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Redução da viscosidade de emulsões água em óleo pela inversão de fase: desempenho e caracterização do surfactante

Viscosity reduction of water-in-oil emulsion by phase inversion: surfactants performance and characterization

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Resumo: A técnica de inversão de fase tem recebido atenção na indústria do petróleo com o objetivo de diminuir o consumo de energia. Emulsões de petróleo bruto preparadas com soluções modelo de salmoura contendo 1,5% em peso de NaCl e 1,0% em peso de surfactantes foram produzidas e avaliadas quanto à condutividade elétrica, estabilidade cinética, microestrutura e reologia. Verificou-se que a inversão de fase ocorreu na faixa de 20-40% em peso de salmoura. Emulsões com 10-40% em peso de salmoura e Triton-X-100 manifestaram menor separação de fases do que sem surfactante ou com Tween 80, enquanto emulsões óleo em água com 50 e 60% em peso de salmoura e Triton-X-100 alcançou o menor valor de viscosidade. Assim, estes resultados elucidam a influência de parâmetros selecionados nas propriedades das emulsões visando melhorar a mobilidade e fluidez por inversão de fase de emulsões água em óleo de alta viscosidade.
Palavras-chave: óleo crú; reologia; transição de fase; estabilidade cinética; Triton-X-100; Tween 80.

***Abstract**: The phase inversion technique has received attention in the petroleum industry in order to decrease energy consumption. Crude oil emulsions with model brine solutions containing 1.5% wt NaCl and 1.0 wt.% surfactants were produced and evaluated on electrical conductivity, kinetic stability, microstructure and rheology. It was found that phase inversion occurred in the range of 20-40 wt.% of brine. Emulsions having 10-40 wt.% of brine and Triton-X-100 manifested lower phase separation than without surfactant or with Tween 80, while oil-in-water emulsions having 50 and 60 wt.% of brine and Triton-X-100 achieved the lowest value of viscosity. Thus, these results elucidate the influence of selected parameters on emulsions properties aiming to improve mobility and flowability by phase inversion of high viscous water-in-oil emulsion.*
Keywords: crude oil; rheology; phase transition; kinetic stability; Triton-X-100; Tween 80.

1 Introduction

Energy sources demand remarkably increased during the past years, which makes petroleum one of the most traded commodities in the world (Guo et al., 2018). In the petroleum extraction, seawater is typically mixed within the oily phase (crude oil) due to the turbulence generated in valves and pumps (Silva et al., 2018). This may induce emulsion formation due to contact between two immiscible liquids, as well as turbulence during production activates and the presence of emulsifying compounds in crude oil, as asphaltenes, resins and waxes (Shi et al., 2018; Silva et al., 2018; Umar, Saaid and Pilus, 2018). Such compounds can be defined as chemical agents with an emulsifying activity that reduce the interfacial tension between immiscible fluids (Meriem-Benziane et al., 2012).

According to Mironova and Ilyin (2018) emulsions take place when an immiscible fluid is dispersed in another in a form of droplets. Water-in-oil (W/O) emulsions consist of water droplets in a continuous oil phase, being the most common in the petroleum production area - due to the hydrophobic nature of petroleum stabilizing compounds (Zolfghari et al., 2016). Oil-in-water (O/W) emulsions are composed of oil droplets dispersed in a continuous aqueous phase, having lower viscosity than W/O (Foudazi et al., 2015).

The oil processing, production and transportation in a form of W/O emulsion are challenges for the petroleum industry (Silva et al., 2018; Souas, Dafri and Benmounah, 2021). The presence of water increases the W/O emulsion viscosity, which often changes its rheological behavior (MEDINA-SANDOVAL, 2018). This usually results in higher energy consumption by the pumping system (HASAN, GHANNAM and ESMAIL, 2010) and causes an increase in the cost of oil processing and transportation. It also induces corrosion of equipment when oil is extracted and transported (FAIZULLAYEV et al., 2022).

Currently, there are several strategies aiming to reduce heavy crude oil or W/O emulsion viscosity (MIRONOVA, ILYIN, 2018; DORVAL NETO et al., 2019), including dilution with lighter petroleum or organic solvents, forming of heavy crude oil emulsions in water (O/W), heating heavy crude oil and pipelines, electrically heated submarine pipelines, the use of pour point depressants (PPD), the application of drag reduction additives, core annulus flow (CAF) and partial upgrading (SOUAS, SAFRI and BENMOUNAH, 2021) such as the possible alternative to use surfactant(s) to emulsify the heavy crude oil in water or brine and to transport the low viscosity emulsion in a pipeline (SUN, SHOOK, 1996).

Phase inversion phenomenon is an important phenomenon for the petroleum processes that need techniques for improve mobility and flowability (TAN et al., 2020), reduce the viscosity of the pumped fluid, and reduce lifting and transportation costs (BULGARELLI et al., 2022). One of them is the catastrophic phase inversion, the process by which one type of emulsion (such as W/O) is converted to another (such as O/W) by the change in the volume ratio of oil to water. The size and number of droplets increase with volume fraction of dispersed phase. The imbalance between coalescence and breakup of droplets results in phase inversion, in which the dispersed phase is transformed in the continuous phase (Zi et al., 2022). The emulsion inversion point (EIP) is the critical water volume that induces W/O to O/W inversion.

The emulsion viscosity during phase inversion process initially increases up to a point of phase inversion region. From that point forward, it starts to decrease with the amount of brine added (Fonseca et al., 2016). Al-Wahaibi et al. (2015) evaluated the viscosity reduction (VR) of heavy crude oil of Omani oil field using Triton X-100 as a surfactant. The authors showed a VR of about 90% at around 50 wt% input water fraction. The inversion occurred at 30% water content.

As stated by Zadymova et al., (2017), the preparation of O/W emulsions can be conducted with assistance of amphiphilic surfactants and enough energy of agitation. In general, a more soluble emulsifier in the oil phase favors the formation of a W/O emulsion, stabilizing this emulsion and making the system more prone to inversion at higher water cutoff values. The formation of O/W emulsion induced by phase inversion may occur when a sufficient amount of water containing surfactant is added into a W/O emulsion (HASAN, GHANNAM and ESMAIL, 2010). Kokal (2005) shows that emulsifying agents have an effective action in stabilizing the emulsion, as they are concentrated at the oil-water interface, forming a rigid film, providing a reduction in interfacial tension, contributing to the dispersion of droplets and stabilization of the emulsion.

The mechanism and inversion region are also affected by water salinity (SOUAS, SAFRIAND and BENMOUNAH, 2021). The salts can interact with asphaltenes and resins by ionic interactions, changing droplet size distribution (DSD) and stability of the emulsions. Da Silva et al., (2018) observed that W/O emulsions prepared with FW (formation water) had a higher DSD than those prepared with SS (saturated water) and DW (deionized). This difference can be related to the amount of monovalent, bivalent and trivalent ions that are present in the formation water.

Another aspect to be considered is that water must be removed from oil before any further process or refining. By minimizing the water fraction, it is possible to maximize the use of pipelines, eliminating severe operational problems. Hence, it is important to know the phase inversion regions in order to use the optimized water and surfactant volumes. This knowledge is important because a technique must involve both the formation and breakdown of emulsions and the removal of water from the oil after transport and before the crude oil is refined (MARTÍNEZ-PALOU et al., 2015). Thus, the lack of knowledge about the phase inversion region of emulsions becomes a technology obstacle (SUN, SHOOK, 1996).

The proposed study evaluates the phase inversion from W/O to O/W emulsion using crude oil from Brazil oilfield, synthetic seawater (brine) and two commercial surfactants. The characterization of the emulsion was performed by combined analysis, including electrical conductivity, kinetic stability, microstructure and flow curve. Emulsion composition and properties were both evaluated as important criteria for improving emulsion transport and thus the cost of pumping crude oils.

2 Experimental

The emulsion synthesis procedure was based on Fortuny et al. (2007) and was prepared by the agent-in-water method (Becher, 1966) where surfactant was first dissolved in brine. The pseudoplastic crude oil (°API 32, 29.5 mPa.s at 100 s-1) was obtained from Brazilian territory. Triton-X-100 (Neon, Brazil) and Tween 80 (Synth, Brazil) were used as non-ionic surfactants, being low sensitive to electrolytes presence and pH changes. Triton-X-100 and Tween 80 show high hydrophilic-lipophilic balance (HLB) of 13.4 and 14.9, respectively, promoting the conversion of W/O to O/W emulsion. Emulsions were prepared by homogenizing known amounts of crude oil (32 API gravity) and model brine solutions containing specified amounts of NaCl (1.5 wt%) and surfactants (Triton-X-100 or Tween 80). The emulsion synthesis procedure involved two stages: a pre-emulsification stage and an emulsification stage. Prior to the pre-emulsification stage, the crude oil was shaken vigorously to ensure homogeneity before sampling. During the pre-emulsification stage, a known amount of brine solution was added stepwise to the hydrocarbon phase, while the mixture was hand-shaken to completely incorporate the brine, resulting in a pre-emulsion. In the second stage, this mixture was homogenized using a rotor stator homogenizer (Ultra-Turrax T-25, IKA), with S25-18G dispersing tool (rotor diameter 12.7 mm). The ratio of brine and crude oil in the mixture was varied to make up W/O or O/W emulsion with the desired value of 60, 50, 40, 30, 20 and 10 wt % of water. The homogenization conditions, such as the stirring frequency and the time of homogenization, were kept constant at 15 000 rpm and 2 min, respectively.

Afterward, the emulsion was characterized by measuring its electrical conductivity, kinetic stability, and DSD. All the procedures and measurements were conducted in triplicate at room temperature (25°C) under the same conditions to ensure repeatability.

2.1 Emulsion Characterizations

The ratio of brine and crude oil in the mixture markedly affects the emulsions properties such as electric conductivity (FORTUNY et al., 2007). Then, the emulsion inversion from W/O to O/W type was evaluated by electric conductivity. The measures were taken immediately after homogenization in an electrical conductimeter W12D (BEL Engineering, Italy).

Kinetic stability is traditionally measured by macroscopic observation of phase separation along time (MORAN, 2007) and it is affected by oil and water content percentage, density difference between water and oil, viscosity of continuous phase, salinity, pH, surfactant, and DSD (KUMAR and MAHTO, 2016). Therefore, the emulsions were transferred into 50 ml glass cone-shaped tubes scaled in 0.1 ml immediately after homogenization and the aqueous phase volume recorded twice a day for seven days. Brine separated volume (SV%) was calculated according to Eq. (1):

$$SV\% = \frac{V_0 - V_m}{V_0} \times 100 \tag{1}$$

where V0 and Vm are the original brine volume and Vm is the brine volume determined at different times.

Emulsion properties such as DSD were characterized immediately after homogenization and after 7 days of storage by optical microscopy (Leica, Germany).

It is known that the reliability of a DSD result obtained via optical microscopy is directly related to the measured drops number. In this way, an ideal number of drops to be counted was determined in preliminary tests so that the distribution obtained was representative.

The samples were poured onto microscope slides and observed at a magnification of 40x. At least 10 images were taken for each sample and the best 5 sharp pictures analyzed using the software Image J 1.50i (http://rsb.info.nih.gov/ij/).

Micrographs were analyzed by measuring the diameter of at least 300 droplets (one by one). The droplet size data were used to plot a histogram of frequency versus droplet size category. Considering spherical droplets, the surface mean diameter (d32) was calculated according to Eq. (2):

$$d_{32} = \sum \frac{n_i d_i^3}{n_i d_i^2} \qquad (2)$$

where n_i is the number of particles with diameter d_i.

Steady shear measurements were carried out using a viscosimeter OFITE model 900 (United States). The samples were analyzed immediately after homogenization. The experimental data were fitted by the Power Law. Flow curves were obtained by an up-down-up steps program using a shear rate range between 0 and 300 s^{-1}.

3 Results and discussion

3.1 Electrical conductivity

Conductivity, as a property of a solution, can reflect the type of emulsion and provide an important basis for the investigation of the phase transition and stability of the emulsion system. Figure 1 shows the electrical conductivity of emulsions without surfactant (A), with 1.0 wt.% of Tween 80 (B) and 1.0 wt.% of Triton-X-100 (C). Emulsions without surfactant (Figure 1A) showed low conductivity (lower than 0,002 mS/cm2) on 10, 20 and 30 wt.% of brine, increasing to values higher than 5.0 mS/cm2 with 40, 50 and 60 wt.% of brine. Emulsions with Tween 80 (Figure 1B) showed low conductivity up to 20 wt.% of brine and higher than 3.3 mS/cm2 for samples containing more than 30 wt.% of brine. Emulsions with Triton-X-100 (Figure 1C) containing 10 wt.% of brine showed low conductivity (0.019 mS/cm2) that increased continuously with brine from 6.4 to 30 mS/cm^2 with 20 and 60 wt.% of brine, respectively. According to Moran (2007), water droplets coalescence drastically increases on emulsion inversion, destabilizing emulsion and producing O/W emulsions with high electrical conductivity (Moran, 2007). The catastrophic phase inversion depends on system formulation (Kumar et al., 2015). When surfactants are present, phase inversion is induced by changing the volume fraction of the dispersed phase and by the affinity of the surfactant for each phase. The continuous phase tends to be the one in which the surfactant is more soluble (Maffi, Meira and Estenoz, 2020). Both surfactants used show high hydrophilic-lipophilic balance (HLB), favoring inversion from W/O to O/W.

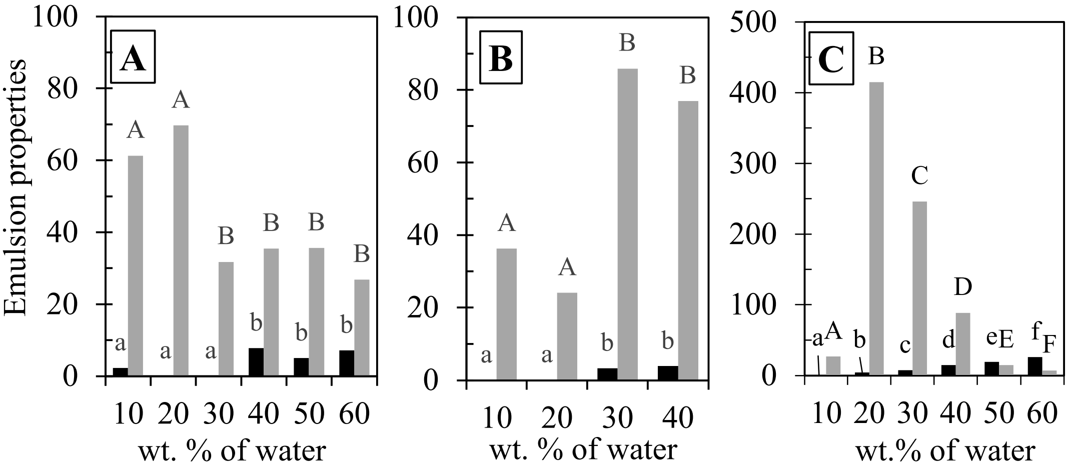

Figure 1. Conductivity (mS/cm^2) (■) and viscosity (mPa.s) (▨) of emulsions without surfactant (A), with 1 wt.% of Tween 80 (B) and with 1 wt.% of Triton-X-100 (C). Different letters mean a significant ($p>0.05$) difference of emulsion properties in different water contents. Small (a, b, c, d, e, and f) and capital (A, B, C, D, E, and F) letters correspond to statistical analysis on emulsion conductivity and viscosity, respectively.

Identification of the inversion point is essential to ensure the minimum water content of the emulsion. In this way, the lowest energy consumption in the fluid flow is ensured and minimizes problems in the separation stage.

3.2 Rheology

The rheological behavior of emulsions is shown in Figure 2 and Table 1. Emulsion inversion was confirmed on both conductivity and rheological analysis. The evaluation of combined analysis to detect emulsion inversion was used by Oliveira Honse et al. (2018) who used electrical conductivity and near-infrared spectroscopy. Emulsions without surfactant showed viscosity increased up to 20 wt.% of brine, and a lower viscosity at higher brine content, suggesting O/W emulsions production at 30 wt.% of brine. Since emulsions with 10 and 20 wt.% of brine showed low conductivity values, it can also indicate W/O emulsions. Generally, the emulsion viscosity increases with water content up to intermediate concentrations (20-30 % w/w), as observed by Abd, Nour, and Sulamain (2014) and Ariffin, Yahya and Husin (2016), and decreased at higher water concentrations, as seen by Fonseca et al. (2016). The decrease of O/W viscosity with water was also observed by Ahmed et al. (1999), Hasan, Ghannam, and Esmail (2010) and Nadirah, Abdurahman and Rizauddin (2014).

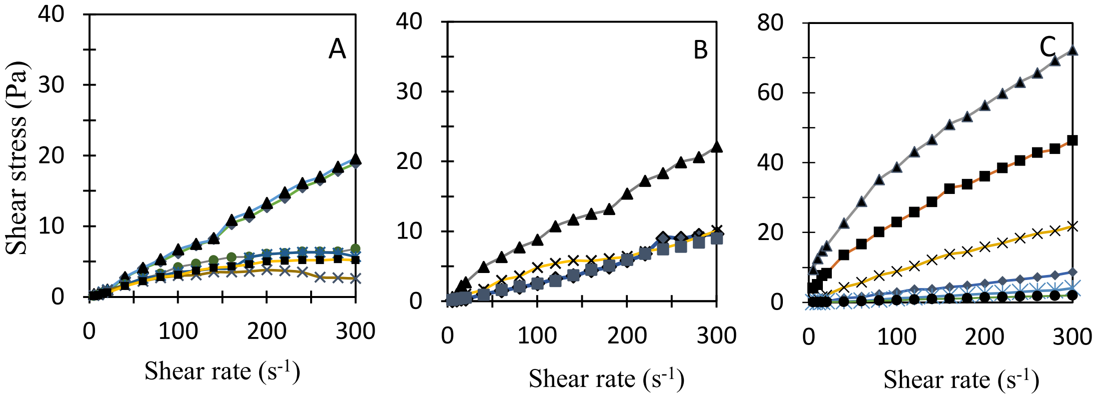

Figure 2. Flow curves of emulsions without surfactant (A), with 1 wt.% of Tween 80 (B) and with 1 wt.% of Triton-X-100 (C), with different water concentrations (wt.%): 10 (♦), 20 (▲), 30 (■), 40 (x), 50 (*), and 60 (●).

Table 1. Rheological parameters k (consistency index) and n (behavior index) of shear-thinning emulsions. * Different letters mean significant (p>0.05) difference between emulsions indexes (k or n) in the same column.

Surfactant	wt.% of water	k (Pa·s)	n (-)
Without surfactant	50	0.066 ± 0.004^{a}	0.83 ± 0.02^{a}
	40	0.039 ± 0.002^{b}	0.92 ± 0.07^{a}
Tween 80	30	0.19 ± 0.02^{c}	0.83 ± 0.02^{a}
Triton-X-100	40	0.18 ± 0.03^{c}	0.85 ± 0.04^{a}
	30	1.8 ± 0.6^{cd}	0.58 ± 0.05^{b}
	20	4.4 ± 0.9^{d}	0.50 ± 0.02^{b}

Emulsions with Tween 80 showed a substantially viscosity increase at 30 wt.% of brine. As emulsion with 30 wt.% of brine showed high electrical conductivity, it can be concluded that emulsions with 10 and 20 wt.% of brine are W/O, while emulsions with 40 wt.% of brine are O/W. W/O emulsions with Tween 80 showed lower viscosity than without surfactants. However, O/W emulsions with Tween 80 showed higher viscosity than without surfactant up to 40 wt.% of brine.

Emulsion with Triton-X-100 showed a viscosity increase up to 20 wt.% of brine. Since emulsion with 10 wt.% of brine showed low electrical conductivity values, it is probably W/O type, while emulsions with 30, 40, 50 and 60 wt.% of brine are O/W type.

Water addition makes emulsion non-Newtonian at intermediary water content (Martínez-Palou et al., 2015), being affected by surfactant composition. In general, shear-thinning behavior was observed on O/W emulsion next to phase inversion. Shear-thinning behavior is described by τ= 〚Kγ˙〛 ^n, where τ is shear stress, γ˙ is shear rate, K is the consistency behavior parameter and n is behavior index parameter.

Emulsions without surfactant with 10, 20 and 30 wt.% of brine are Newtonian fluids, while emulsions with 50 and 40 wt.% of brine are shear thinning fluids without expressive difference on their behavior index (n) of 0.83 and 0.92, respectively (Table 1). Emulsion with 60 wt.% of brine without surfactant did not show a characteristic flow curve, presenting a decrease of shear stress at a high shear rate. Emulsion contained Tween 80 are Newtonian, except emulsion with 30 wt.% of the brine that showed shear thinning behavior with behavior index (n) of 0.83 (Table 1). Emulsions contained Triton-X-100 and 10, 50 and 60 wt.% of brine showed Newtonian behavior, while emulsions with intermediary brine content showed shear thinning behavior, with a pronounced pseudoplasticity (index behavior between 0.5 and 0.58) on emulsions with 20 and 30 wt.% of brine.

3.3 Phase separation

The phase separation increased with the increment of brine content (Figure 3), as observed by Vegad and Jana (2021), Abdurahman et al. (2012), and Ahmed et al. (1999). It takes place due to effective collisions between water droplets, increasing coalescence on W/O emulsions (Ahmed et al., 1999), despite their high viscosity (Figure 1). The decrease of O/W emulsion stability with brine addition is associated with the low viscosity of the continuous phase, which favors oil droplets movements and creaming phenomena. This phenomenon is characterized by the droplets of the emulsion that tends to rise to the top of the storage flask. Moreover, the increase in brine content reduces surfactant concentration at the oil-water interface, creating an interfacial film of insufficient strength and formation of large droplets (Vegad and Jana, 2021). Modeling studies of coalescence and creaming phenomena such as Deoclecio, Ribeiro and Meneguelo (2019) show that the coalescence models fitting parameters are function of the liquids properties only, such as phases viscosity, specific mass and surface tension, since they modeled the decay curve of experiments with different initial conditions, but composed of the same liquids, with the same value.

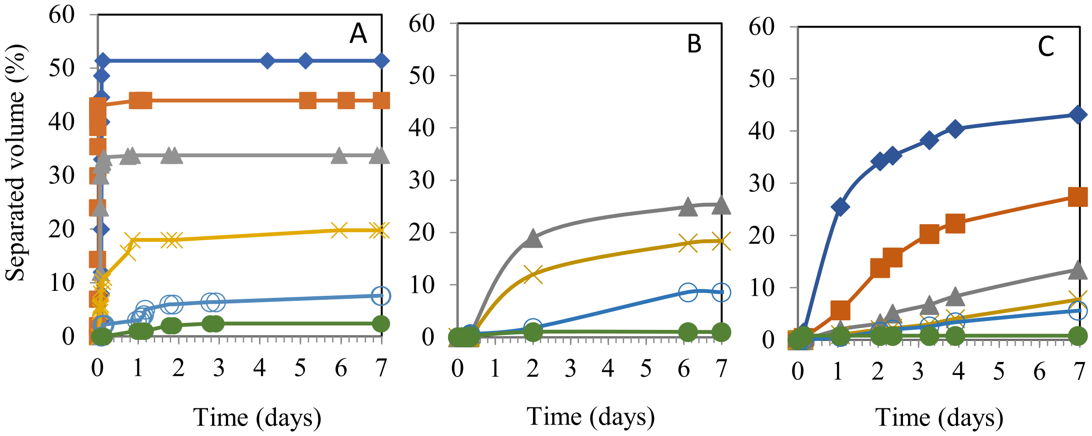

Figure 3. Percentage of aqueous phase separated (vol.%) of emulsions without surfactant (A), with 1 wt.% of Tween 80 (B) and with 1 wt.% of Triton-X-100 (C), with different water concentrations (wt.%): 10 (●), 20 (○), 30 (x), 40 (▲), 50 (■), and 60 (♦).

The use of surfactant increased emulsion stability. This behavior may be due to the carbon number of the alkyl chain of emulsifiers that increases the mechanical stability of the adsorbed emulsifier molecules on the interface of O/W emulsion (AL-SABAGH, 2002). Emulsion without surfactant showed the highest volume of phase separation, while emulsions with Triton-X-100 showed half of phase separation compared with emulsions composed of Tween 80 (Figure 3). The use of surfactant increases the number of barriers between the two phases as a result of reduced interfacial tension (VEGAD and JANA, 2021). The high viscosity of O/W emulsions with surfactant, decreased droplets movements, as well as destabilization phenomenon, and thus phase separation. The major phase separation for most emulsions without surfactant occurred on the first day, while emulsions with surfactant showed slower kinetic separation, with expressive phase separation during the 7 days of storage. According to Souas, Safari and Benmounah (2021), the surfactant must stabilize the emulsion during transportation and must also be able to separate from the emulsion at the point of destination. Thus, the results are corroborated by the study by Bulgarelli et al., (2022), where unstable emulsions have the lowest water cutoff for the EIP, and its maximum value is observed for the stable emulsion. The stability test performed in this study refers to the ease in breaking emulsion to two-phase. Crude oil should contain less than 0.2% water and sediment and less than 10 pounds of salt per thousand barrels of crude oil (PBT) to be sent to the refinery or transported in pipelines. So, demulsification techniques, such as electric separation and others, should be used to remove impurities, salt and water from the mixture (Abdulredha, Hussain and Abdullah, 2020).

3.4 Emulsion droplet size

The mean droplet size of all emulsions is shown in Table 2. For some W/O emulsions with 10 wt.% of brine, no droplets were observed on optical microscopy, probably because their size was smaller than 1 µm. The other ones presented polydisperse droplets in a continuous medium (Figure 5). Emulsions with Triton-X-100 showed larger droplets size than emulsions without surfactant or with Tween 80. Despite coalescence observed on emulsion with Triton-X-100, these systems showed higher stability due to the high viscosity of O/W emulsions with 20, 30 and 40 wt.% of brine. Surfactant acts on emulsion by lowering the interfacial tension and inhibits coalescence of oil droplets. However, the surfactant eventually loses its effectiveness by migration into the oil droplets (Gillies, Sun and Shook, 2000).

According to Table 2 emulsions without surfactant showed mean droplet size between 1.4 µm and 1.7 µm immediately after the homogenization process. The size of the droplets after 7 days of the homogenization has shown little increase as the creaming process occurred, varying between 1.6 and 2.0 µm. Emulsions prepared with Tween 80 showed mean droplet size immediately after homogenization ranging from 1.5 to 4.4 µm while emulsions analyzed 7 days after homogenization showed values between 1.2 and 5.4 µm. The slight decrease in mean droplet size with time passed for 20 and 30 wt.% of brine can be associated with the optical microscope resolution. It is limited by the size of submicron particles approaching the wavelength of visible light (400-700 nm) of optical microscope (Ebnesajjad, 2014), nearby the emulsion droplet size observed (around 1 micrometer).

Table 2. Mean droplet size (d32/µm) of emulsions immediately homogenization process and after 7 days of storage.

	Without surfactant		Tween 80		Triton-X-100	
wt. % water	Immediately	7 days	Immediately	7 days	Immediately	7 days
60	1.5 ± 0.1^{ac}	1.6 ± 0.1^{a}	-	-	3.2 ± 0.2^{d}	6.9 ± 0.5^{b}
50	1.6 ± 0.2^{ac}	2.0 ± 0.09^{b}	-	-	3.9 ± 0.8^{c}	8.5 ± 1^{a}
40	1.4 ± 0.09^{bc}	1.7 ± 0.07^{a}	4.4 ± 0.8^{b}	5.4 ± 0.6^{c}	3.2 ± 0.3^{d}	9.5 ± 2^{a}
30	1.7 ± 0.2^{a}	1.8 ± 0.1^{a}	1.6 ± 0.1^{a}	1.2 ± 0.2^{b}	4.0 ± 0.3^{c}	8.1 ± 0.4^{a}
20	1.6 ± 0.06^{a}	1.8 ± 0.07^{a}	1.5 ± 0.09^{a}	1.2 ± 0.09^{b}	5.2 ± 0.3^{b}	7.6 ± 0.7^{a}
10	-	1.8 ± 0.2^{a}	1.6 ± 0.1^{a}	1.4 ± 0.1^{a}	1.9 ± 0.1^{a}	-

* Different letters mean significant ($p>0.05$) difference between the emulsion droplet size in the same column.

Emulsions containing Triton-X-100 exhibited, immediately after homogenization, mean droplet size values between 1.9 µm and 5.2 µm, which increased after 7 days of preparation to values ranging from 6.9 to 9.5 µm.

The droplet size distribution (DSD) of an emulsion is influenced by the interfacial tension between the oil and aqueous phases, by oil emulsifying agents, by the presence of solids and by the shear (KOKAL, 2005). The force necessary to deform and disrupt a droplet should be larger than the interfacial force of water-oil systems (WALSTRA, 1993), which is lowered by a surfactant (UMAR, SAAID and PILUS, 2018). Surfactant acts on lowering interfacial tension, increasing surface elasticity, and increasing surface elasticity, increasing electric double layer repulsion and possibly increasing surface viscosity (SCHRAMM, STASIUK and MARANGONI, 2003).

Figure 4 presents the optical microscopy and DSD data of the emulsions immediately after homogenization. Emulsions containing Triton-X-100 showed a more dispersed distribution with droplets ranging 1 µm to 9 µm. The sample containing Tween 80 showed a higher frequency of droplets between 1 and 2 µm, except emulsion with 40 wt.% of brine which presented droplets size up to 9 µm.

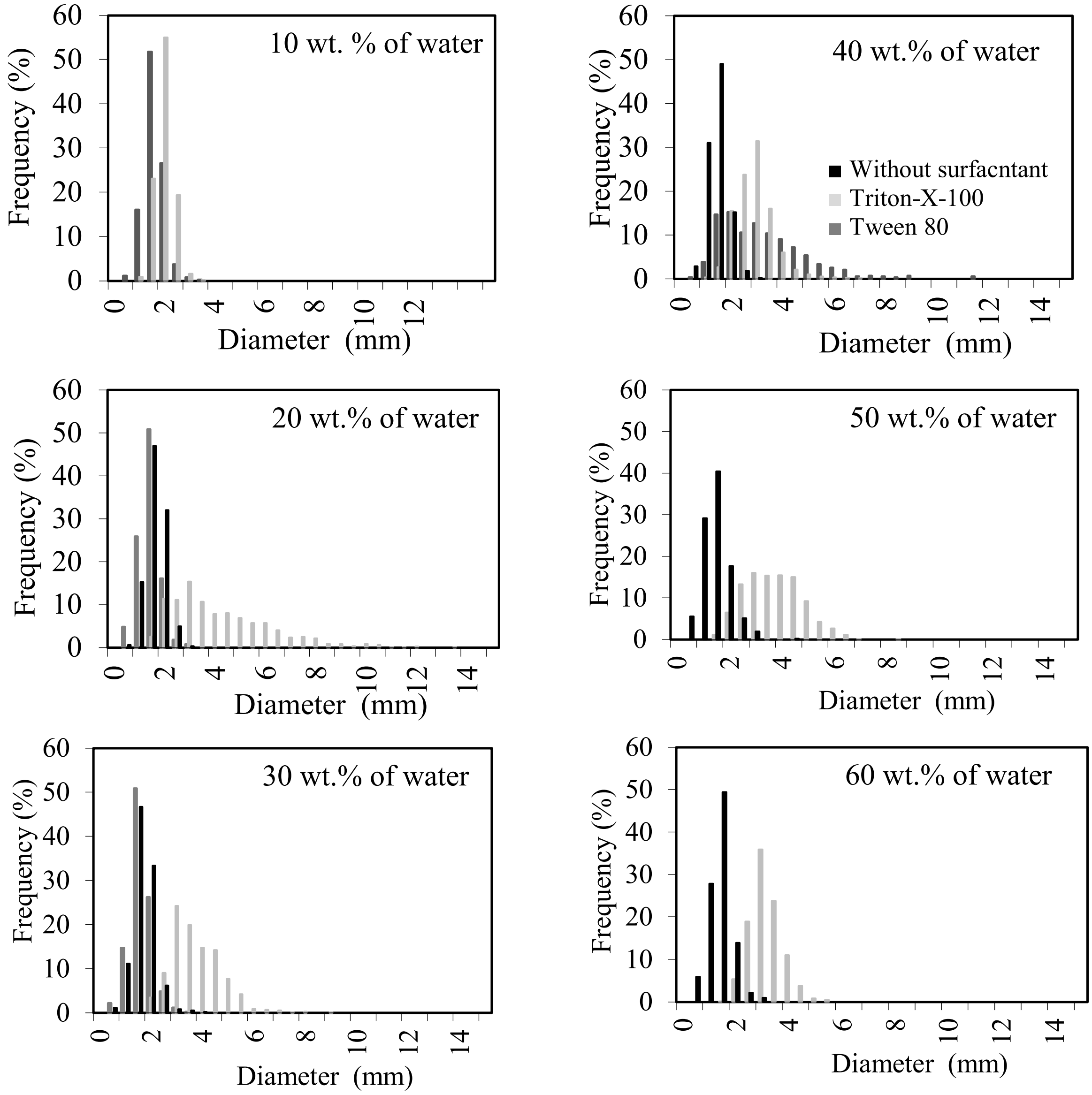

Figure 4. Distribution of droplet size immediately after homogenization for the samples containing 10, 20, 30, 40, 50, and 60 wt.% of water without the addition of a surfactant (■), with Triton-X-100 (■) or Tween 80 (■).

Figure 5 shows the optical microscopy and DSD of the emulsions 7 days after the homogenization process. Comparing Figures 4 and 5, the emulsions showed droplets with a bigger size and more dispersed distribution after 7 days of storage. As observed on mean droplet size results (Table 2), emulsions with Tween 80 and without surfactant showed smaller droplet size than emulsions with Triton-X-100. Emulsion without surfactant showed droplet size smaller than 5 µm. Emulsions containing Triton-X-100 exhibit a dispersed distribution with droplets size between 1 and 15 µm. As an interfacial activity substance, Triton-X-100 changed the interactions of crude oil surfactants (as asphaltenes, resins, and fatty acids) on water-oil interface and resulted on droplet coalescence probably due to the decrease of structural mechanical properties of surfactants in the interfacial layer (UMAR, SAAID and PILUS, 2018).

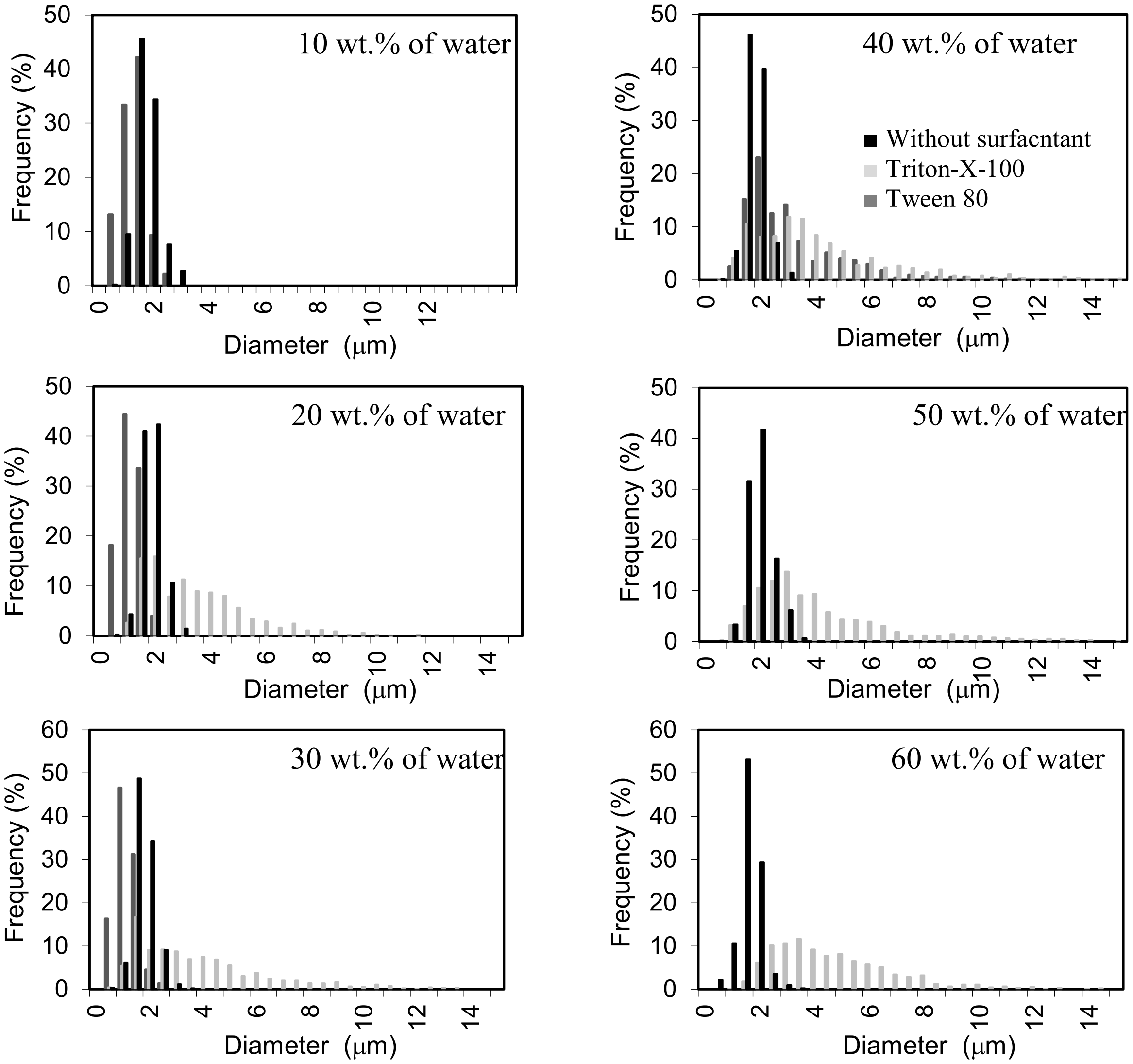

Figure 5. Distribution of droplets size after 7 days of storage for the samples containing 10, 20, 30, 40, 50, and 60 wt.% of water without the addition of a surfactant (■), with Triton-X-100 (■) or Tween 80 (■).

Comparing droplet size of emulsion after homogenization and after 7 days of storage, the droplet sizes increased over time reducing the total interfacial energy stored within their interfaces due to emulsion destabilization phenomena, such as coalescence and Ostwald ripening. Besides, droplet size dispersion increased with brine addition.

4 Conclusions

The inversion of phases from W/O to O/W was detected clearly at low brine content, nearby 20 to 40 wt.% of brine. The magnitude of the viscosity reflects the type of emulsion in O/W or W/O. This is interesting in order to reduce the viscosity of the oil by adding less volume of brine and surfactants. Decrease in the oil-water ratio leads to an increase in the volume fraction of the dispersed phase and the number of small water droplets. This increases the probability of collisions and interactions between small droplets. Therefore, the viscosity of the W/O emulsion increases (Chen et al., 2023). On the other hand, when the emulsion inversion occurs, the continuous phase (water) becomes the one with the lowest viscosity, abruptly decreasing the viscosity on the overall fluid. The strategy used in this research to detect emulsion inversion by evaluating emulsion properties (rheology, microstructure, conductivity and kinetic stability/ phase separation) was more effective than using only one measurement.

The emulsion stability decreases with brine content due to surfactant concentration reduction at the oil-water interface, a high droplet concentration and lower viscosity. Besides, emulsions with 10 to 40 wt.% of brine containing Triton-X-100 present lower phase separation than emulsion without surfactant or with Tween 80, due to the latest higher viscosity. On the other hand, O/W emulsions composed of 50 and 60 wt.% of brine containing Triton-X-100 achieved the lowest viscosity. Triton-X-100 produced O/W emulsions with 50 wt.% of brine with only 5% (v/v) of phase separation after 1 day of storage. And, from the kinetic stability and rheological point of view, being interested in fluid transportation despite the high proportion of water.

5 Future perspectives

The catastrophic inversion phase depends on several variables: composition, density and viscosity of dispersed and continuous phase, interfacial tension, and shear rate. The evaluation of the effect of each parameter in isolation is challenging. It is a multivariable, nonlinear and complex process (Maffi, Meira and Estenoz, 2020). Besides rheology, droplet size, microscopy and conductivity, other experimental analyses have been used in the literature to evaluate the phase inversion point. Pu et al. (2021) estimated the inversion point by measuring the actual moisture of the separated emulsion phase. FTIR (Fourier transform infrared spectroscopy) was used by Jiang et al. (2022) to correlate the weakening of the hydroxyl absorption peak of water molecules with the phase inversion from O/W to W/O emulsions. Honse et al., (2018) monitored phase inversion by NIR (near-infrared spectroscopy), He et al., (2023) analyzed phase inversion point by theoretical models of free energy and Maffi, Estenoz (2021) by machine learning algorithms.

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