



Influence of salt and acrylamide copolymer on the stability and TOG of brine/crude oil emulsions

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Abstract

The formation of water/oil (w/o) emulsions is undesirable for the oil industry since they negatively impact extraction and transport. Resins and asphaltenes are considered the main interfacially active natural components responsible for the stability of these emulsions, although other parameters can also affect this stability. Injection of polymer solutions is one of the methods aiming to increase oil production, but its influence on w/o emulsions' stability and the quality of the separated water is still not clear, mainly for heavy oils. Therefore, in this work we used a heavy oil to prepare w/o emulsions without and with 450 ppm of acrylamide copolymer (FLOPAAM AN 125) in brine, without and with 650 ppm of demulsifier in the oil phase. The influence of the salt concentration on the stability of the w/o emulsions and on the total oil and grease (TOG) of the separated water was evaluated by the bottle test and fluorimetry, respectively. Increasing salinity in the range of ~35,000 ppm to ~63,000 ppm was associated with lower emulsion stability and TOG of separated water. These parameters then remained almost constant from ~63,000 to 90,000 ppm of salts, except the emulsion containing only acrylamide copolymer, in which the stability kept decreasing. The acrylamide copolymer and demulsifier provoked a decrease in the emulsion stability, although the effect of both together was not additive. Low TOG was achieved using only the demulsifier. Acrylamide copolymer alone provoked a decrease in the quality of the separated water, an effect that was enhanced in the presence of the demulsifier.

Keywords Water-in-crude oil emulsion · Emulsion Stability · Total oil and grease · Polyacrylamide copolymer

Introduction

Approximately 80% of crude oil extracted is in the form of water-in-oil (w/o) emulsions (Kang et al. 2011). The formation of w/o emulsions is undesirable for the oil industry, since they negatively impact extraction and transport, and

consequently increase the cost of oil production (Yang et al. 2014; Subramanian et al. 2017; Umar et al. 2018). The formation of an emulsion occurs by mixing two liquids that are immiscible. One of these liquids will be in the form of microdroplets suspended in the mixture's other component. In a w/o emulsion, water (brine) will be found as microdroplets, suspended in the oil phase. The oil phase impairs the mobility of the droplets, hampering their collision and the resulting coalescence process. However, emulsions are thermodynamically unstable systems, so aqueous and oil phases tend to separate to reduce the interfacial area (Kilpatrick 2012; Wong et al. 2015; Umar et al. 2018; Kamkar et al. 2020). This separation can take a long time, so demulsifiers are used to accelerate the emulsion's destabilization (Le Folloc et al. 2010; Maia Filho et al. 2012; Del Carpio et al. 2014).

Since reservoirs contain crude oils with different characteristics, it is necessary to study the factors that lead to the formation of emulsions to apply effective destabilization

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actions (Thomas et al. 2001; Oliveira et al. 2018; Umar et al. 2018). Regarding the crude oil composition, asphaltenes are considered to be the main cause of emulsions' stability, since they form a resistant viscoelastic interfacial film at the water-oil interface, hindering the process of droplet coalescence and making the emulsion more stable (Le Folletec et al. 2010; Hazrati et al. 2018; Umar et al. 2018). Several factors can impact the stability of w/o emulsions, such as: surface tension; oil composition; salt concentration; temperature; pH; water content; oil and grease content; size and size distribution of droplets; speed and time of shearing; and presence of solid particles, nanoparticles or amphiphilic polymers (Ghannam 2005; Le Folletec et al. 2010; Kang et al. 2011; Yang et al. 2014; Kamkar et al. 2020).

Studies have reported that rising temperature generates an increase in the kinetic energy of the droplets and a decrease in the viscosity of the oil, increasing the probability of collisions between the oil droplets, which facilitates their coalescence and increases the size of the droplets, thus generating less stable emulsions (Fan et al. 2018).

Solid particles present in the reservoir rock can affect the stabilization mechanism of the water droplets emulsified in the oil. This type of emulsion is known as a Pickering emulsion (Wang and Alvarado 2011; Umar et al. 2018). Unlike conventional emulsions, which have surfactants at their interface, solid particles are present at the Pickering emulsion droplet interface, generally promoting greater emulsion stability. Therefore, coalescence is hampered and more resistant interfacial films are formed (Wang and Alvarado 2011; Kilpatrick 2012; Silva 2018; Kolotova et al. 2018; Radnia et al. 2019). Poindexter and Marsh (2009) evaluated the influence of inorganic salts on the stability of emulsions, using a filtered crude oil sample to remove polar components from petroleum (resins and asphaltenes). They observed from bottle test results that the effect of inorganic salts overlapped the effect of asphaltenes on the formation of stable emulsions.

The presence of salts in the formation water (connate water) and/or in the injected water (used in primary recovery) can affect the w/o emulsions' stability, but their effect is not consistent in the literature (Subramanian et al. 2017; Oliveira et al. 2018). Some studies have indicated that an increase in the salt concentration in the aqueous phase tends to stabilize emulsions (Ghannam 2005). On the other hand, data exist suggesting that instability is due to the presence of salt in the aqueous phase (Subramanian et al. 2017). Ghannam (2005) investigated 10/90 and 50/50 (v:v) w/o emulsions, varying the sodium chloride concentration (1 and 5%), without and with emulsifier addition. The stability increased with rising salt concentration, and the 10/90 emulsion containing emulsifier and 5% salt remained completely stable during the test period (48 h). Subramanian et al. (2017) investigated the effect of acid-base interactions and salts

on the stability of water-in-oil emulsions using nine types of crude oil (light, medium, heavy and extra heavy). Four types of saline water were used: using 4 to 30% by weight of sodium chloride (NaCl), 4 to 20% by weight of calcium chloride (CaCl_2), sea water and formation water. The behavior regarding the stability of the emulsion was attributed to the acid-base interactions between the asphaltenes and the aqueous phase. The authors also revealed that by increasing the salt concentration of 4–30 wt % for monovalent salt and of 4–20 wt % for divalent salts, there is a destabilization of light oil emulsions and the non-formation of emulsions with medium, heavy and extra heavy. One of the explanations provided by the authors is that the water molecules can hydrate the ions instead of interacting with the acidic and basic portions of the asphaltenes.

Other agents that can affect the stability of w/o emulsions are the amphiphilic polymers (Umar et al. 2018; Kamkar et al. 2020). This class of polymers promotes interaction between aqueous and organic environments, which may or may not contribute to higher emulsion stability (Lu et al. 2018; Yang et al. 2021). Depending on the water content, amphiphilic polymers can hinder the formation of emulsions.

The most common amphiphilic polymers used in EOR are based on acrylamide, which is used due to its relative low cost and good thickening power, which provokes an increase in oil displacement to the production well, consequently increasing oil productivity (Kang et al. 2011; Lucas et al. 2015; Umar et al. 2018; Yang et al. 2021). Nevertheless, no conclusive studies were found in the literature evaluating specifically the influence of these kind of polymers on the emulsion stability and the quality of separated water, using heavy oils.

Due to the controversy in the literature and the difficulty of dealing with heavy oils, we evaluated the influence of salt concentration and the addition of acrylamide copolymer and/or a demulsifier on the stability of w/o emulsions by using bottle tests. Moreover, we also investigated the influence of these parameters on the TOG (total oil and grease) of the separated water, using fluorimetry. The study was conducted using synthetic emulsions prepared with a heavy crude oil sample.

Materials and methods

Materials

A crude oil sample ($^{\circ}\text{API} = 13.2$, water content by Karl Fischer = 2.8 wt%, density = 0.9770 g/cm^3 , total acid number = 0.98 and fraction of asphaltenes insoluble in n-heptane (C7I) = 12.9 wt%), a commercial sample FLOPAAM AN125, called in this work simply as polymer (copolymer of acrylamide and acrylamido propyl sulfonated acid,

molar mass: $\sim 8,000,000$ g/mol and 25 mol% of sulfonate monomer), and a commercial demulsifier were supplied by Equinor (Brazil). Acetic acid (CH_3COOH) (ACS), sodium bicarbonate (NaHCO_3) (ACS), strontium chloride hexahydrate ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$) (ACS), potassium chloride (KCl) (ACS), sodium chloride (NaCl) (ACS) and sodium hydroxide (NaOH) (PA) were acquired from Isofar (Duque de Caxias, Brazil). Barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) (PA), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) (PA), calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) (PA), hydrochloric acid (HCl) (PA) and n-hexane (PA) were purchased from Labsynth (Diadema, Brazil). Silicon dioxide (SiO_2) (Emprove Ph Eur brand) was acquired from Merck Brasil (Rio de Janeiro, Brazil). Distilled water was used to prepare the emulsions.

Preparation of synthetic w/o emulsions

The following procedure was established to prepare w/o emulsion using the heavy oil: (1) brine was previously prepared at room temperature with magnetic stirring for 30 min; (2) brine and oil, in different flasks, were put in an oven for 30 min at 80°C ; (3) brine was slowly added in the oil under stirring with a glass rod at room temperature; and (4) the mixture was stirred using Polytron at 15,000 rpm with external heating of 60°C for 6 min. Step (2) was required to facilitate the preparation of the emulsion due to the high viscosity of the oil.

The brines were prepared by dissolving the salts in distilled water under magnetic stirring at room temperature. The brine at 55,000 ppm was prepared with NaCl and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, at 10:1 proportion. The brines at 35,000, 63,000 and 90,000 ppm were prepared using the following addition order of the different salts: NaCl (31,800 mg/L), $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (2520 mg/L), NaHCO_3 (200 mg/L), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (523.8 mg/L), KCl (424 mg/L), $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ (236 mg/L), $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (20.7 mg/L), SiO_2 (23.9 mg/L) (all salts were previously dissolved in distilled water). Finally, CH_3COOH (300 mg/L) was added, followed by pH 7 adjustment using HCl or NaOH.

The acrylamide copolymer addition to the brine was carried out under magnetic stirring and heating using a capped flask, for 1.5 h.

All samples were prepared by the same operator, using a balance presenting a standard deviation of 0.0000 g.

Bottle test

The freshly prepared w/o emulsion was poured into a graduated conic glass flask, which was placed in a thermostatic bath until the test temperature was reached. Then the demulsifier was added using a micropipette and the glass flask was shaken manually for 1 min. After that, the flask was put into

the thermostatic bath again and the test began. For the first 30 min, at every 5 min the flask was removed from the bath and the volume of separated water was read. From 30 to 60 min of testing, the volume was read at every 10 min. This generated a kinetic curve of percentage of separated water in function of time. The water separated at the end of the test was used to determine TOG. For the preliminary results to select the analyses conditions, only some experiments of bottle test were done in duplicate. For the conclusive results, both bottle test and TOG measurement were carried out in duplicate. The results were expressed as the average and the respective errors.

TOG determination by fluorimetry

To obtain enough water for TOG determination, the bottle test was conducted in quadruplicate for each system. At the end of the bottle test, the oil was removed from the conical tube using a pipette and then the water was removed also using a clean pipette. Water separated from the four tests was mixed, and 45 mL was poured into a separation funnel, followed by the addition of 5 mL of n-hexane to enable oil extraction. After centrifugation, the organic phase was analyzed by fluorimetry (Turner Design TD-3100 fluorimeter) with excitation and wavelength ranges of 300–400 nm and 410–600 nm, respectively, to determine TOG. The device requires previous calibration with pure solvent and a solution of 225 ppm crude oil in n-hexane. To the maximum concentration is attributed 25 ppm, which corresponds to 1/9 of 225 ppm, since the oil extraction from aqueous phase is carried out using 1 part of n-hexane and 9 parts of oily water. It is important to highlight that calibration is required whenever the type of oil is changed.

The 225 ppm of crude oil in n-hexane was obtained from diluting a 1000 ppm of a stock solution, which was prepared under magnetic stirring for 48 h, followed by ultrasound for 30 min.

Results and discussion

Selecting the conditions

In order to select the w/o emulsion composition and the demulsifier concentration, preliminary tests were performed. 20/80 and 40/60 volumetric ratio (v:v) w/o synthetic emulsions were prepared to evaluate the stability by the bottle test at 100°C : the aqueous phase was prepared using brine at 55,000 ppm (NaCl: CaCl_2 10:1), without and with 450 ppm of polymer. In the oil phase, the demulsifier concentration was varied (0, 50, 350 and 650 ppm). The concentrations of brine, acrylamide copolymer, and demulsifier were selected based on, respectively, average

values found for several produced waters, average values found in produced water from reservoirs where EOR was applied, and the range of demulsifier used to break w/o emulsions.

Figure 1 shows the kinetic curves obtained from bottle test for the 40/60 w/o emulsion without polymer at different demulsifier concentrations. Increasing demulsifier concentration, in the range used, increased the amount of separated water during the entire test, i.e., the demulsifier destabilized the emulsion, as expected. Similar curves were obtained for 40/60 w/o emulsions, at different demulsifier concentrations, containing 450 ppm of polymer in brine, and for 20/80 w/o emulsions at different demulsifier concentrations, without and with 450 ppm of polymer. The results of the percentage

of separated water at the end of the bottle tests (after 60 min) are summarized in Table 1.

As expected, the emulsion with the highest water content (40/60) was the least stable when comparing the same conditions. Without adding polymer, increasing demulsifier concentration caused reduced emulsion stability for both the 40/60 and 20/80 w/o proportions. At 40/60 w/o, we observed 12.5, 37.5, 62.5 and 70% separated water at the end of the bottle test, while at 20/80 w/o, these values were 0.0, 2.5, 10.5 and 15% separated water by addition of 0.0, 50, 350 and 650 ppm of demulsifier, respectively. The same effect was not observed when the demulsifier was added to emulsions containing polymer in brine, i.e., when adding 50, 350 and 650 ppm of demulsifier, the respective emulsion stability

Fig. 1 Kinetic curves of volume of separated water by bottle test (at 100 °C) for the 40/60 (v:v) w/o emulsion containing different concentrations of demulsifier (0, 50, 350 and 650 ppm)

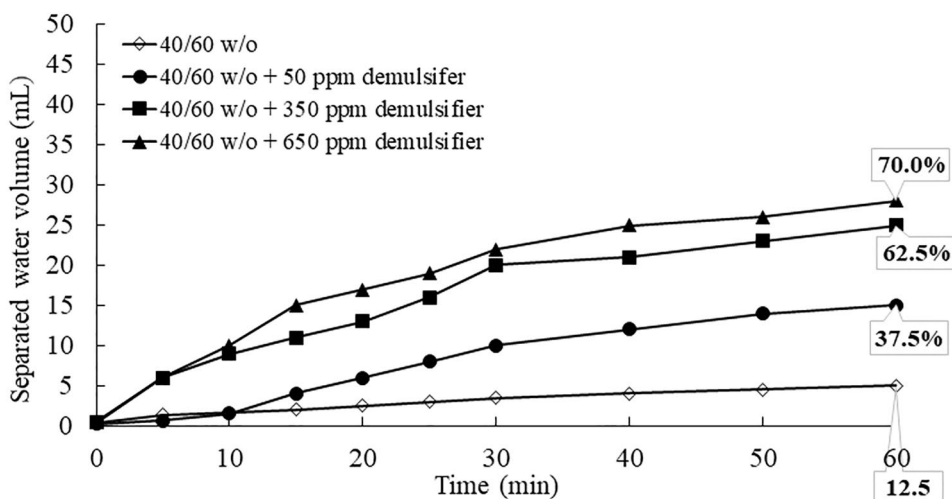


Table 1 Evaluation of emulsion stability by bottle test (100 °C) after 60 min, without or with demulsifier and polymer

| w/o composition (v:v) | Acrylamide copolymer in brine (ppm) | Demulsifier (ppm) | Separated water after 60 min of stability test at 100 °C (%) |
|-----------------------|-------------------------------------|-------------------|--|
| 40/60 | 0 | 0 | 12.5 |
| | 450 | 0 | 43.75 ± 1.25 |
| | 0 | 50 | 37.5 |
| | 450 | 50 | 33.75 ± 1.25 |
| | 0 | 350 | 62.5 |
| | 450 | 350 | 42.5 |
| | 0 | 650 | 70.0 |
| | 450 | 650 | 67.5 |
| 20/80 | 0 | 0 | 0.0 |
| | 450 | 0 | 15.75 ± 1.75 |
| | 0 | 50 | 2.5 |
| | 450 | 50 | 7.0 ± 0.5 |
| | 0 | 350 | 10.5 |
| | 450 | 350 | 15.0 |
| | 0 | 650 | 15.0 |
| | 450 | 650 | 25.0 |

values increased, remained the same as the emulsion containing only polymer, and decreased, for both 40/60 and 20/80 w/o proportions.

The addition of 450 ppm of polymer in brine, without adding demulsifier, decreased the emulsion stability: the percentages of separated water increased from 12.5 to 43.75% and from 0.0 to 15.75% for the 40/60 and 20/80 w/o emulsions, respectively.

For the 20/80 w/o emulsion, the addition of 450 ppm of polymer promoted an increase in the percentage of separated water in comparison with the emulsion containing only demulsifier at the respective concentrations tested (50, 350 and 650 ppm). On the other hand, for the 40/60 w/o emulsion, the presence of 450 ppm of polymer contributed to decrease the demulsification efficiency in comparison with the same demulsifier concentrations.

It is curious to notice that the addition of polymer and demulsifier together did not have a synergistic effect in relation to the individual effects for both 20/80 and 40/60 w/o emulsions. For the 20/80 w/o emulsion, the water separation levels were 15.75, 15 and 25% with addition of 450 ppm of polymer, 650 ppm of demulsifier, and 450 ppm of polymer + 650 ppm of demulsifier. For the 40/60 w/o emulsion, the corresponding separation levels were 43.75, 70 and 67.5% with addition of 450 ppm of polymer, 650 ppm of demulsifier, and 450 ppm of polymer + 650 ppm of demulsifier. This suggests the presence of a competitive effect between polymer and demulsifier at the w/o interface. A recent literature (Mouret et al. 2022) has stated no influence of EOR polymer on w/o emulsion stability, only on the quality of water, highlighting that the findings depend on the type of the polymer, crude oil, water cut and, most likely other parameters.

From these results, the emulsion composition of 40/60 w/o and demulsifier concentration of 650 ppm were selected because they presented a larger volume of separated water without complete phase separation, facilitating observation of the influence of the variables under study.

Influence of polymer and salt on emulsion stability and TOG of separated water

The investigation of the influence of salt concentration on the emulsion stability and TOG of the separated water was conducted using 40/60 w/o emulsions: oil phase without and with 650 ppm of demulsifier; and aqueous phase without and with 450 ppm of polymer, with varying salinity levels of ~ 35,000 ppm, ~ 63,000 ppm and ~ 90,000 ppm using a mixture of salts that was representative of the same field from which the crude oil was extracted. In these analyses, we again examined the emulsion stability by bottle test and the TOG of the separated water by fluorimetry.

Table 2 presents the results of percentage of water separated at the end of the bottle test and TOG of this water. The influence of polymer and demulsifier added together and individually, using brine containing 55,000 ppm of NaCl:CaCl₂ (10:1), was confirmed for all brine concentrations using mixtures of different salts.

To verify if the presence of polymer or demulsifier interferes in the TOG values measured by fluorimetry, pure brine, identified in Table 2 as 100/0 w/o composition, was analyzed with 650 ppm of demulsifier or 450 ppm of polymer. The results confirmed 0.0 ppm for the TOG, as expected.

Concerning the influence of brine concentration on the emulsion stability and TOG of separated water, we observed a decrease of both with increasing salinity in the range between ~ 35,000 ppm and ~ 90,000 ppm. However, the effect was more pronounced from 35,000 to 63,000 than from 63,000 to 90,000. The decrease in the emulsion stability induced by rising salt concentration has been attributed to the increase of the ionic force, provoking faster water droplet coalescence, increasing the droplet sizes and separating the emulsion (Moradi et al. 2011). It is worth mentioning that the effect of salinity is not the only variable that must be taken in account, mainly because it is a heavy oil. The combination of demulsifiers with asphaltenes present in oil, which are very lipophilic, leads to destabilization of the

Table 2 Evaluation of emulsion stability after 60 min using bottle test at 100 °C and TOG of the separated water determined by fluorimetry using n-hexane as extraction solvent

| w/o composition (v:v) | Acrylamide copolymer in brine (ppm) | Demulsifier (ppm) | Total salts concentration ~ 35,000 ppm | | Total salts concentration ~ 63,000 ppm | | Total salts concentration ~ 90,000 ppm | |
|-----------------------|-------------------------------------|-------------------|--|--------------|--|--------------|--|--------------|
| | | | Separated water (%) | TOG (ppm) | Separated water (%) | TOG (ppm) | Separated water (%) | TOG (ppm) |
| 100/0 | 0 | 650 | – | 0.00 | – | 0.00 | – | 0.00 |
| | 450 | 0 | – | – | – | – | – | 0.00 |
| 40/60 | 0 | 0 | 10.5 ± 0.5 | – | 15.0 | – | 22.5 | – |
| | 0 | 650 | 65.00 ± 2.50 | 12.28 ± 2.25 | 74.40 ± 0.60 | 6.28 ± 0.46 | 75.90 ± 0.30 | 8.64 ± 1.75 |
| | 450 | 0 | 33.75 ± 1.25 | 41.27 ± 2.62 | 44.40 ± 0.60 | 17.63 ± 1.04 | 53.75 ± 1.25 | 14.22 ± 1.66 |
| | 450 | 650 | 58.75 ± 1.25 | 55.31 ± 2.20 | 68.75 ± 1.25 | 29.85 ± 0.21 | 71.25 ± 1.25 | 32.70 ± 1.00 |

system when the so-called ideal formulation is reached. This formulation is related to hydrophilicity and the concentration of added demulsifier (Rondon et al. 2006).

The decrease in TOG of separated water with rising salt concentration can be attributed to the salting-out effect. This occurs when the brine concentration increases, inducing phase separation, and the oil content in the water becomes lower because it becomes more difficult to mix the oil in water containing ions. This mechanism agrees with the finding of Fan et al. (2018), who reported an increase in oil droplet size with rising NaCl concentrations in the range from 0 to 250,000 ppm, contributing to the destabilization of o/w emulsions.

The TOG level of separated water after the bottle test was around 10 ppm when using only demulsifier (650 ppm of emulsifier) for all salinity levels tested (from ~35,000 to ~90,000 ppm). The addition of 450 ppm of polymer significantly increased the TOG of the separated water, when compared with the results obtained for the emulsions containing only demulsifier. This is related to the ability of polymer in stabilizing the oil droplets in the aqueous phase, mainly due to its high hydrophilic character imposed by ions of sulfonated groups. This effect caused by the polymer on the TOG occurs mainly for the emulsion presenting lower salt concentrations: for 35,000 ppm of salts, TOG was close to 40 ppm, and decreased to around 15 ppm when using higher salinity (63,000 and 90,000 ppm). The addition of polymer (450 ppm) and demulsifier (650 ppm) together provoked a significant increasing in TOG in comparison with the addition of demulsifier and polymer separately, at all salinities tested. At ~35,000 ppm of salts, the TOG values were 12.28, 41.27 and 55.31 ppm, respectively, with the addition of demulsifier, polymer and demulsifier + polymer, while at ~63,000 of salts, the TOG values were 6.28, 17.63 and 29.85 ppm, respectively, with demulsifier, polymer and demulsifier + polymer, and at ~90,000 ppm of salts, the TOG values were 8.64, 14.22 and 32.70 ppm, respectively, with demulsifier, polymer and demulsifier + polymer.

Conclusions

This study helps to predict what could happen in terms of breaking w/o emulsion and quality of separated water during the demulsification process when producing a heavy oil with a high salinity produced water from a reservoir where EOR was applied.

For brine in heavy oil emulsions, both the salinity degree and the presence of acrylamide copolymer affect the demulsification process, that is, they affect the efficiency of demulsifier in breaking the emulsion and the

quality of the separated water. Increasing the salinity from 35,000 to 63,000 ppm, the emulsion stability and the TOG of the separated water decreases, being possible to separate higher amount of water from the oil with a better quality of this water. The increase in salinity from 63,000 to 90,000 ppm does not significantly affect the emulsion stability nor TOG of separated water. It happens for all systems: with demulsifier or/and acrylamide copolymer.

The presence of 450 ppm of acrylamide copolymer provokes a decreasing in emulsion stability, although it is less effective than the addition of 650 ppm of demulsifier. Despite the demulsifier and polymer act to destabilize the emulsion, the presence of both together does not exhibit an additive effect, seeming to exist a competition between them because the efficiency of demulsifier is decreased in the presence of polymer. It means that emulsions produced from reservoir treated with EOR will require larger concentration of demulsifier to separate the same amount of water when EOR was not applied. Another consequence caused by the presence of polymer coming from EOR is related to the significantly increasing in TOG of the separated water during the demulsification process, that is, the quality of water becomes worse, even in oil field with salinity so high as 90,000 ppm. The polymer hydrophilicity seems to be enough to stabilize the oil droplets in the aqueous phase. Although TOG of the separated water is very low when using the demulsifier, the quality of water in a system containing polymer and demulsifier is even worse than that when using only polymer. Since the demulsifier is required to break the emulsion, special attention must be paid with the water treatment process in this case.

Author contributions Study conception and design were proposed by EL and RN. Material preparation, data collection and analysis were performed by VF, PR, ES, CS and RN. The first draft of the manuscript was written by VF, RN, CS and EL. All authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Data availability Not applicable.

Code availability Not applicable.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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