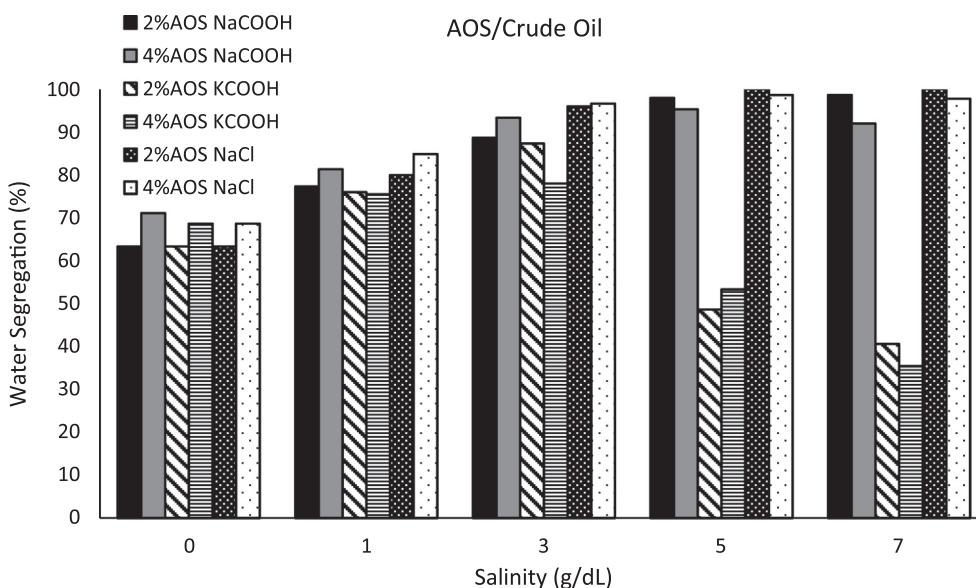


Fig. 10. Water segregation for AOS/Crude oil emulsions with different brine compositions.

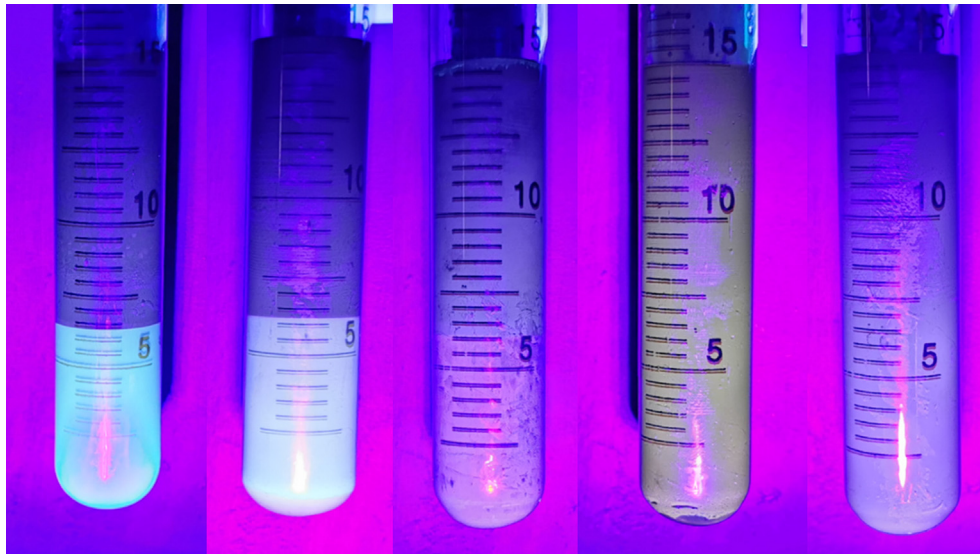


Fig. 11. Emulsion behaviour with CG and medium oil with KCOOH from 0, 1, 3,5 and 7 g/dL taken under UV light to see the interfaces.

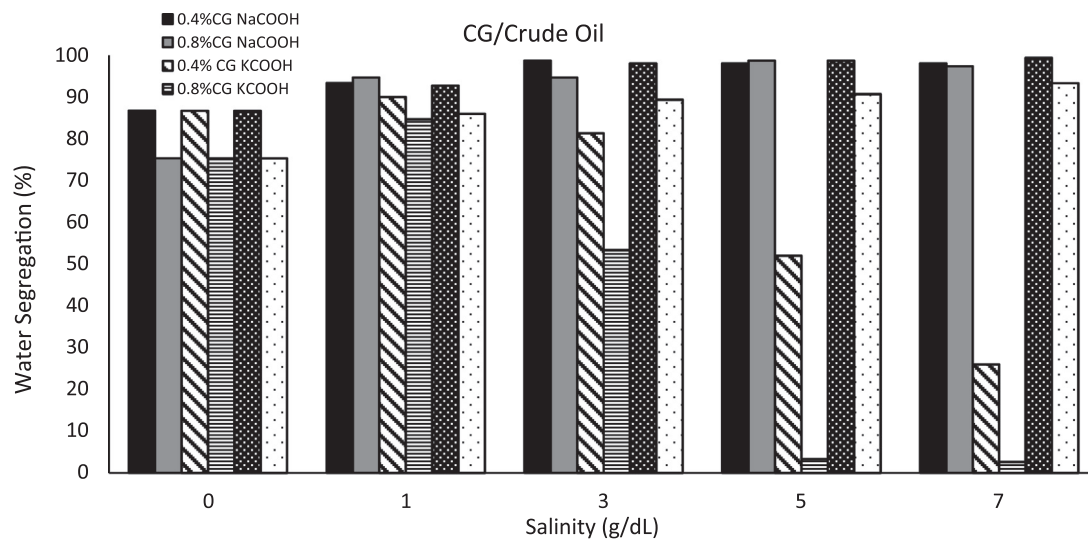


Fig. 12. Water segregation for Coco Glucoside/Crude Oil emulsions with different brine compositions.



Fig. 13. Emulsion behaviour of 0.8 % Coco Glucoside/Crude Oil with 9.5 g/dL KCl brine.

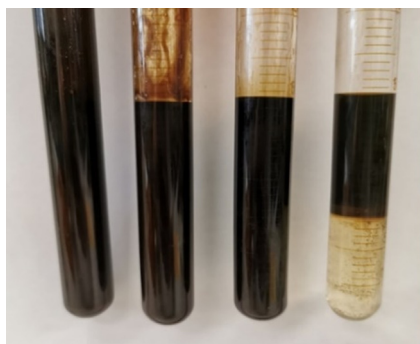


Fig. 14. Emulsions with increasing petroleum ether content, from left to right: 20%, 30%, 50% and 80%.

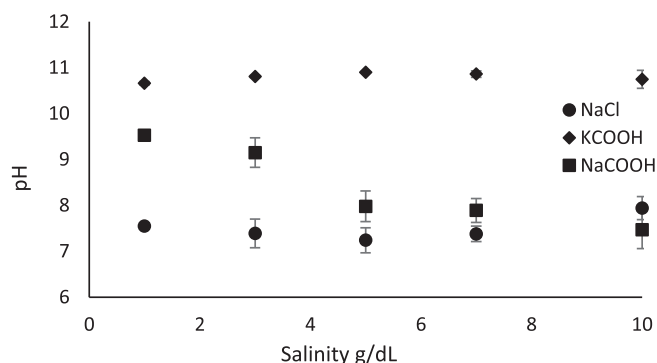


Fig. 15. pH obtained for several concentrations of solutions containing a) a) Sodium Formate (NaCOOH), b) Potassium Formate and c) Sodium Chloride (NaCl).

tral side, slightly acidic. Sodium formate gave a more stable result for salinities of 5 and 10 g/dL, between 7.34 and 7.47 also laying on the neutral side. However, potassium formate brines with salinities from 1 to 7 g/dL gave high pH values, basic mediums of 10.7 to 11.08. This high pH allows the creation of a very stable water in oil emulsion for this specific type of crude oil. In these conditions the natural surfactants present in the crude oil substitute or could also aid commercial surfactants and environmental-friendly surfactants at the interphase stabilizing the emulsion.

Since there was a considerable change in the pH response for these brines, it would be of significance to study the zeta potential of these emulsions. However, these emulsions are considerably stable and therefore it can be presumed that a high zeta potential (either negative or positive) can be attributed to them (Moradi et al., 2011). As a result, zeta potential may not be a critical parameter and therefore not examined further in this study.

This characteristic of potassium formate can be beneficial and detrimental at the same time, depending on the objective that it is desired in the petroleum industry. If this salt is used to create good emulsification with the heavy to medium crude oil present in the reservoir when applying EOR techniques this would be very beneficial, since the high salinity concentration would not affect the emulsion stability. However, if this salt is used for well cleaning and completion, the results would not be the desired since this could create emulsions at the surface which would lead to separation problems in order to retrieve the oil phase for commercial purposes.

The emulsification of Greenzyme appears to be better when crude oil is the oil phase to emulsify. The oil eating bacteria part that is the base of Greenzyme could be behind this better affinity for crude oil. In Fig. 16 it can be observed that there is not an enormous difference in water separation for all the types of brines.

However, in the case of sodium formate the performance of the surfactant is marginally better with a water segregation of 88 %, than for the other two brines for which the segregation is 92 % for 1 g/dL. At 1.5 g/dL the segregation increases to 94 %. This surfactant did not present the same reaction with KCOOH as observed with AOS and CG. Since this surfactant is noticeably acidic in concentrated form with a pH range of 3.5–5 (Deen et al., 2016), and potassium formate brine is basic (as seen on Fig. 15), the overall pH of the brine might had come down towards neutral values of pH. Therefore, affecting the ability of asphaltenes and resins to function as a surfactant/stabilizer and portraying a different outcome.

Table 5 presents a compendium of the solubilization ability for the surfactants tested with medium-heavy crude oil at different salt concentrations. As seen by the colour dominance there was an increase in emulsification from NaCOOH to NaCl to KCOOH.

4.5. Emulsion with condensate oil

The emulsification ability with condensate was also tested, however, with only high surfactant concentrations. As observed in Table 6, the emulsification with condensate oil was not as good as that observed with heptane or medium-heavy crude oil. Most of the emulsions separated with a slight increase in the salinity concentration.

4.6. Emulsion polymerization

A polymer (xanthan gum) was added to emulsions and the samples were tested to determine if the emulsions could demonstrate better stability. The highest surfactant concentration was tested with heptane, condensate and medium-heavy crude oil with DIW, and 5 and 10 g/dL of salt content for all the brines. It was found that adding 0.5 g/dL of xanthan gum to the brine solutions increased the emulsification considerably. Emulsions with heptane and CG or AOS all presented a full emulsion phase with just 0.5 mL of excess oil phase at the top of the emulsion on the highest salt concentrations. Greenzyme attained full emulsification only for DIW, any salt concentration even with the polymer added had full separation when the phases were mixed. Emulsions with condensate had the same trend but the excess oil was present at both salinities 5 and 10 g/dL for CG and AOS. Greenzyme could only be emulsified with DIW. In the case of heavy-medium crude oil there was no excess oil present neither for CG nor AOS. Greenzyme emulsions with this type of oil and xanthan gum could only hold with DIW and 5 g/dL Sodium Formate but other types of salt or concentrations resulted in full separation.

4.7. Droplet size analysis

The classifications referring to droplet size and stability consider the physical and thermodynamic properties of the emulsion system. Therefore, the emulsions can be divided into macroemulsions, nanoemulsions and microemulsions (Moradi et al., 2011). Macroemulsions comprise droplet sizes of a range between 100 nm and 100 μ m, this large size contributes to its thermodynamic instability. These are the most commonly found forms of emulsions. Nanoemulsions have droplets between 20 and 100 nm. The size of the droplets makes them stable, yet they are still thermodynamically unstable. Microemulsions with a droplet size in the range of 5 to 100 nm are the only emulsions considered thermodynamically stable. This range is almost identical to nanoemulsions. However, microemulsions can be formed through spontaneous emulsification and normally have an alcohol phase as a co-surfactant. They also tend to withhold their stability

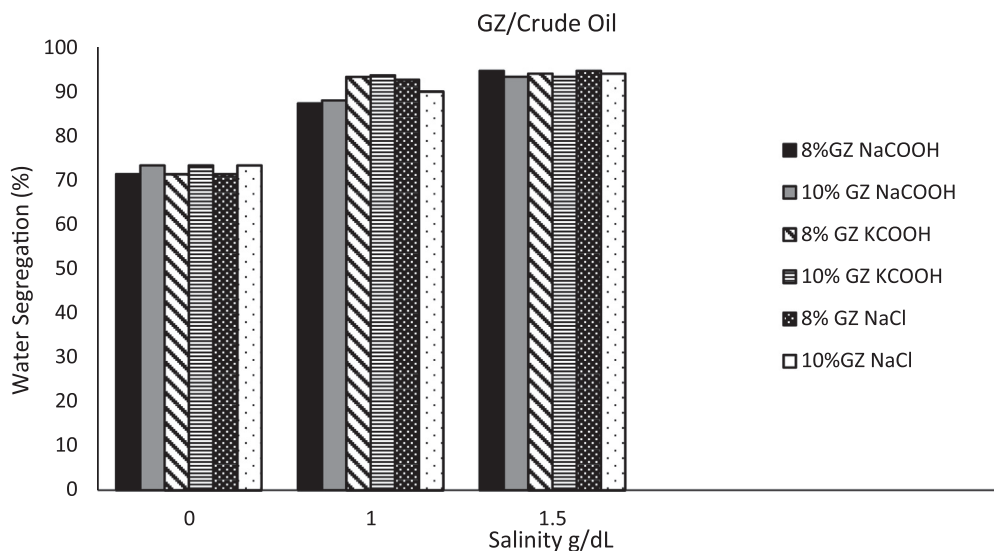


Fig. 16. Water segregation for GZ/Crude oil emulsions with different brine compositions.

Table 5
Water in emulsion phase for medium-heavy crude oil according to surfactant and salinity.

Surfactant% in water		Sodium Formate g/dL				
		0	1	3	5	7
0.4 %-0.8 %	CG	14-25 %	6-7 %	2-6 %	2 %	2 %
2-4 %	AOS	32-37 %	22-23 %	7-12 %	2-5 %	2-5 %
8 %-10 %	GZ	27-29 %	12-13 %	0	0	0
Surfactant% in water		Sodium Chloride g/dL				
		0	1	3	5	7
0.4 %-0.8 %	CG	14-25 %	10-16 %	2-11 %	2-10 %	1-7 %
2-4 %	AOS	32-37 %	15-20 %	4 %	2 %	2 %
8 %-10 %	GZ	27-29 %	8-10 %	0	0	0
Surfactant% in water		Potassium Formate Salt g/dL				
		0	1	3	5	7
0.4 %-0.8 %	CG	14-25 %	8-14 %	19-47 %	48-97 %	74-98 %
2-4 %	AOS	32-37 %	24-25 %	13-22 %	26-52 %	40-74 %
8 %-10 %	GZ	27-29 %	7 %	0	0	0

Water % in emulsion
 Loose emulsion separating in a few minutes
 Emulsion formed but will retain a very small amount of water (1-3 %)
 Emulsion formed but will retain a small amount of water (4-12 %)
 Emulsion formed and will retain a considerable amount of water (13-98 %)

Table 6
Water in emulsion phase for condensate crude oil with AOS, CG and GZ at different salinity conditions.

Surfactant% in water		Salinity g/dL NaCl, Sodium and Potassium Formate				
		0	1	3	5	7
0.8 %	CG	16 %	0	0	0	0
4 %	AOS	12 %	16-20 %	2 %	0	0
10 %	GZ	5 %	0	0	0	0

Water % in emulsion
 Loose emulsion separating in a few minutes
 Emulsion formed but will retain a very small amount of water (1-3%)
 Emulsion formed but will retain a small amount of water (4-12%)
 Emulsion formed and will retain a considerable amount of water (13-20%)

increasing the temperature which creates the difference between all of them.

The size distribution in the emulsion phase tends to have an impact on the emulsion ability to resist flocculation, creaming and coalescence which would lead to phase separation (Abdulredha et al., 2018).

For the light phase heptane was selected to produce the droplet size study as emulsions with condensate were quite unstable and tended to separate faster under the microscope than those containing heptane. The droplet size analysis for 4 % of AOS concentration with NaCl was selected to display by frequency percentage in Fig. 17. Most of the emulsions present a peak at 20 μm for 0-

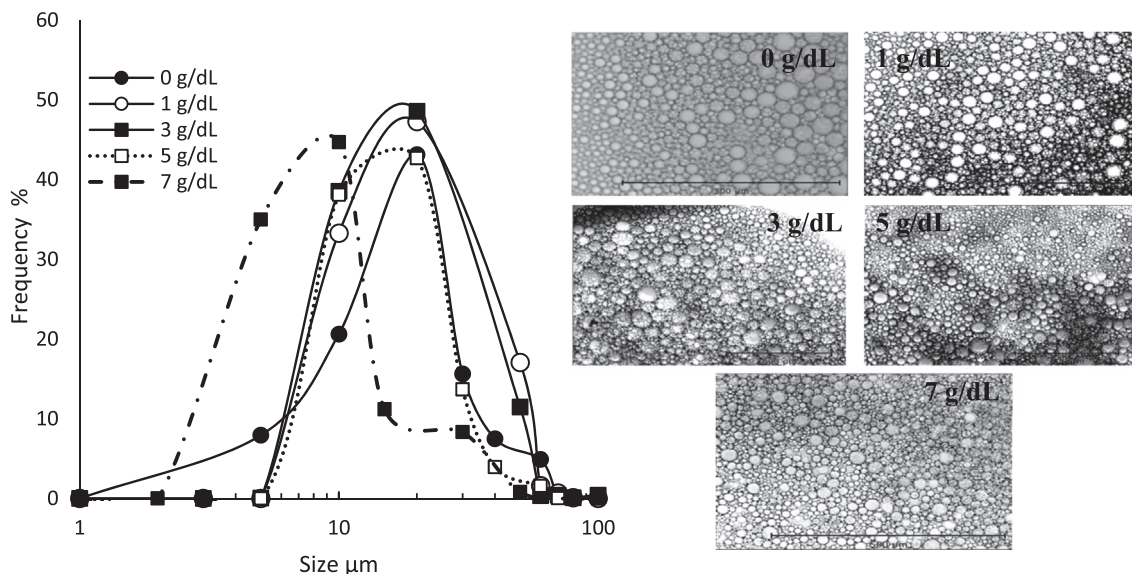


Fig. 17. Droplet size count of emulsions with 4 % AOS/C7 and Sodium Chloride at different salt concentrations. On the right from top to bottom representative images of the emulsions from 0 to 7 g/dL, scale 500 μm .

5 g/dL with an occurrence on this range of 42–48 %. This indicates that about 50 % of the droplets are falling in this size classification. The highest salinity presents the lowest droplet size with a peak at 10 μm , correlating with the rheology data, as seen in next section, which presents the highest viscosity at 7 g/dL with sodium chloride for AOS. Smaller droplets would result in higher viscosity (Li et al., 2019). Yet, these high salinity emulsions seem to be more difficult to study for their droplet size, since at a prolonged contact with the air tends to evaporate it faster than with the other concentrations.

For the emulsions created with crude oil the analysis of the droplet size with KCOOH brine at different concentrations is displayed in Fig. 18 as it presented a different emulsification compared with the other two types of salt. Emulsions with 4 % AOS with crude oil

have a shorter size range than the observed for heptane. This could be attributed to the effect of air on the vaporization of heptane which tended to show larger droplets. The highest salinity portrays the highest droplet count at the smallest size, between 1 and 3 μm , also correlating with the rheology (as seen in section 4.8) and the water content (as in section 4.4). Emulsions with 1 g/dL present the same range, but overall have slightly less droplets in that array when compared indicating a similar emulsion tightness. Following closely 5 g/dL has almost the same response, yet considerably less incidence in droplet sizes between 1 and 2 μm . Increasing salt concentrations portray smaller droplet size as it is affected by the pH as previously discussed. This smaller droplet size produces a tighter emulsion phase giving them stabilities of more than 6 months at room temperature. The droplet size range for CG and NaCl brine

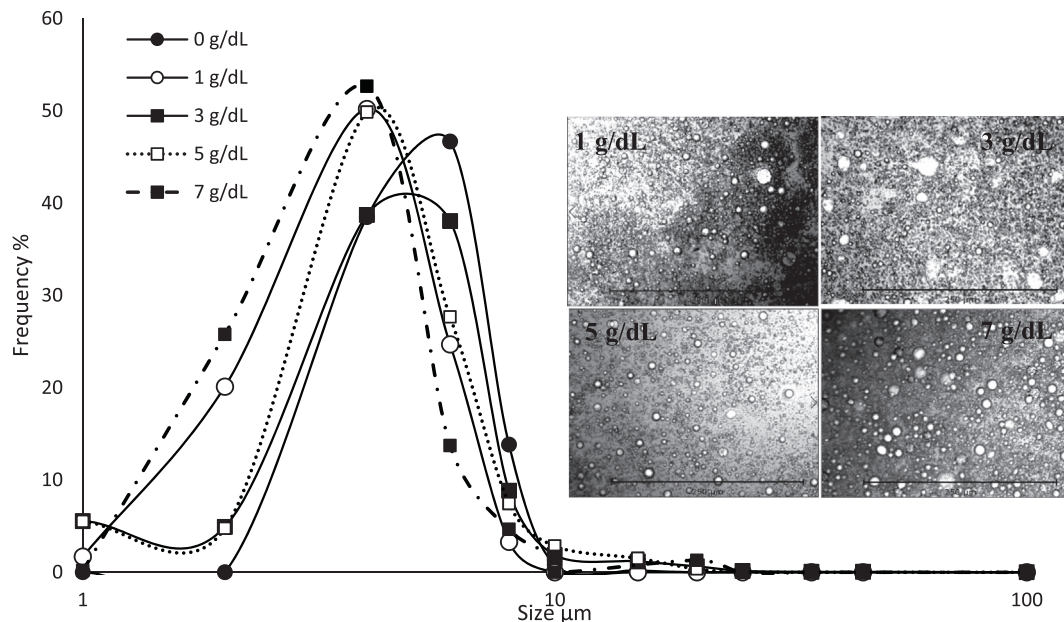


Fig. 18. Droplet size count of emulsions with 4 % AOS/Crude oil and KCOOH brine at different salt concentrations. On the right from top to bottom representative images of the emulsions from 0 to 7 g/dL, scale 500 μm .

(Fig. 19) presents an analogous array for heptane when compared to AOS. However, CG has peaks at a lower diameter of 10 μm . Yet, AOS presented more incidence at higher droplet sizes of 50 μm which did not occur as prominently with CG. The frequency of smaller droplets is also slightly higher for CG. 1 and 5 g/dL present more than 62 % of the droplets with a size of 10 μm . DIW, 3 and

7 g/dL have between 54 and 57 % of the droplets in a range of 15–20 μm .

Emulsions with CG and crude oil presented more droplets per image than both AOS and Greenzyme as shown in Fig. 20. As with AOS it is also presented the results with KCOOH; in this case with a concentration of 0.8 % CG. All the emulsions presented a shorter

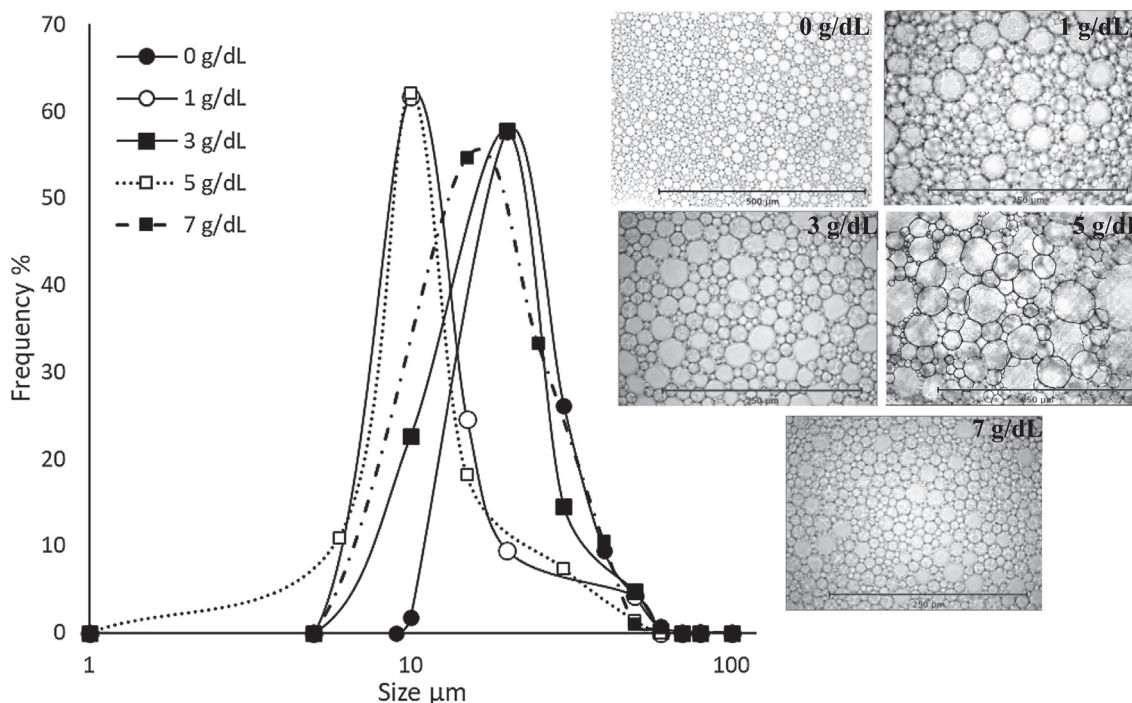


Fig. 19. Droplet size count of emulsions with 0.8 % CG/NaCl brine and heptane at different salt concentrations. On the right from top to bottom, left to right, representative images of the emulsions from 0 to 7 g/dL, scale 250 and 500 μm .

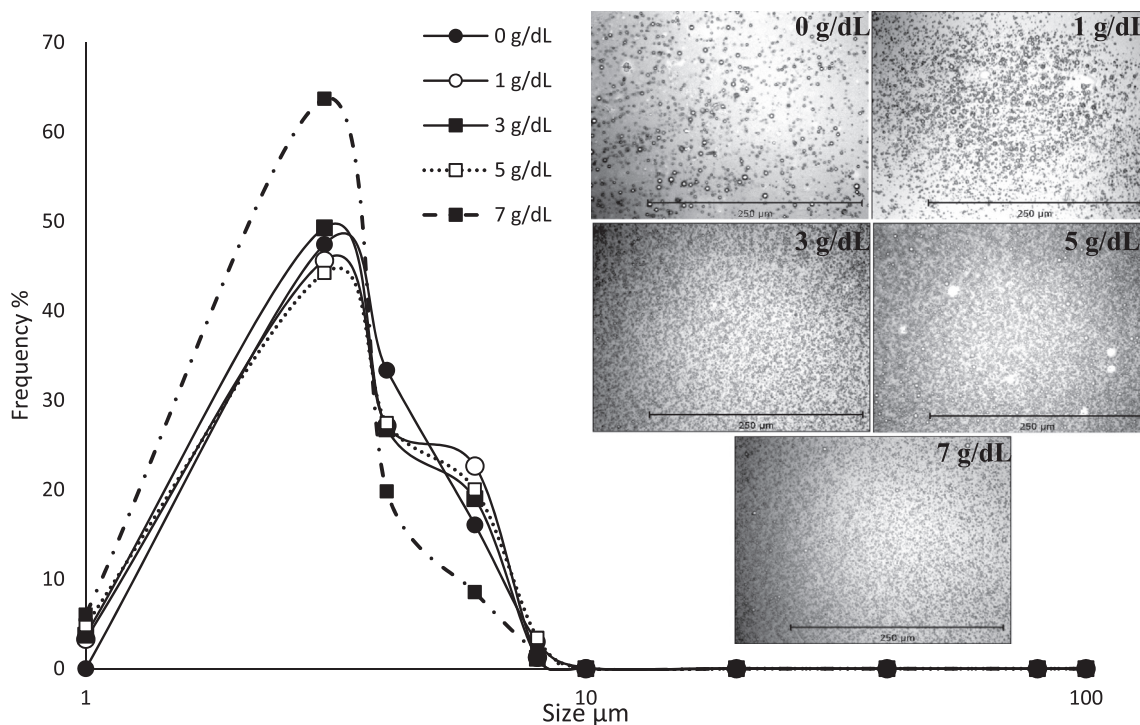


Fig. 20. Droplet size arrangement of 0.8 % Coco Glucoside and Crude oil emulsions with KCOOH brine at different concentrations. Scale of 250 μm .

and more uniform range of droplet size, between 1 and 5 μm . From the micrographs an increase in droplet occurrence as the salinity is augmented is observed, indicative of more water solubilized into the emulsion phase. The topmost peak at 3 μm with an incidence of 63 % corresponds to 7 g/dL, representative of high tightness and stability. Deionized water and the increasing salt concentration samples behaved similarly, with an incidence of 50 % for droplets between 1 and 3 μm , with no droplets larger than 10 μm . The micrographs obtained for KCOOH brine are similar to those reported in 2019 with alkyl polyglycoside of 2–6 μm which were obtained at 90 °C (Kundu et al., 2015). The effect obtained with KCOOH is comparable to that seen with high temperature emulsification ability, which in the case of surfactants classified as APG rises with the surge of temperature.

For Greenzyme the displayed example in Fig. 21 shows the arrangement in droplet size for the emulsion with heptane as the oil phase and 10 % Greenzyme in a NaCl brine. The droplet size range is very similar when compared with the other two surfactants in the case of heptane. This could indicate that the stability of these emulsions is analogous to those obtained with AOS and CG. Greenzyme presents peaks at 15 and 20 μm , with a frequency between 40 and 65 %. The highest salinity tested has the highest incidence at the lowest droplet size diameter, denoting a more stable emulsion. Nevertheless, the droplet size incidence could not be recorded for higher salinities since the emulsions were too unstable. As mentioned, Greenzyme (Fig. 22), seems to present a better performance with crude oil. The highest droplet frequency for emulsions with 8 % Greenzyme in KCOOH brine and medium-heavy crude oil corresponds to DIW with 60 % incidence at 3 μm , frequency % decreases to only 40 % for the peaks in the cases of 1 and 1.5 g/dL. Higher incidence with small droplet size could indicate that the emulsion is more stable for zero salinity. It needs to be noted that the droplet count diminishes as the salinity is augmented, as seen on the micrographs, suggesting that there is less water solubilized into the emulsion phase confirming that the surfactant performance decreases with salinity.

Rheology of Emulsions

Emulsion rheology reflects the internal structure of the emulsion itself and their particle–particle interactions (Pal, 2000). Fig. 23 shows the response of viscosity against shear rate of emul-

sions with AOS and CG with heptane as the oleic phase. Both emulsions presented shear thinning responses. However, those formed with CG have slightly higher viscosity even though they had less surfactant present in the mixture and presented the same oil phase. The considerably large chain length present in polyglucosides yielded an entanglement of rod-like micelles into a densely packed system (Jiang et al., 2011). These systems are formed due to enhanced hydrophobic interactions producing high viscosity and shear thinning with increasing shear rate.

The increase in salinity presents an increase in viscosity, even when the amount of water solubilized into the emulsion phase is less than that contained in emulsions with DIW. Literature mentions that as the amount of solubilized phase decreases in the emulsion, the viscosity should also decrease accordingly (Ariffin et al., 2016). Nevertheless, the presence of salt ions creates more friction between the molecules producing the increase in the viscosity for the emulsions with increased salt content.

The Herschel-Bulkley equation was fitted to AOS rheology data. However, there was a better fit on the response of the data from CG with the power law model. The specific values for the fitting are found in Appendix.

In the case of AOS, the rheology response was similar in classification as most of the cases were shear thinning for the medium-heavy crude oil as shown on Fig. 24. However, there was a clear change in response for Sodium Formate and Sodium Chloride at 7 g/dL. Both cases presented an independent response for viscosity as the shear rate was increased, indicating Newtonian behaviour. This variation might be due to the decrease in water content to about 1–3 % as the droplet–droplet interactions are reduced these yields to a decrease in friction, reducing the viscosity. This could be considered almost as the reading of just bare crude oil. The increase in the dispersed phase directly affects the emulsion behaviour. As it rises, the shear thinning response is more evident. For Sodium Chloride brine with a low salinity of 1 g/dL at low shear rates the response was shear thinning, and from 0.9 1/s onwards the response became Newtonian. This tends to occur due to the unpacking of the molecules from one another and they start to align in the same direction of the flow (Kolotova et al., 2018).

For CG there was a complete change for the rheological behaviour compared with either the response with heptane or the

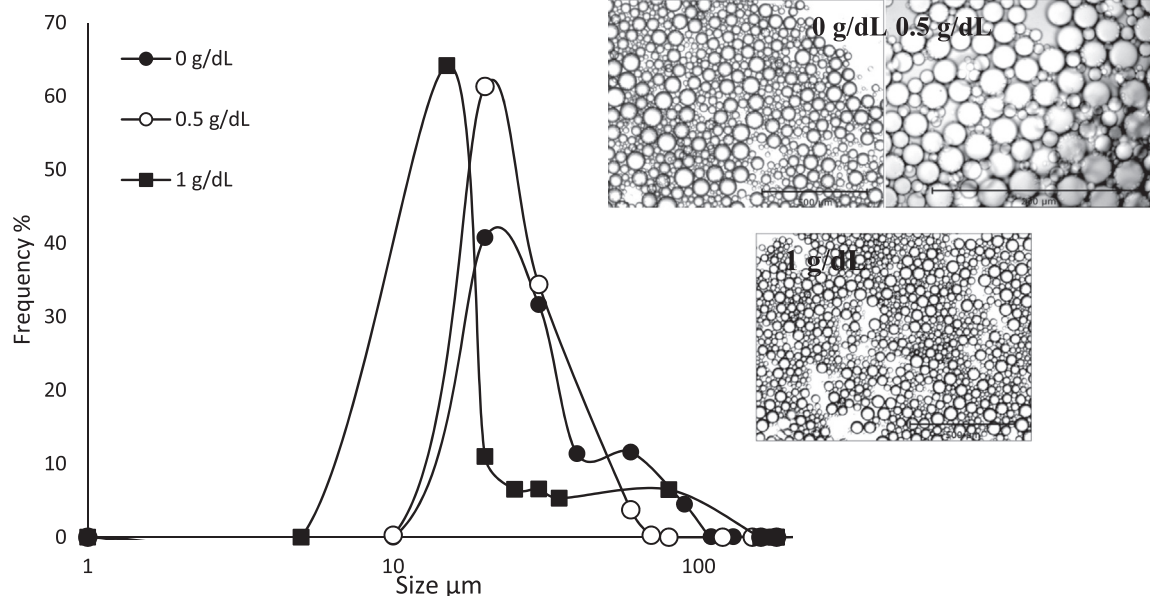


Fig. 21. Emulsion droplet size for 10 % Greenzyme and Heptane. On the right side, from left to right representative images of the droplets for emulsions with 0–1 g/dL with a scale of 250 μm for 0.5 g/dL and 500 μm for 0 and 1 g/dL.

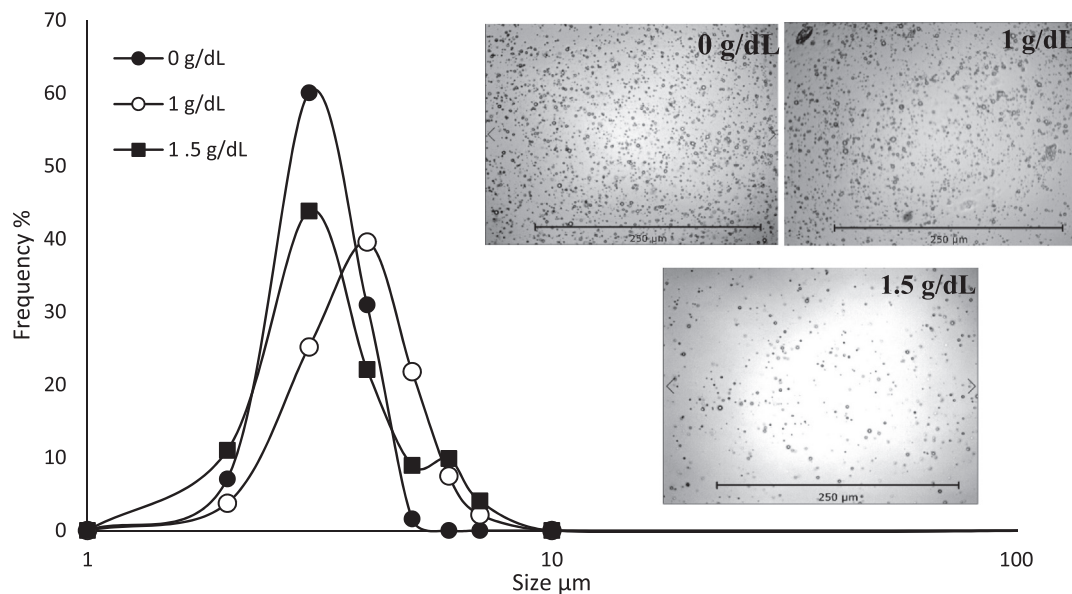


Fig. 22. Droplet size analysis for 8 % Greenzyme in KCOOH brine with medium heavy crude oil. On the right representative micrographs for 0, 1 and 1.5 g/dL can be observed. Scale 250 μm .

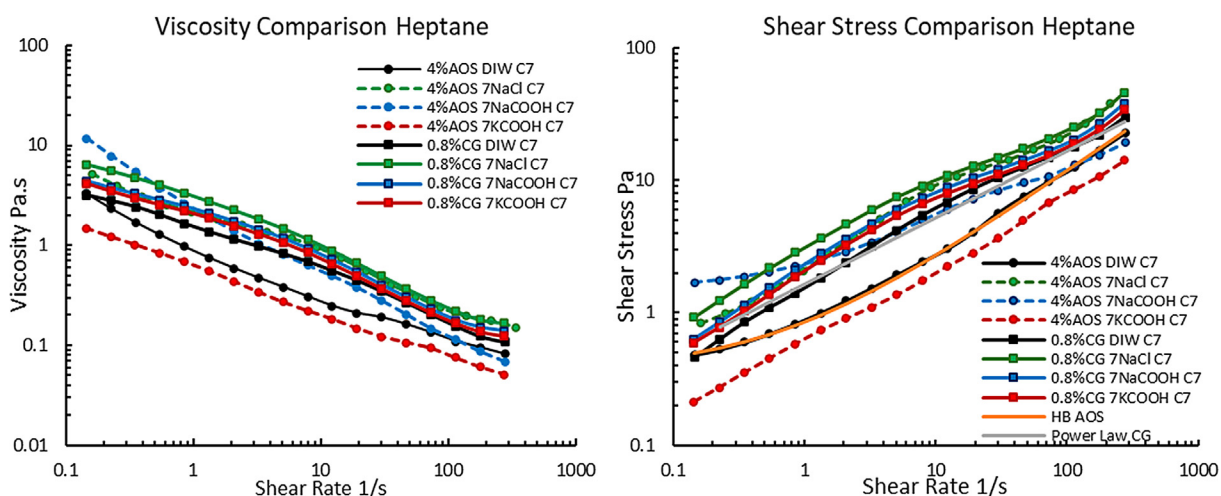


Fig. 23. Viscosity response against shear rate of emulsions with heptane as the oleic phase with AOS and CG at different brine conditions.

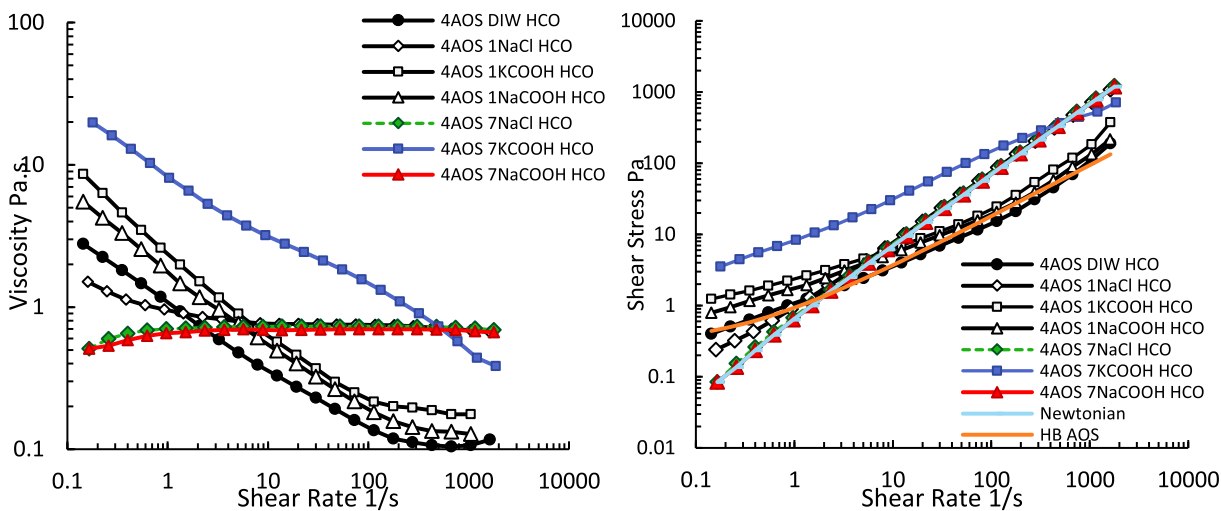


Fig. 24. Rheology response for AOS emulsions with medium-heavy crude oil at different brine conditions.

AOS response with crude oil. All the emulsions presented a Newtonian behaviour instead of shear thinning as previously observed in the other compositions (Fig. 25). The lowest viscosity registered was obtained with DIW which contained about 15–25 % water content into the emulsion phase. But since it did not contain any type of salt the viscosity was still lower compared to the salted emulsions. There is a slight increase in viscosity for 1 g/dL NaCl and 7 g/dL NaCl and sodium formate which overall presented less solubilized water but since they have an increased salt content the viscosity tended to augment. Highest viscosities were obtained for potassium formate brines, higher for the uppermost salt concentration, correlating with the enhanced emulsification at this salt concentration that presented a water content of almost 100 % in the emulsion phase. As a result, incrementing the viscosity considerably as the drop-drop interactions precede an augment in friction producing an increase in viscosity [70]. The change of the type of behaviour could be attributed to being more influenced by the presence of asphaltenes in the crude oil.

As seen on Fig. 26 emulsions formed with condensate presented shear thinning response similar to the emulsions obtained with

heptane. For condensate oil, AOS showed a higher viscosity than that obtained with CG. This prove out to be appropriate since emulsions for CG were not stable when the salinity was increased, hence the only recorded data for CG was for DIW.

4.8. Polymerized emulsion rheology

A clear shear thinning response that was fitted with the Herschel-Bulkley equation was found for both AOS and CG emulsions made with 0.5 g/dL of Xanthan Gum and heptane at different salt conditions. In Fig. 27 the responses for the highest salinity concentration with NaCl are shown. The measurements were almost identical for these emulsions indifferent of the surfactant type or the salt concentration, indicating that the polymer was the main factor accountable for the increase in viscosity. DIW was the lowest response recorded for AOS and CG. Although the difference is not that large. When compared to emulsions without the presence of polymer the viscosity increased approximately 9.65 times at a low shear rate of 0.3 1/s, at shear rates higher than 100 1/s the increment decreased to just about 1.9 times.

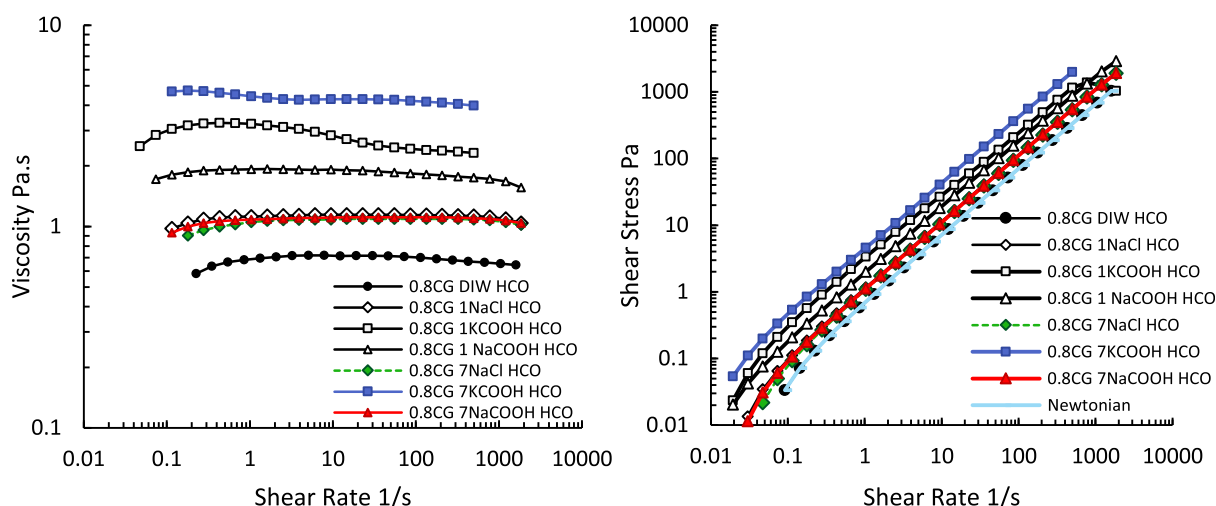


Fig. 25. Rheology response for CG emulsions with medium-heavy crude oil with different brine conditions.

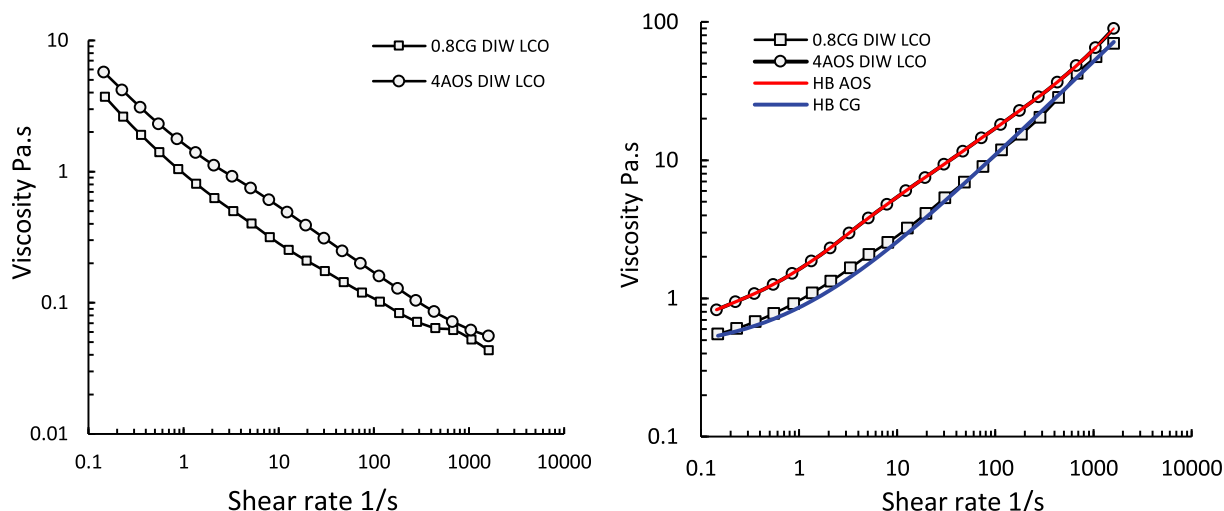


Fig. 26. Rheology response for emulsions with condensate for CG and AOS with Herschel-Bulkley (HB) fit.

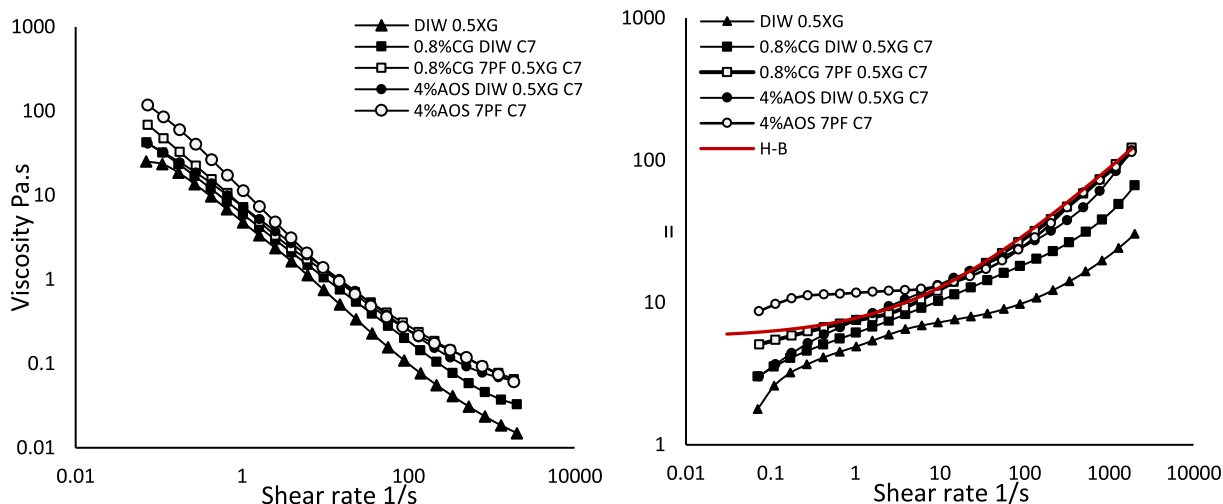


Fig. 27. Viscosity and shear stress responses as a function of shear rate for AOS and CG polymerized emulsions with 7 g/dL NaCl brine and heptane as the oleic phase.

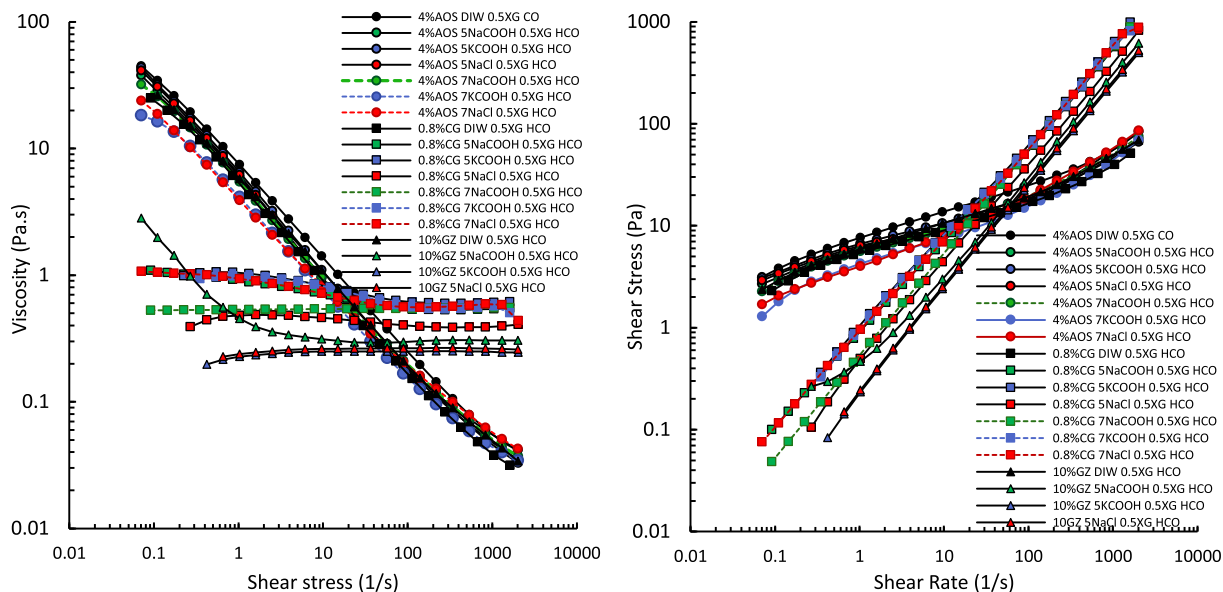


Fig. 28. Viscosity and shear stress responses as a function of shear stress for emulsions with medium heavy crude oil for AOS, CG and GZ.

In the case of medium heavy crude oil rheology recordings can be observed in Fig. 28. For AOS all of the behaviours presented were shear thinning. For CG only the emulsion made with DIW had a strong shear thinning behaviour. The emulsions with increased salinity had a Newtonian behaviour at high shear rates. Greenzyme had similar responses when compared with CG and AOS for emulsions made with DIW, even followed the same trend. However, when salinity was increased the only brine that created a considerably more stable emulsion was sodium formate as the other two had complete phase separation. It also had a shear thinning behaviour. For AOS, when emulsions with and without polymer are compared there is an increase in viscosity at a low shear rate of 0.3 1/s from 2.2 without polymer to 17.3 with polymer, which would be an increase of 690 % in viscosity. In the case of CG, the increase at 0.3 1/s is 1750 %.

For emulsions with XG, all surfactants and condensate had shear thinning behaviour alike those responses found for heptane, as both types of emulsions are made with light crude oils (Fig. 29).

However, the slope is steeper for the condensate, as at the highest shear rates, the viscosity is even lower than that of heptane.

5. Conclusions

The surface tension, emulsification ability and rheology of emulsions created with commercial, sugar based and enzymatic surfactant with sodium and potassium formate and sodium chloride as a base case brine were evaluated. It was observed that the reduction of the surface tension in the presence of electrolytes rests on mechanisms related to the type of surfactant used. For ionic surfactants it is attributed to the reduction of the repulsion between head groups in the presence of salts. For polyglucosides it is a similar effect, the micelle is believed to be more negatively charged, which could be linked to the OH groups present in the molecule and these interact with the water phase hence the similarities with the anionic surfactant. The added electrolytes had a strong effect lowering both surface and interfacial tension regard-

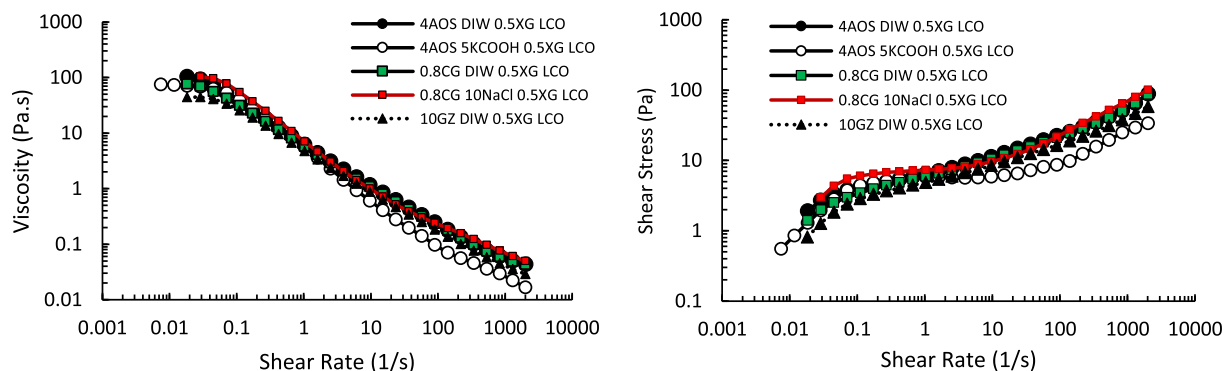


Fig. 29. Viscosity and shear stress responses as a function of shear rate for AOS, CG and Greenzyme polymerized emulsions at various salinities and condensate oil as the oleic phase.

less of the type of surfactant used. Thermodynamical properties of the surfactants indicate that the smallest surface area corresponds to that of CG which allows it to be packed more tightly into the surface. This correlates to the highest surface energy from the three surfactants tested. AOS followed closely the thermodynamical properties of CG. Hence CG could be used instead of Sulfonates when environmental restrictions are in place. Since the Greenzyme molecule is significantly bigger it generates a looser binding of the molecules in the surface obtaining a weak effect on decreasing the interfacial tension.

Emulsification properties of AOS and CG for heptane are equivalent as well as for medium-heavy crude oil. Emulsification with Greenzyme is not possible if the salinity is just slightly high with the salts tested (Sodium and Potassium Formate and Sodium Chloride). In the case of condensate, the emulsion is more stable with AOS than with CG. This stability could be linked to their higher water solubility. Emulsions with Sodium Formate and Chloride behave similarly as there is no considerable change in the pH to create an effect on the crude oil to foment more emulsification. Nevertheless, the readings for surface and interfacial tension are lower for Sodium Formate than for Sodium Chloride which could be attributed to the $-\text{COOH}$ chain as behaves also as a surfactant chain. For emulsions created with Potassium Formate brines and medium-heavy crude oil, the increase of pH activates the heavy hydrocarbon particles creating a very stable emulsion phase. This could be detrimental from the oil production point of view since emulsions are not desirable. However, this needs to be considered if the emulsion is the anticipated or required phase. It was observed that Potassium Formate tended to lower the interfacial tension more than the other two types of salts. The addition of xanthan gum effectively stabilizes emulsions with CG or AOS even at high salt concentrations for all types of salts and oils. All the emulsions obtained in this study can be classified as a macroemulsions due to their droplet size. CG emulsion phase presented a Newtonian behaviour, indicating that even at high shear rates this behaviour could be achieved in the production stage of a well and the emulsion will remain stable. AOS and Greenzyme presented a shear thinning behaviour which could be beneficial since the emul-

sion would not be as stable and it might be able to be separated during the production phase itself.

CRediT authorship contribution statement

Linda Tatiana Lezama: Conceptualization. **Roozbeh Rafati:** Conceptualization, Supervision. **Amin Sharifi Haddad:** Conceptualization, Supervision.

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors would like to thank BTP Solutions for providing the Greenzyme samples to perform the experiments, the School of Engineering at the University of Aberdeen for providing research facilities to conduct this research. They acknowledge the National Council of Science and Technology (CONACYT) and the Secretariat of Energy (SENER) of Mexico for providing funding. The authors also need to express their special thanks to our Laboratory Technicians, Jennifer Freeman and Iona Copley for helping us throughout the way.

Appendix

Rheology fitting parameters for AOS, CG and GZ with different brines and oil compositions.

See [Table 7](#), [Table 8](#), [Table 9](#).

Table 7

Fitting parameters and for AOS. HB-Herschel-Bulkley, PL-Power Law, DIW-Deionized water, KCOOH-Potassium Formate, NaCOOH-Sodium Formate, NaCl-Sodium Chloride, C7-Heptane, MCO-Medium Crude Oil, LCO-Condensate, XG-Xanthan Gum. 1, 5 7 g/dL.

AOS/C7	HB	HB	HB	HB	HB	HB	HB
Parameter	DIW	1 KCOOH	1 NaCOOH	1 NaCl	7 KCOOH	7 NaCOOH	7 NaCl
Yield Stress	0.37	0	0	0	0.05	1.47	0.37
Consistency Index	0.48	1.62	1.4	1.56	0.58	0.89	1.75
Flow Index	0.69	0.52	0.6	0.48	0.58	0.55	0.57
AOS/C7/XG	HB	HB	HB	HB	HB	HB	HB
Parameter	DIW	5 KCOOH	5 NaCOOH	5 NaCl	7 KCOOH	7 NaCOOH	7 NaCl
Yield Stress	6.38	7.09	4.97	4.97	8.67	5.97	5.90
Consistency Index	0.83	1.51	2.24	2.24	1.13	1.12	1.74
Flow Index	0.64	0.55	0.45	0.45	0.60	0.62	0.57
AOS/MCO	PL	HB	PL	PL	PL	Newtonian	Newtonian
Parameter	DIW	1 KCOOH	1 NaCOOH	1 NaCl	7 KCOOH	7 NaCOOH	7 NaCl
Yield Stress		2.86					
Consistency Index	1.14	0.25	1.63	1.14	8.54	0.67	0.70
Flow Index	0.60	0.94	0.59	0.89	0.60		
AOS/MCO/XG	HB	HB	HB	HB	PL	HB	PL
Parameter	DIW	5 KCOOH	5 NaCOOH	5 NaCl	7 KCOOH	7 NaCOOH	7 NaCl
Yield Stress	5.14	4.68	5.21	4.72		7.41	
Consistency Index	2.38	1.61	0.79	1.04	7.10	0.78	6.80
Flow Index	0.45	0.47	0.60	0.54	0.30	0.58	0.31
AOS/LCO	HB	HB	HB	HB			
Parameter	DIW	1 KCOOH	1 NaCOOH	1 NaCl			
Yield Stress	0.50	0.02	0.02	0.02			
Consistency Index	0.89	1.40	1.45	1.51			
Flow Index	0.62	0.50	0.50	0.58			
AOS/LCO/XG	HB	HB	HB	HB	HB	HB	HB
Parameter	DIW	5 KCOOH	5 NaCOOH	5 NaCl	7 KCOOH	7 NaCOOH	7 NaCl
Yield Stress	3.46	3.10	2.37	3.94	3.86	3.45	5.08
Consistency Index	2.01	0.66	0.04	0.46	0.33	1.62	1.64
Flow Index	0.48	0.51	0.89	0.58	0.63	0.49	0.51

Table 8

Fitting parameters and for CG. HB-Herschel-Bulkley, PL-Power Law, DIW-Deionized water, KCOOH-Potassium Formate, NaCOOH-Sodium Formate, NaCl-Sodium Chloride, C7-Heptane, MCO-Medium Crude Oil, LCO-Condensate, XG-Xanthan Gum. 1, 5 7 g/dL.

CG/C7	Power Law	PL	PL	PL	PL	PL	Newtonian
Parameter	DIW	1 KCOOH	1 NaCOOH	1 NaCl	7 KCOOH	7 NaCOOH	7 NaCl
Yield Stress							
Consistency Index	1.7	2.5	1.9	1.8	1.8	1.8	1.0
Flow Index	0.5	0.5	0.5	0.7	0.6	0.6	
CG/C7/XG	HB	HB	HB	HB	HB	HB	HB
Parameter	DIW	5 KCOOH	5 NaCOOH	5 NaCl	7 KCOOH	7 NaCOOH	7 NaCl
Yield Stress	3.12	3.73	4.73	4.31	5.17	5.00	5.31
Consistency Index	1.82	1.40	0.65	1.97	1.69	1.81	2.18
Flow Index	0.45	0.56	0.67	0.52	0.56	0.54	0.53
CG/MCO	Newtonian	Newtonian	Newtonian	Newtonian	Newtonian	Newtonian	Newtonian
Parameter	DIW	1 KCOOH	1 NaCOOH	1 NaCl	7 KCOOH	7 NaCOOH	7 NaCl
Yield Stress							
Consistency Index	0.650	2.77	1.86	1.15	4.30	1.10	1.05
Flow Index							
CG/MCO/XG	HB	HB	Newtonian	Newtonian	Newtonian	Newtonian	Newtonian
Parameter	DIW	5 KCOOH	5 NaCOOH	5 NaCl	7 KCOOH	7 NaCOOH	7 NaCl
Yield Stress	3.35	0.05					
Consistency Index	1.69	1.37	0.58	0.43	0.88	0.55	0.58
Flow Index	0.50	0.93					
CG/LCO	HB						
Parameter	DIW						
Yield Stress	0.42						
Consistency Index	0.44						
Flow Index	0.69						
CG/LCO/XG	HB	HB	HB	HB	HB	HB	HB
Parameter	DIW	5 KCOOH	5 NaCOOH	5 NaCl	7 KCOOH	7 NaCOOH	7 NaCl
Yield Stress	3.35	2.70	1.70	3.40	5.04	3.35	4.80
Consistency Index	2.20	0.02	0.08	0.02	3.23	1.29	1.48
Flow Index	0.46	0.92	0.75	0.96	1.46	0.54	0.54

Table 9

Fitting parameters and for GZ. HB-Herschel-Bulkley, PL-Power Law, DIW-Deionized water, KCOOH-Potassium Formate, NaCOOH-Sodium Formate, NaCl-Sodium Chloride, C7-Heptane, MCO-Medium Crude Oil, LCO-Condensate, XG-Xanthan Gum. 1, 5 7 g/dL.

GZ/C7				
Parameter	DIW			
Yield Stress	N/A Unstable			
Consistency Index				
Flow Index				
GZ/C7/XG				
Parameter	DIW	HB	HB	HB
Yield Stress	0.05	5 KCOOH	5 NaCOOH	5 NaCl
Consistency Index	0.30	-0.18	0.05	-0.22
Flow Index	1.00	0.27	0.30	0.29
GZ/MCO	1.00	0.99	1.00	0.98
Parameter	Newtonian			
Yield Stress	DIW			
Consistency Index	0.612			
Flow Index				
GZ/MCO/XG				
Parameter	HB	Newtonian	HB	Newtonian
Yield Stress	DIW	5 KCOOH	5 NaCOOH	5 NaCl
Consistency Index	3.35		0.20	
Flow Index	1.69	0.25	0.30	0.27
GZ/LCO	0.50		1.00	
Parameter	HB			
Yield Stress	DIW			
Consistency Index	0.01			
Flow Index	1.1			
GZ/LCO/XG	0.63			
Parameter	HB			
Yield Stress	DIW			
Consistency Index	1.566			
Flow Index	2.118			
GZ/LCO	0.427			

References

- Abdulredha, M.M., Hussain, S.A., Abdullah, L.C., 2018. Overview on petroleum emulsions, formation, influence and demulsification treatment techniques. *Arab. J. Chem.*
- Ahmed, N.S., Nassar, A.M., Zaki, N.N., Gharieb, H.K.H., 1999. Stability and rheology of heavy crude oil-in-water emulsion stabilized by an anionic-nonionic surfactant mixture. *Pet. Sci. Technol.* 17 (5-6), 553-576.
- N. Akhlaghi, S. Riahi, and R. parvaneh, "Interfacial Tension Behavior of a Nonionic Surfactant in Oil/Water System; Salinity, pH, Temperature, and Ionic Strength Effects," *J. Pet. Sci. Eng.*, vol. 198, no. April 2020, p. 108177, 2020.
- Ananda, K., Yadav, O.P., Singh, P.P., 1991. Studies on the surface and thermodynamic properties of some surfactants in aqueous and water+1,4-dioxane solutions. *Colloids and Surfaces* 55, 345-358.
- Ariffin, T.S.T., Yahya, E., Husin, H., 2016. The rheology of light crude oil and water-in-oil-emulsion. *Procedia Eng.* 148, 1149-1155.
- Balzer, D., 1993. Cloud Point Phenomena in the Phase Behavior of Alkyl Polyglucosides in Water. *Langmuir* 9 (12), 3375-3384.
- Bansal, D.O.S.V.K., 1978. The Effect of Ethoxylated Sulfonates on Salt Tolerance and Optimal Salinity of Surfactant Formulations for Tertiary Oil Recovery. *Soc. Pet. Eng.*, 1-6
- Y. Barakat et al., "The Phase Behavior of Simple Salt-Tolerant Sulfonates," no. December, pp. 913-918, 1983.
- Bashir, A., Sharifi Haddad, A., Rafati, R., 2022. A review of fluid displacement mechanisms in surfactant-based chemical enhanced oil recovery processes: Analyses of key influencing factors. *Pet. Sci.*, Nov. 19 (3), 1211-1235.
- Baviere, M., Bazin, B., Noik, C., 1988. Surfactants for EOR: Olefin Sulfonate Behavior at High Temperature and Hardness. *SPE Reserv. Eng.* 3 (2), 597-603.
- Bermúdez-Salguero, C., Gracia-Fadrique, J., 2015. Gibbs excess and the calculation of the absolute surface composition of liquid binary mixtures. *J. Phys. Chem. B* 119 (17), 5598-5608.
- Beunen, J.A., Ruckenstein, E., 1982. The effect of salting out and micellization on interfacial tension. *Adv. Colloid Interface Sci.* 16 (1), 201-231.
- Bybee, K., Nov. 2006. Formate-Based Reservoir-Drilling Fluid Meets High-Temperature Challenges. *J. Pet. Technol.* 58 (11), 57-59.
- M. Byrne et al., "Formate Brines : A Comprehensive Evaluation of Their Formation Damage Control Properties Under Realistic Reservoir Conditions," 2002.
- Caenn, R., Darley, H.C.H., Gray, G.R., 2016. *Introduction to Drilling Fluids*.
- D. K. Chattoraj and K. S. Birdi, *Adsorption and the Gibbs Surface Excess*, vol. 114, no. 2859. Boston, MA: Springer US, 1984.
- G. R. Deen, J. Skovgaard, and J. S. Pedersen, 6 - Formation and properties of nanoemulsions. Elsevier Inc., 2016.
- Downs, J.D., Killie, S., Whale, G.F., Inglesfield, C., Inti, S., Mij, P., 1994. "Development of Environmentally Benign Formate-Based Drilling and Completion Fluids".
- J. J. D. Downs, "Formate Brines: Novel Drilling and Completion Fluids for Demanding Environments," *SPE Int. Symp. Oilf. Chem.*, no. March 1993, pp. 267-279, 1993.
- Farajzadeh, R., Krastev, R., Zitha, P.L.J., 2008. Foam films stabilized with alpha olefin sulfonate (AOS). *Colloids Surfaces A Physicochem. Eng. Asp.* 324 (1-3), 35-40.
- U. Felix, T. O. Ayodele, and O. Olalekan, "Surfactant-Polymer Flooding Schemes (A Comparative Analysis)," *Niger. Annu. Int. Conf. Exhib. held Lagos, Nigeria*, 2015.
- Herschel, W.H., Bulkley, R., 1926. Konsistenzmessungen von Gummi-Benzollösungen. *Kolloid-Zeitschrift* 39 (4), 291-300.
- Howard, S.K., 1995. Formate Brines for Drilling and Completion: State of the Art. *Soc. Automob. Eng.*, 1-14
- S. Iglauer, Y. Wu, P. J. Shuler, M. Blanco, Y. Tang, and W. A. Goddard, "Alkyl Polyglycoside Surfactants for Improved Oil Recovery," in *SPE/DOE Symposium on Improved Oil Recovery*, 2004.
- Jha, N.K., Iglauer, S., Sangwai, J.S., 2018. Effect of Monovalent and Divalent Salts on the Interfacial Tension of n -Heptane against Aqueous Anionic Surfactant Solutions. *J. Chem. Eng. Data* 63 (7), 2341-2350.
- L. C. Jiang, M. Basri, D. Omar, M. B. Abdul Rahman, A. B. Salleh, and R. N. Z. Raja Abdul Rahman, "Self-assembly behaviour of alkylpolyglucosides (APG) in mixed surfactant-stabilized emulsions system," *J. Mol. Liq.*, vol. 158, no. 3, pp. 175-181, 2011.
- Jones, G., Ray, W.A., 1941. The surface tension of solutions of electrolytes as a function of the concentration. III. Sodium chloride. *J. Am. Chem. Soc.* 63 (12), 3262-3263.
- Kanicky, J.R., Pandey, S., Shah, D.O., 2001. "Surface Chemistry in the Petroleum Industry".
- Khusainova, A., Nielsen, S.M., Pedersen, H.H., Woodley, J.M., Shapiro, A., 2015. Study of wettability of calcite surfaces using oil-brine-enzyme systems for enhanced oil recovery applications. *J. Pet. Sci. Eng.* 127, 53-64.
- M. Kjellin and I. Johansson, *Surfactants from Renewable Resources*, 1st ed. Chichester, UK: John Wiley & Sons, Ltd, 2010.
- Kolotova, D.S., Kuchina, Y.A., Petrova, L.A., Voron'ko, N.G., Derkach, S.R., 2018. Rheology of Water-in-Crude Oil Emulsions: Influence of Concentration and Temperature. *Colloids and Interfaces* 2 (4), 64. <https://doi.org/10.3390/colloids2040064>.
- Kundu, P., Kumar, V., Mishra, I.M., 2015. Modeling the steady-shear rheological behavior of dilute to highly concentrated oil-in-water (o/w) emulsions: Effect of temperature, oil volume fraction and anionic surfactant concentration. *J. Pet. Sci. Eng.* 129, 189-204.
- Li, G., Chen, L., Ruan, Y., Guo, Q., Liao, X., Zhang, B., 2019. Alkyl polyglycoside: a green and efficient surfactant for enhancing heavy oil recovery at high-temperature and high-salinity condition. *J. Pet. Explor. Prod. Technol.* 9 (4), 2671-2680.
- Majeed, T., Sølling, T.I., Kamal, M.S., 2019. Foamstability: The interplay between salt-, surfactant- and critical micelle concentration. *J. Pet. Sci. Eng.* 187 (December), 2020.
- Messler, D., Kippie, D., Broach, M., Benson, D., 2007. "A Potassium Formate Milling Fluid Breaks the 400° Fahrenheit Barrier in a Deep Tuscaloosa Coiled Tubing. Clean-out".

- Minofar, B., Jungwirth, P., Das, M.R., Kunz, W., Mahiuddin, S., 2007. Propensity of formate, acetate, benzoate, and phenolate for the aqueous solution/vapor interface: Surface tension measurements and molecular dynamics simulations. *J. Phys. Chem. C* 111 (23), 8242–8247.
- Miyagishi, S., Okada, K., Asakawa, T., 2001. Salt effect on critical micelle concentrations of nonionic surfactants, N-acyl-N-methylglucamides (MEGAN). *J. Colloid Interface Sci.* 238 (1), 91–95.
- Moradi, M., Alvarado, V., Huzurbazar, S., 2011. Effect of Salinity on Water-in-Crude Oil Emulsion: Evaluation through Drop-Size Distribution Proxy. *Energy & Fuels* 25 (1), 260–268.
- Mueller, S., Llewellyn, E.W., Mader, H.M., 2010. The rheology of suspensions of solid particles. *Proc. R. Soc. A Math. Phys. Eng. Sci.*, Apr. 466 (2116), 1201–1228.
- Mukherjee, I., Moulik, S.P., Rakshit, A.K., Mar. 2013. Tensiometric determination of Gibbs surface excess and micelle point: A critical revisit. *J. Colloid Interface Sci.* 394 (1), 329–336.
- Pal, R., 2000. Shear viscosity behavior of emulsions of two immiscible liquids. *J. Colloid Interface Sci.* 225 (2), 359–366.
- Pantelic, I., Cuckovic, B., 2014. "Alkyl Polyglucosides: An emerging class of sugar surfactants", *Alkyl Polyglucosides From Nat. Surfactants to Prospect.* *Deliv. Syst.*, 1–19
- Para, G., Jarek, E., Warszyński, P., Adamczyk, Z., 2003. Effect of electrolytes on surface tension of ionic surfactant solutions. *Colloids Surfaces A Physicochem. Eng. Asp.* 222 (1–3), 213–222.
- Puerto, M.C., Gale, W.W., 1976. Estimation of Optimal Salinity and Solubilization Parameters for Alkylorthoxylylene Sulfonate Mixtures. *Spe-Aime* 5814, 193–200.
- M. Rahayem, P. Mostaghimi, Y. A. Alzahid, A. Halim, L. Evangelista, and R. T. Armstrong, "Enzyme Enhanced Oil Recovery EOR: A Microfluidics Approach," in March 21, 2019, 2019, no. Sep 2008.
- W. Renpu, "Completion and Perforating Fluids," *Adv. Well Complet. Eng.*, pp. 171–220, 2011.
- M. J. Rosen and J. T. Kunjappu, *Surfactants and Interfacial Phenomena*. Hoboken, NJ, USA: John Wiley & Sons, Inc., 2012.
- Saasen, A. et al., 2002. Drilling HT / HP Wells Using a Cesium Formate Based Drilling Fluid. *IADC/SPE Drill. Conf.*, 1–6
- V. Santanna, T. D. C. Dantas, and A. Neto, "The Use of Microemulsion Systems in Oil Industry," *Microemulsions - an Introd. to Prop. Appl.*, no. Figure 2, pp. 161–174, 2012.
- Savic, S., Pantelic, I., Lukic, M., Markovic, B., Milic, J., 2014. "Behind the Alkyl Polyglucoside-based structures: Lamellar liquid crystalline and lamellar gel phases in different emulsion systems", in *Alkyl Polyglucosides*. Elsevier, 21–52.
- Schick, M.J., Atlas, S.M., Eirich, F.R., 1962. Micellar structure of non-ionic detergents. *J. Phys. Chem.* 66 (7), 1326–1333.
- Schindelin, J., Arganda-Carreras, I., Frise, E., Kaynig, V., Longair, M., Pietzsch, T., Preibisch, S., Rueden, C., Saalfeld, S., Schmid, B., Tinevez, J.-Y., White, D.J., Hartenstein, V., Eliceiri, K., Tomancak, P., Cardona, A., 2012. Fiji: An open-source platform for biological-image analysis. *Nat. Methods* 9 (7), 676–682.
- L. L. Schramm, *Surfactants. Fundamentals and Applications in the Petroleum Industry*. Cambridge University, 2000.
- Shinoda, K., Yamaguchi, T., Hori, R., 1961. The Surface Tension and the Critical Micelle Concentration in Aqueous Solution of β -D-Alkyl Glucosides and their Mixtures. *Bull. Chem. Soc. Jpn.* 34 (2), 237–241.
- Staszak, K., Wieczorek, D., Michocka, K., 2015. Effect of sodium chloride on the surface and wetting properties of aqueous solutions of cocamidopropyl betaine. *J. Surfactants Deterg.* 18 (2), 321–328.
- Strassner, J.E., 1968. Effect of pH on Interfacial Films and Stability of Crude Oil-Water Emulsions. *J. Pet. Technol.* 20 (03), 303–312.
- Tadros, T.F., 2013. *Emulsion Formation, Stability, and Rheology*. *Emuls. Form. Stab.*, 1–76
- T. F. Tadros, *Applied Surfactants*. Wiley, 2005.
- A. S. Technologies, "Greenzyme MSDS." Houston, Texas, 2018.
- Udoh, T., Vinogradov, J., 2019. Experimental Investigations of Behaviour of Biosurfactants in Brine Solutions Relevant to Hydrocarbon Reservoirs. *Colloids and Interfaces* 3 (1), 24.
- Walstra, P., 1993. Principles of emulsion formation. *Chem. Eng. Sci.* 48 (2), 333–349.
- Y. Wang, A. Kantzas, B. Li, Z. Li, Q. Wang, and M. Zhao, "New Agent for Formation-Damage Mitigation in Heavy-Oil Reservoir: Mechanism and Application," *Proc. SPE Int. Symp. Exhib. Form. Damage Control*, 2008.
- Wang, Y., Liu, X., Bai, L., Niu, J., 2017. Influence of alkyl chain length of alpha olefin sulfonates on surface and interfacial properties. *J. Dispers. Sci. Technol.* 38 (12), 1764–1769.
- Wang, Y., Liu, X., Jiao, T., Niu, J., 2017. Performance Comparison Between Internal Olefin Sulfonates and Alpha Olefin Sulfonates. *J. Surfactants Deterg.* 20 (1), 183–191.
- Wang, C., Wang, X., Liu, F., Jiang, Z., Lin, X., 2018. Surface concentration or surface excess, which one dominates the surface tension of multicomponent mixtures? *Colloid Polym. Sci.* 296 (1), 89–93.
- Weissenborn, P.K., Pugh, R.J., 1996. Surface Tension of Aqueous Solutions of Electrolytes: Relationship with Ion Hydration, Oxygen Solubility, and Bubble Coalescence. *J. Colloid Interface Sci.* 184 (2), 550–563.
- Winsor, P.A., 1948. Hydrotropy, solubilisation and related emulsification processes. *Trans. Faraday Soc.* 44, 376. <https://doi.org/10.1039/tf9484400376>.
- Zana, R., 1995. Aqueous surfactant-alcohol systems: A review. *Adv. Colloid Interface Sci.* 57, 1–64.
- Zeppieri, S., Rodríguez, J., López De Ramos, A.L., 2001. Interfacial tension of alkane + water systems. *J. Chem. Eng. Data* 46 (5), 1086–1088.