Effect of Formation Water and Its Individual Salts on the Stability of Water-in-heavy Crude Oil Emulsions

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Abstract

Due to stability problems, petroleum emulsions are still considered a major challenge for the industry. Heavy oil contains high levels of polar compounds and forms highly stable emulsions that are difficult to treat. The aqueous phase of these emulsions, composed of formation water (FW), has high salinity, and these salts can influence the behavior of the emulsions differently. Therefore, the main objective of this study was to evaluate the effect of different saline species on the stability of heavy-oil emulsions. The emulsions were prepared by adding increasing volumes (0.1, 1.0, 10, 20, and 30% w/v) of an aqueous phase containing deionized water (DW), FW, and saturated saline solutions. The emulsions were homogenized at 5,000 rpm for 3 min. The relevant factors were evaluated, including salt type, gravitational separation, temperature, droplet size distribution (DSD), and interfacial tension. The results revealed that emulsions prepared with some acid pH salts and high ionic strength showed kinetic instability with separation from 3.33 to 21.17% of the aqueous phase after 15–25 days of preparation. In contrast, the others remained stable after 30 days, even heating up to 80 °C. Concerning the average DSD, emulsions with acid pH salts showed higher values (1.67±0.36 to 9.03±2.81 μm), whereas lower values (1.09±0.23 to 4.83±1.06 μm) were found in emulsions with DW. The interfacial tension of the dehydrated oil increased in the presence of the salts, especially those with acid pH and high ionic strength, presenting values from 5.37±0.43 to 22.37±0.77 mN/m. Conversely, basic saline solutions decreased the interfacial tension considerably to values below 0.01 mN/m. These results can contribute to a better understanding of heavy oil W/O emulsions stability, considering water phase properties such as pH, ionic strength, and ionic radius of the cation..

Keywords: Heavy Oil, Water-in-oil Emulsion, Stability, Saline Effect.

Introduction

The appearance of water-in-oil (W/O) emulsions is inevitable during petroleum extraction. Oil-reservoir conditions, such as the presence of saline (formation) water, intense agitation, and shear in the drill-pipes, promote the occurrence of emulsions [1]. Natural emulsifiers favor this phenomenon in the chemical composition of petroleum, the most cited of which are (especially in heavy-oil emulsions) asphaltenes, resins, and naphthenic acids [2,3].

Asphaltenes and resins have polar to nonpolar regions in their molecules that allow them to have an amphiphilic character, an affinity for both water and oil. When concentrated at the oil-water interface in the form of asphaltene aggregates solvated with resins, they form a stable film that reduces the interfacial tension, thereby contributing to the dispersion of droplets and the stabilization of the emulsion [1,3]. Due to their hydrophilicity, naphthenic acids aggregate at the oil-water interface and dissociate in the aqueous phase, being able to react with cations and form naphthenate salts. These salts, in turn, can promote the reduction of interfacial tension, thus the stability of the emulsions is increased [4].

Further to asphaltenes, resins, and naphthenic acids, inorganic salts can also be found at the interface of W/O emulsions. It occurs because the produced water or formation water (FW) and injected water, obtained together with the oil in the production field, is a saline solution composed of several salts, such as chlorides

(Cl-), sulfates (SO_4^{2-}), sodium carbonates (Na_2CO_3), calcium (Ca^{2+}), and magnesium (Mg^{2+}) [5]. While salts' effect on emulsion stability has been widely discussed in the literature, disagreement remains. Some authors have reported that the salts may improve the migration of asphaltenes to the water-oil interface, thus increasing emulsion stability [6–8]. It is found Perles et al. [9] that ions in the saline solutions interacted with the polar groups of the asphaltenes, resins, and naphthenic acids to form a strong interfacial film. Rostami et al. [10] determined that cationic elements present in the aqueous phase could interact with compounds with the anionic charge of asphaltenes (due to their heteroatoms, such as nitrogen [N], oxygen [O], and sulfur [S], in their structures) also to increase emulsion stability. Alves et al. [11] evaluated the influence of salinity on the interfacial properties of W/O emulsions with medium oil (°API 28.4) with low asphaltene content (0.33% w/w). They observed that the presence of salt (at concentrations of 250 g/L) leads to a more stable emulsion.

Conversely, other studies have shown that the presence of such salts can decrease the stability of emulsions because they can neutralize the loads in the asphaltenes and reduce their rate of consolidation at the interface [12–14]. Maaref and Ayatollahi [15] evaluated the effect of different seawater salinities on the stability of W/O emulsions. They observed that the W/O emulsion droplets became larger as the brine concentration increased due to the higher aggregation rate and coalescence. In a previous study [14], it was found that emulsions prepared using deionized water (DW) had smaller droplets than those prepared using a saturated sodium chloride (NaCl) solution and FW, respectively. It was observed that increasing the ionic strength and conductivity of the aqueous phase produced emulsions with wider droplet size distribution (DSD) [14]. Rayhani et al. [16] reported that the lower the salinity and ionic strength of the aqueous phase, the higher the resistance of the interfacial film of oil W/O emulsions against droplet coalescence.

Regarding the effect of the type of ion on the stability of emulsions, Wang et al. [17] investigated the stability of W/O emulsions of crude oil using saline solutions composed of divalent and monovalent cations. They observed that cations, such as Ca^{2+}, formed stronger emulsions than the monovalent ion, sodium (Na^+). Muñoz and Solling [18] studied the nature of the cation in W/O oil emulsions with the addition of potassium chloride (KCl) and NaCl solutions at different concentrations, finding that the type of cation present in the aqueous phase affected the droplet size. Kazemzadeh et al. [7] investigated W/O emulsions prepared using magnesium chloride ($MgCl_2$), calcium chloride ($CaCl_2$), sodium sulfate (Na_2SO_4), and magnesium sulfate ($MgSO_4$). Among the cations evaluated, they observed that Ca^{2+} formed less-stable emulsions than Mg^{2+}. In the same year, Mahmoudvand et al. [19] studied the interfacial activity of crude oil against different saline solutions of NaCl, $CaCl_2$, $MgCl_2$, and Na_2SO_4. The authors observed that the divalent cations Ca^{2+} and Mg^{2+} had a more significant effect on the interfacial properties of the oil, while Na^+ had no influence [19]. Such results may be related to the size of the cation and its charge density. In light of the above, it seems clear that the type of ion influences the stability of the emulsion, not just the concentration of

the salt. The pH of the aqueous phase is another factor to be considered when it comes to emulsion stability since this property strongly influences the interfacial properties of the droplet film [1]. When the aqueous phase is alkaline, the naphthenic acids present in the oil can interact to form surfactants, increasing the emulsion's stability. Moreover, the interfacial activity of acids extracted from petroleum and a NaCl aqueous phase with variable pH was studied by Hoeiland et al. [20]. A decrease in interfacial tension was observed at high pH values due to the dissociation of the acidic components of the petroleum. A similar study was conducted by Dong et al. [21], wherein the interfacial tension between a heavy oil and a saline solution was significantly reduced by the presence of basic species, such as sodium hydroxide (NaOH) and Na_2CO_3. In addition, Lashkarbolooki and Ayatollahi [22] investigated how surfactants in petroleum influenced the interfacial tension with water at different salinities and pH values. They also found that, at basic pH values, the acidic compounds of petroleum could dissociate and decrease the interfacial tension value [22].

In a recent review study, Mahdavi and Moghadam [23] showed that most work on the effect of ions on the stability of petroleum W/O emulsions isolates the system interface as if it were representing the whole. That is, only the components present in the interface are evaluated, from which inferences about the behavior of emulsions can be made. Under real conditions, saline water is mixed with petroleum, and many ionic species can contribute to the stability of emulsions.

As presented, previous studies in the W/O emulsion literature have been conducted using an oil phase composed of petroleum fractions and an aqueous phase consisting of DW or synthetic FW, comprising a mixture of salts containing anions Cl-, SO_4^{2-} and carbonates (CO_3^{2-}) with different ionic charges. It is worth highlighting that studies on laboratory-made emulsions that resemble real petroleum emulsions are scarce. Also, the effect of the chemical composition of the aqueous phase is a factor that requires further clarification. Considering that the influence of salts on the stability of oil emulsions remains controversial, the novelty of the present study concerns deepening knowledge about the effect of isolated salts and their constituent ions present on the chemical composition of an FW, which can provide information for academic and industrial application. In addition to evaluating the ionic strength and valence of ions present in the aqueous phase of oil emulsions, the present study considered the hydrolysis of salts that influence the pH and their interactions with the natural emulsifiers of the oil, which can aid in understanding the stability of emulsions. In this context, this study aimed to evaluate the saline effect on the stability of W/O emulsions of heavy oil. Relevant factors, such as pH, conductivity, and ionic strength, were evaluated from the aqueous phases (saturated saline solutions, DW, and FW collected in an oil-producing field) used to prepare the emulsions. Kinetic stability regarding gravitational stability, droplet size, and interfacial tension were all considered for these assessments.

Materials and Methods

A study was conducted on W/O emulsions of heavy oil with different contents and types of aqueous phases containing

DW, FW, and saturated saline solutions. Firstly, the oil was treated and characterized regarding the following physicochemical properties: density, °API, total acid number (TAN), dynamic viscosity, and the content of saturates, aromatics, resins, and asphaltenes (SARA) (as seen in Fig. 1). The emulsions were then prepared and characterized regarding gravitational separation, determination of DSD by optical microscopy, and interfacial tension using the pendant drop method (Fig. 1).
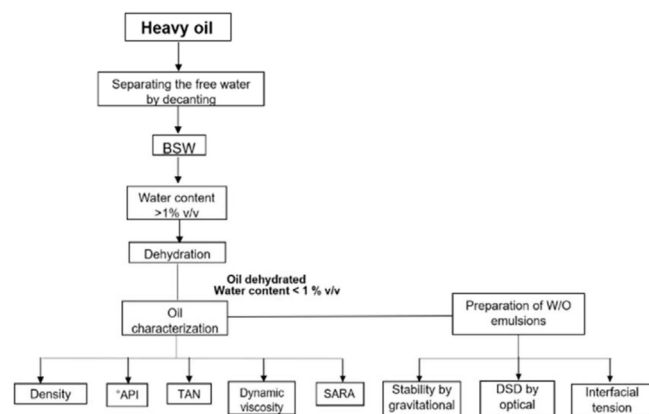

Fig. 1 Experimental procedure flowchart.

Oil

The oil sample used in this study was the same as in previous ones [14,24]. First (Fig. A1 Appendix), the oil underwent a process of separating the free water (non-emulsified) by decanting for one hour [45]. Then, the emulsified water was separated from the oil through a dehydration process, with the addition of 250 µL of commercial demulsifier (a surfactant containing oligomeric species of isoprene and propylene glycol) with 100 mL of oil and centrifugation at 2,000 rpm for 20 min at 60 °C [25]. Following this procedure, the final water content was quantified according to the ASTM D4377 [26] standard, and the final water content was confirmed to be less than 1% v/v; that is, the oil was considered dehydrated. Although oil has undergone dehydration, it is not always possible to separate all emulsified water. The maximum water content accepted by the oil production stage is 1% v/v [27]. Under these conditions, the oil is considered dehydrated. On a laboratory scale, the same parameter is followed because water contents in oil above 1% v/v interfere with determining the physical-chemical properties and in the study of emulsions.

Oil Characterization

The dehydrated oil prepared as per subsection of "Oil" has been previously characterized [14,24] in terms of its physicochemical properties, including its density at 20 °C (ASTM D5002) [28], the American Petroleum Institute (API) gravity (ASTM D1250 and ISO 12185) [29,30], TAN (ASTM D664) [31], dynamic viscosity at 60 °C (ASTM D4402) [32], and SARA (ASTM D6560 and ASTM D2549) [33,34] (Fig. A2 Appendix).

Conductivity, pH, and Ionic Strength of the Water and Saturated Saline Solutions

To characterize the types of aqueous phases used in the preparation of the W/O emulsions in terms of checking the salt concentration, the conductivity, and pH were determined at room temperature (25 °C; Fig. A3 Appendix). Conductivity was measured in an MS Tecnopon conductivity meter, model mCA 105.1, using an electrode whose cell constant (K) equaled 1.0. It was calibrated using a Dinâmica standard solution with a conductivity value of 1,413±0.5 µS·cm-1 at 20 °C. The pH was measured using a Metrohm brand pH meter, model 827 pH Lab, and calibrated using Neon brand buffer solutions with pH values of 7.00 and 4.00±0.02 at 25 °C.

In addition to the conductivity and pH characterization, the ionic strength of saturated saline solutions was calculated according to Equation 1 (Fig. A3 Appendix) [35]:

$$\text{Ionic strength } (\mu) = \frac{1}{2}\left([A]Z_A^2 + [B]Z_C^2 + [C]Z_C^2\right) \quad (1)$$

where [A], [B], and [C] represent the molar concentration of species of ions A, B, C, and ZA, ZB, and ZC correspond to their charges.

Preparation of W/O Emulsions

The dehydrated oil was heated at approximately 60 °C for 20 min to facilitate homogenization. Following this, the W/O emulsions were prepared (Fig. A4 Appendix) by adding increasing volumes (0.1, 1.0, 10, 20, and 30% w/v) of DW, FW, ($5.50 \cdot 10^4$ mg·L^{-1} NaCl), and saturated solutions of NaCl ($3.82 \cdot 10^5$ mg·L^{-1}; S1), Na_2CO_3 ($3.57 \cdot 10^5$ mg·L^{-1}; S2), NH_4Cl ($2.91 \cdot 10^5$ mg·L^{-1}; S3), KCl ($2.80 \cdot 10^5$ mg·L^{-1}; S4), $CaCl_2$ ($5.04 \cdot 10^5$ mg·L^{-1}; S5), $MgCl_2$ ($8.03 \cdot 10^5$ mg·L^{-1}; S6), $FeCl_3$ ($4.42 \cdot 10^5$ mg·L^{-1}; S7), $MnCl_2$ ($8.46 \cdot 10^5$ mg·L^{-1}; S8), $Ni(NO_3)_2$ ($6.49 \cdot 10^5$ mg·L^{-1}; S9), $SrCl_2$ ($6.98 \cdot 10^5$ mg·L^{-1}; S10), and $NaHCO_3$ ($1.02 \cdot 10^5$ mg·L^{-1}; S11). It has been established that emulsions are thermodynamically unstable systems, requiring an energy supply for their formation [36]. This way, the emulsions were homogenized by mechanical dispersion at 5,000 rpm for 3 min in a Polytron model PT 10-35 GT mechanical stirrer equipped with a PT-DA 30/2 rod. [14,24].

The choice of these volumes was based on previous studies [14,24] on the stability of petroleum emulsions. Volumes below 10% w/v (0.1 and 1.0% w/v) were studied to evaluate whether saturated saline solutions would impact small-dose emulsions. Furthermore, each of the salts above was chosen based on the chemical composition of FW used in previous studies [14,24]. FW is real formation water from an oil-producing field previously characterized by the Inductively Coupled Plasma Optical Emission Spectrometry technique to determine the metals present (Table 1) [14]. Furthermore, saturated saline solutions were used to evaluate the ion's pronounced effect on the behavior of petroleum emulsions. Table 2 clarifies the nomenclatures for the emulsions prepared with some examples for the aqueous phases for DW, FW, and S1. For other saturated saline solutions, the acronyms S2–11 appear at the end of the emulsions. For example, EM10S3 identifies the W/O emulsion with 10% w/v of saturated S3 solution. Some emulsions with salts S2, S3, S4, S5, S6, S8, and S10 did not form in the volume of 30% w/v. Therefore, it was necessary to increase the stirring time to 10 minutes for the emulsion with S2, 4 minutes for S3, and 6 minutes for the S5, S6, S8, and S10, thus giving them kinetic stability.

Table 1 Results obtained for metals determination by ICP OES in the formation water sample with the standard deviation [14].

Ions in formation water	Concentration (mg·L^{-1})
Ba^{2+}	125 ± 4
Ca^{2+}	2787 ± 95
Fe^{3+}	<0.1
K^{+}	959 ± 25
Mg^{2+}	1025 ± 25
Mn^{2+}	<0,1
Na^{+}	41473 ± 957
Ni2^{+}	0.949 ± 0.026
Sr^{2+}	381 ± 12
V2+	<0.1

Table 2 Examples of the preparations and acronyms for the W/O emulsions.

W/O emulsion	Water content (%w/v)	Aqueous phase
EM01DW	0.1	DW
EM1DW	1.0	
EM10DW	10	
EM20DW	20	
EM30DW	30	
EM01FW	0.1	FW
EM1FW	1.0	
EM10FW	10	
EM20FW	20	
EM30FW	30	
EM01S1	0.1	S1
EM1S1	1.0	
EM10S1	10	
EM20S1	20	
EM30S1	30	

Characterization of W/O Emulsions

Immediately after preparation, the W/O emulsions were characterized in terms of stability by gravitational separation, average DSD by optical microscopy, and interfacial tension by the pendant drop method (Fig. A5 Appendix).

Stability by Gravitational Separation

The evaluation of stability by gravitational separation was conducted immediately after sample preparation. Approximately 10 mL aliquots of each W/O emulsion were placed in conical plastic tubes and monitored at 25±3 ºC and 24-hour intervals for 30 days. During this time, the occurrence of W/O phase separation was monitored. Then, the emulsions were heated in a water bath, starting at 30 °C and ending at 80 °C. The emulsion was considered stable if there was no separation of water–oil phases.

Optical Microscopy

The procedure first consisted of preparing the glass slide to carry out the readings under the optical microscope using isopropyl alcohol p.a. as a cleaning agent. Next, a small aliquot of each newly-prepared W/O emulsion was applied to the slide. These procedures were performed in triplicate for each emulsion.

Then, the slide with the emulsion was placed on the platform of the polarized light optical microscope, manufactured by Nikon, model Eclipse LV100POL with LV100's CFI LU Plan Fluor EPI P 20 and 50x objectives with DS-Fi1 digital camera attached. Furthermore, 20x or 50x objectives were selected during measurement to provide a true, magnified image of the emulsions. The position of the digital camera was adjusted so that the image was displayed correctly on a computer monitor and set to the appropriate scene mode for the microscopy method. Once this stage was done, the platform was moved to select the target in the sample. Once selected the target in the sample, the brightness and focus were adjusted, and the image was captured. The photomicrographs obtained were analyzed using the NIS Elements D software (version 3.2) to determine the DSD and verify the shape of the droplets.

Interfacial Tension

The dynamic interfacial tension between the dehydrated petroleum and the different types of aqueous phases was performed using an SEO-Surface Electro-Optics tensiometer model Phoenix MT (M) which employs the pendant drop method [37] (Fig. 2). A 0.4064 mm diameter in the shape of a "U" needle was connected to a 300 uL (ul is underwriters laboratories) plastic syringe filled with oil (i.e., a less dense fluid). The syringe, oil, and needle set were fixed to the manual piston of the equipment and immersed in a transparent cell filled with the same aqueous phase used to prepare the emulsions (i.e., a denser fluid).

Due to the heavy oil used in the study, the measurement of interfacial tension was performed with heating at approximately 45 °C, with the aid of a Jeio Tech ultra-thermostatic bath (model RW3–0525) coupled to the transparent container containing the aqueous phase (Fig. 2).
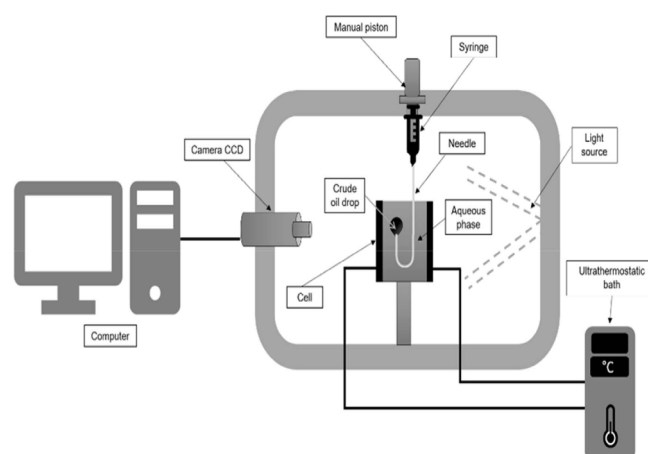
Fig. 2 Schematic diagram of the apparatus used to determine the interfacial tension.

After calibrating the needle diameter, a drop of pendant oil (approximately 5 µL) was formed. This drop was generated through the same needle immersed in the aqueous phase. After stabilizing the drop for roughly 30 seconds, approximately 45 digital images were captured by the CCD camera attached to the equipment and stored sequentially in the Surfaceware software (version 10.11). To ensure repeatability,

this procedure was performed in triplicate for each type of aqueous phase used to prepare emulsions.

The images were analyzed for each droplet image, and the software calculated the interfacial tension using the Young-Laplace equation as a principle (Equation 2) [38]. This equation relates the change in surface pressure separating two liquids to molecular bonding forces. In its most general form, it can be expressed as:

$$\Delta p = \gamma \left(\frac{1}{R1} + \frac{1}{R2} \right) \qquad (2)$$

where Δp is the pressure variation between the surfaces, γ is the surface tension, and R represents the two perpendicular radii of curvature. Modern computational methods, such as the one used by Surfaceware (version 10.11), use interactive approximations that allow finding solutions to the Young-Laplace equation. Thus, the interfacial tension between immiscible fluids with known densities can be determined using the profile analysis approach of the formed drop, according to Equation 3 [39]:

$$\gamma = \frac{\Delta \rho g D E^2}{H} \qquad (3)$$

were $\Delta \rho$ is the density difference, g is the acceleration of gravity, DE is the equatorial diameter of the drop, and H the correction factor of the DS/DE determination, as shown in Fig. 3 below:
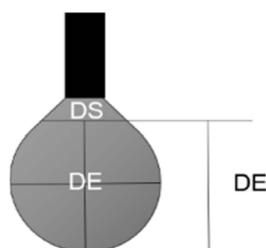

Fig. 3 Pendant drop illustration.

Due to the dark coloration of the saturated saline solutions of $FeCl_3$ (S7) and $Ni(NO_3)_2$ (S9), it was not possible to capture the pendant drop using the tensiometer camera, even when employing the equipment's maximum light intensity. As such, these solutions were not evaluated for interfacial tension using the oil studied.

Results and Discussion
Oil Characterization

The results of the physicochemical characterization of the dehydrated oil are presented in Table 3; these have already been described in previous works [14,24].

The density (0.970 g·cm-3) and API gravity (13.7) of the oil meant that it could be classed as heavy, following the high value obtained for its dynamic viscosity (1.291 at 60 °C). The TAN result (expressed in mg·KOH/g) of the oil presented in Table 3 refers to the mass in milligrams of the KOH base (potassium hydroxide) necessary to neutralize the naphthenic acids present in each gram of oil. The petroleum industry classifies oil that has a TAN greater than 0.500 mg·KOH·g⁻¹ as acidic [40]; therefore, due to its TAN of 1.209 mg·KOH·g⁻¹, the oil could be classed as acidic. Prior research has suggested that naphthenic acid compounds found in oils can act as stabilizers of W/O emulsions due to their ability to

accumulate at the oil-water interface, reducing the interfacial tension of the film formed [1,4]. These acidity results indicate that studies of the saline effect on W/O emulsions should be treated as important to verify the effect of all these species on the interfacial tension of the film surrounding the emulsion's water droplet.

Considering the chemical composition of the studied oil in terms of the SARA (Table 3), its high dynamic viscosity (1.291 Pa·s at 60 °C) and density (0.970 g·cm⁻³) can be correlated and explained by the presence of high-molecular-weight groups, with an emphasis on asphaltenes (7 wt%). It has previously been reported that oils with asphaltene contents greater than 10% and asphaltene/resin (As/R) ratios greater than 0.6 can destabilize W/O emulsions, which it makes them unstable upon water–oil phase separation [41,42]. For the studied oil, the As/R ratio was 0.22, confirming that it would have no such destabilizing effect.

Table 3 Physicochemical characterization of the studied oil, with standard deviation in parentheses.

Property	Result	Standard method
Water content (%v/v)	0.68 ± 0.01	ASTM D437723
Density at 20°C (g·cm⁻³)	0.970 ± 0.003	ASTM D500224
API gravity (°API)	13.7 ± 1.0	ASTM D125025 and ISO 1218526
Viscosity dynamic at 60 °C (Pa·s)	1.291 ± 0.050	ASTM D440228
TAN (mg·KOH·g⁻¹)	1.209 ± 0.023	ASTM D66427
SARA (wt%)		
Saturates	36 ± 1	ASTM D254930
Aromatics	25 ± 1	ASTM D254930
Resins	32±1	ASTM D254930
Asphaltenes	7±1	ASTM D656030

Conductivity, pH, and Ionic Strength of the Water and Saturated Saline Solutions

The water dissociates a dissolved salt and is thus considered as a strong electrolyte. Thus, the properties of saline solutions depend on the constituent cations and anions. Moreover, the reaction that can occur in such systems is called hydrolysis, where the cations and anions of the salts react with the water to generate aqueous hydrogen ($H^+_{[aq]}$) or hydroxide ($OH^-_{[aq]}$) [43,44]. Therefore, saline solutions can be acidic, basic, or neutral.

The results presented in Table 4 show that the saturated solutions of Na_2CO_3 (S2) and $NaHCO_3$ (S11) were basic, with pH values greater than 7 (11.47 and 8.07, respectively). The saturated solutions of DW, FW, NaCl (S1), and KCl (S4) were considered neutral, with pH values close to 7 (7.02, 6.51, 6.60, and 6.95, respectively). The other saturated saline solutions—NH_4Cl (S3), $CaCl_2$ (S5), $MgCl_2$ (S6), $FeCl_3$ (S7), $MnCl_2$ (S8), $Ni(NO_3)_2$ (S9), and $SrCl_2$ (S10)—were acidic, with pH values of less than 7. Thus, most saturated saline solutions used to form W/O emulsions are acidic.

Conductivity is important for determining the degree of an electrolyte's dissociation, the electric current carried by the ions in solution [43]. The higher the conductivity, the greater the degree of the salt's dissociation.

Table 4 Concentration, pH, conductivity, and ionic strength of the water (DW and FW) and saturated saline solutions (S1–S11) were used to prepare the W/O emulsions.

Type of water or salt	Acronym	Concentration (mg·L^{-1})	pH	Conductivity (mS·cm^{-1})	Ionic strength (mol·L^{-1})
Deionized water	DW	<0.001	7.02	1.09·10-3	<8.56·10-9*
Formation water	FW	5.50·104	6.51	577.00	1.15
NaCl	S1	3.82·105	6.60	145.03	6.53
Na$_2$CO$_3$	S2	3.57·105	11.47	83.86	10.11
NH$_4$Cl	S3	2.91·105	3.46	126.3	5.44
KCl	S4	2.80·105	6.95	128.7	3.75
CaCl$_2$	S5	5.04·105	5.17	136.8	13.62
MgCl$_2$	S6	8.03·105	3.91	112.2	25.59
FeCl$_3$	S7	4.42·105	1.99	59.67	16.32
MnCl$_2$	S8	8.46·105	2.38	63.91	20.16
Ni(NO$_3$)$_2$	S9	6.49·105	3.37	102.00	10.65
SrCl2	S10	6.98·105	4.21	136.9	13.20
NaHCO$_3$	S11	1.02·105	8.07	53.6	1.21

*For the calculation, we considered the concentration of DW expressed in NaCl (mol·L^{-1})

Table 4 shows that the FW had the highest conductivity (577.00 mS·cm^{-1}) between the DW and all the saturated saline solutions. This result may relate to the quantity and composition of the ions present in the FW (Table 4) [14]. As expected, the DW had the lowest conductivity value, indicating it contained the lowest number of ions.

The saturated saline solutions with higher concentrations—MgCl$_2$ (S6) with 8.03·105 and MnCl$_2$ (S8) with 8.46·105 mg·L^{-1}—presented intermediate ionic conductivity values. The ionic conductivity was lower (53.6 mS·cm^{-1}) for the saturated NaHCO$_3$ solution at a lower concentration than the others (1.02·10^5 mg·L^{-1}). These results indicate that the conductivity values for the saturated saline solutions did not follow their concentrations. It could be due to each ion having a different ionic mobility. Thus, both the saline concentration and the ionic species' mobility in the solution interfere with the conductivity [43]. Due to the interaction difference between ions, ionic radius, ionic load, and ion migration speed, the most concentrated saturated saline solutions did not necessarily present the highest ionic conductivity values. As saturated saline solutions of S1, S3, S4, and S11 comprised monovalent ions, the ionic strength (Table 4) of this group of salts was identical to its total molar concentration [35]. In general, it was observed that saturated saline solutions with acidic pH presented higher ionic strength values, ranging from 10.65 to 25.26 mol·L^{-1}. On the other hand, lower ionic strength values were found for neutral and basic solutions, with results from 1.21 to 10.11 mol·L^{-1}. The lowest ionic strength values were observed for DW and FW (<8.56·10-9 and 1.15 mol·L^{-1}, respectively.

Preparation of the W/O Emulsions
Immediately after preparation, the behavior of the emulsion was verified visually as a function of the w/o phase separation. Thus, it was observed that some W/O emulsions did not form under the experimental conditions established per subsection of "Preparation of W/O emulsions" in the aqueous phase comprising 30% w/v. It was apparent for the W/O emulsions containing saturated solutions of Na$_2$CO$_3$ (S2), NH$_4$Cl (S3), CaCl$_2$ (S5), MgCl$_2$ (S6), MnCl$_2$ (S8), and SrCl$_2$ (S10), where it was necessary to increase the stirring time to 10 min for S2,

4 min for S3, and 6 min for S5, S6, S8, and S10, to ensure that the entire aqueous phase was emulsified (Table 5). This problem likely occurred due to the high amount of aqueous phase added during the preparation of these emulsions. It should be noted that, for most of the emulsions mentioned above, the aqueous phase contained inorganic minerals with cosmotropic ions from the Hofmeister series: the cations Na$^+$, Mg^{2+}, Ca^{2+}, and the anions CO$_3^{2-}$ and Cl$^-$ [45,46]. According to this series, cosmotropic ions interact more with water molecules than the water molecules do with each other. Due to this behavior, strongly-hydrated ions were considered [47]. In emulsions, cosmotropic ions compete with surfactants for hydration water, acting as salting-out ions. Thus, the destabilization of the surfactants at the interface may have occurred, hindering the formation of the described emulsions. For the remaining samples, the agitation speed, time, and amount of aqueous phase added (5,000 rpm, 3 min, and 0.1, 1.0, 10, 20, and 30% w/v) were sufficient for emulsion formation. It is worth mentioning that anomalous behavior was observed in forming the emulsions containing a saturated solution of FeCl$_3$ (S7). During homogenization of the oil with 10% w/v of the aqueous phase of S7, it was noted that the resulting mixture had practically solidified, thus hindering its flow through the mechanical stirrer. Part of the iron found in petroleum has an oil-soluble structure or is in the form of compounds [48]. The instability of heavy oil can occur by a drastic change of pH at the site or an increase in the concentration of iron ions. These two factors can promote the formation of asphaltenic sediments [49]. In the present study, as the pH of the iron chloride solution was the lowest (most acidic), and due to the high concentration of iron ions, the resulting mixture during emulsion preparation increased viscosity. It showed lump formation, which, according to the literature, could well be asphaltic sediments. It is worth mentioning that the oil used in the study was heavy and had an asphaltenes content of 7 wt%. Consequently, preparing the emulsions with 20 and 30% w/v aqueous phases was impossible. This effect was less pronounced for the emulsions with 0.1 and 1.0% w/v of S7, making it possible to prepare and characterize these emulsions.

Characterization of W/O Emulsions
Stability by Gravitational Separation

The stability test results by gravitational separation of the W/O emulsions using different amounts and types of aqueous phases suggest that most emulsions were stable throughout the 30-day monitoring period. Fig. A1 (Appendix) shows an example of a stable and unstable emulsion with phase separation. S8–10 were considered unstable, except at small aqueous-phase volumes of 0.1 and 1% w/v. In solution, EM20S8, 4.54% of the aqueous phase had separated from the oil after 15 days of monitoring. In solution, EM20S9, 5.56% of the aqueous phase had separated from the oil after 25 days of monitoring, and in EM30S9, after 1 week, 3.33% had separated. Among all the W/O emulsions studied, those prepared with S10 (pH 4.21) (Table 4) were considered the most unstable at room temperature. It is because EM10S10, EM20S10, and EM30S10 showed instability after 10 days of monitoring, with 8.00, 29.17, and 2.56% of the saturated saline solution separating from the oil, respectively. This difference observed in the amount of aqueous phase separated from EM20S10 to EM30S10 occurred because preparing the 30% w/v emulsion required increasing the dispersion time from 3 to 6 minutes (per subsection of "Preparation of W/O emulsion" in "Results and Discussion"). The emulsion with 20% w/v of aqueous phase was prepared under the established experimental conditions (i.e., 3 minutes; see subsection of "Preparation of W/O emulsion" in "Results and Discussion"). Therefore, as the dispersion application time doubled to prepare the emulsion with 30% w/v, higher stability occurred in the same period in which the gravitational separation was evaluated. Thus, EM30S10 showed a lower amount of separated aqueous phase when compared to EM20S10.

These results demonstrate that, at ambient temperature, a high aqueous-phase content (20 and 30% w/v) of acidic, saturated saline solution (S8–S10 with pH values of 2.38–4.21) caused instability in the W/O emulsions. It is worth remembering that these saline solutions were the most concentrated and had the highest ionic strength values of all those studied (Table 4). It is likely that, at high salt concentrations (6.5 – 8.5·105 mg·L^{-1}) and ionic strength (10.65–20.16 mol·L^{-1}), the water molecules preferred to hydrate the ions rather than interact with the asphaltenes to promote emulsion stability. Consequently, the interfacial film of these emulsions is not sufficiently strong to prevent coalescence of the droplets, which results in the separation of the water and oil phases. For the oil used in this study, it can be seen that the acidic aqueous phase emulsified with high ionic strength can promote the instability of the formed emulsions.

According to the studies by Shojaati et al. [50], polar groups remain stable up to a certain concentration of ions. When the concentration of ions in the aqueous phase is very high (around 2·105 ppm), a phenomenon known as "salting-out" occurs. In this phenomenon, the polar groups return to the oil phase. In high concentrations, the salts can break the hydrogen bond between the aqueous phase and the polar groups, causing the instability of asphaltenes and resins at the interface. To improve the explanation, the mechanism in Fig. 4 should be followed. Where in (1), the water-oil interface is stabilized by polar groups. Aqueous phase without ions; (2) in the presence of ions in the aqueous phase, there are interactions between the ions and the molecules of polar groups. Cationic elements interact with the anionic elements of polar groups; (3) when the concentration of ions in the aqueous phase is very high, salting-out occurs; (4) the salts can break the hydrogen bonds between the aqueous phase and the polar groups, thus destabilizing the interface.
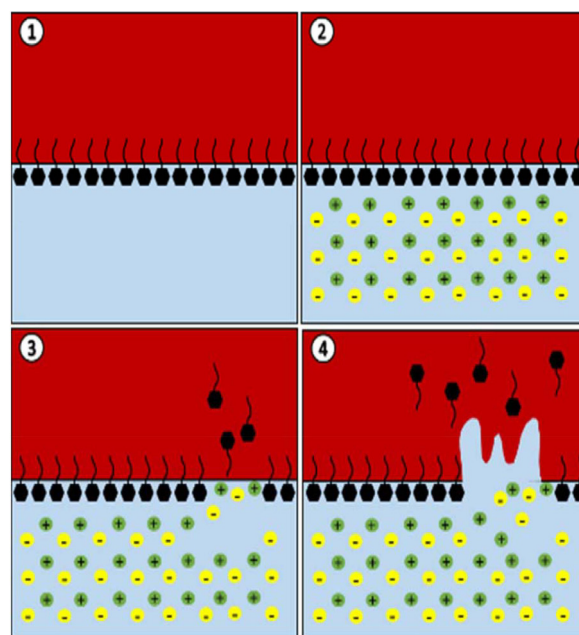

Fig. 4 On the destabilization Mechanism of the water-oil interface in the presence of ions.

Considering the high concentrations of the solutions used in the study (Table 4), it was expected, according to the salting-out theory, that all saline emulsions could present instability with phase separation. However, it was observed that, further to the saline concentration, other properties of the aqueous phase, such as pH and ionic strength, must be considered. For example, basic-character salts can chemically react with naphthenic acids and acid groups in resins and asphaltenes, causing these compounds to be easily adsorbed at the interface. According to the literature, the interaction between asphaltenes and carboxylic acids facilitates molecular arrangement at the interface, which favors the stability of emulsions. The results of the present study show that W/O emulsions with an aqueous phase of acid pH showed instability, likely due to the interactions of asphaltenes with carboxyl acids at the interface being less tensoative [51].

It is worth noting that the W/O emulsions prepared using aqueous phases containing DW, FW, neutral, and basic saturated saline solutions showed no instability, even after 30 days. Compared to the others, the neutral and basic saline solutions had low ionic strength values, and pH ranges from 6 to 11 (Table 4). These results indicate that, for the oil in particular, the aqueous phase with low ionic strength forms more stable emulsions, which aligns with Moradi et al. [11] and Rayhani et al. [16]. Furthermore, the pH range of these saline solutions contributed to the stability of W/O emulsions, especially at high pH due to the ionization of carboxylic acids present in petroleum. These results support Arla et al., Hutin et al., and Poteau et al. [51–53].

When subjected to testing with heating (30 days after preparation), an increase in the amount of aqueous-phase separation in the EM20S10 emulsion was observed, with approxi

mately 8.33% more separated water being observed at 80 °C. Thus, this emulsion, after submission to the two tests, presented a total separated aqueous-phase volume of approximately 37.50%. That is, the increase in temperature from 25 to 80 °C was sufficient to promote the separation of a greater volume of acidic aqueous phase (pH 4.21). For the other W/O emulsions, there was no increase in the amount of aqueous phase that separated during the heating procedure. The different types of aqueous phase that were used (basic, neutral, and acidic) exerted an influence on the interfacial properties of the W/O emulsions. Previous studies have reported that, depending on the pH, the functional chemical groups present in the polar compounds of petroleum can dissociate in the aqueous phase after emulsification, generating high-charge densities on the surface of the film around the droplets, thereby producing internal repulsion, rupture of the film, and droplet coalescence and phase separation [54]. Even when the high asphaltene content of the studied oil (7±1 wt%) (Table 3) and the As/R ratio of 0.22 are considered, which indicates that this oil is favorable to the formation of stable emulsions, unstable emulsions were still found. It suggests that depending on the amount and composition of the aqueous phase, oils that are theoretically considered to form stable W/O emulsions can form unstable ones several days after preparation.

Optical Microscopy

The morphology of the emulsions was visually evaluated using an optical microscope, and their stability by the mean DSD. It should be noted that all of the photomicrographs were obtained in triplicate immediately after the preparation of each emulsion. The smallest standard deviation obtained between the triplicates ensures the reliability of the DSD measurement.

The results showed that, in general, the W/O emulsions had an average DSD of between 1–10 µm (Table A1 Appendix), thus indicating their stability [2]. As expected, an increase in DSD was observed with increasing volumes of aqueous phase (0.1 to 30% w/v). Emulsions with higher water content showed grater data variability (Table A1). Of the emulsions prepared using S7, the only one containing observable droplets was EM1S7 (Table A1). Observing droplets in the

EM01S7 solution was impossible, so they are not discussed further.

The average DSDs of the W/O emulsions prepared using DW and FW classed them as stable, ranging from 1.09 with standard deviation ±0.23 to 5.97 ±2.44 µm. The FW emulsions had a larger mean DSD than the DW emulsions (Table A1), as shown by a previous study [14]. To provide an overview, only the photomicrographs of emulsions with an aqueous-phase volume of 10 w/v% are presented, together with the DSD curve (Fig. 5). Visually, smaller droplets were observed in EM10DW and some larger droplets in EM10FW, in agreement with the mean DSD result obtained. In general, compared to all the evaluated emulsions, smaller mean DSD values typified the emulsions with salt-free DW (Table A1), indicating that the composition of the oil itself, in terms of resins (32 wt%), asphaltenes (7 wt%), and TAN (1.209 mg·KOH·g^{-1}) (Table 3), was able to form stable emulsions without water–oil phase separation, even when heated to 80 °C. In this case, the main mechanism in operation is the interaction between the polar functional groups of the asphaltenes (heteroatoms) with the water molecules through hydrogen (H) bonds [55].

Several studies have been published on the interactions between oil's chemical composition (asphaltenes, resins, and naphthenic acids) and saline solutions. As mentioned in the introduction, several authors have argued that the presence of salts can increase the stability of W/O emulsions. Despite this, this saline effect regarding reduced droplet size was not observed in the present study because the emulsions prepared with DW had a lower mean DSD than the others. However, other authors have suggested that the presence of salts can decrease the stability of emulsions [12–14,16]. The present study's findings align more with these, as indicated by the gravitational separation test and mean DSD results (Table A1).

The emulsions prepared with the studied salts (S1–11) can be evaluated and discussed concerning the pH of each saline solution. The emulsions prepared with salts with basic pH values (S2 and S11) and ionic strength 10.11 e 1.21 mol·L^{-1}, respectively (Table 4), showed average DSDs in the range of 2.33±0.85 to 4.60±2.26 µm and 1.63±0.62 to 4.56±1.58 µm, respectively; these were classed as stable (Table A1).
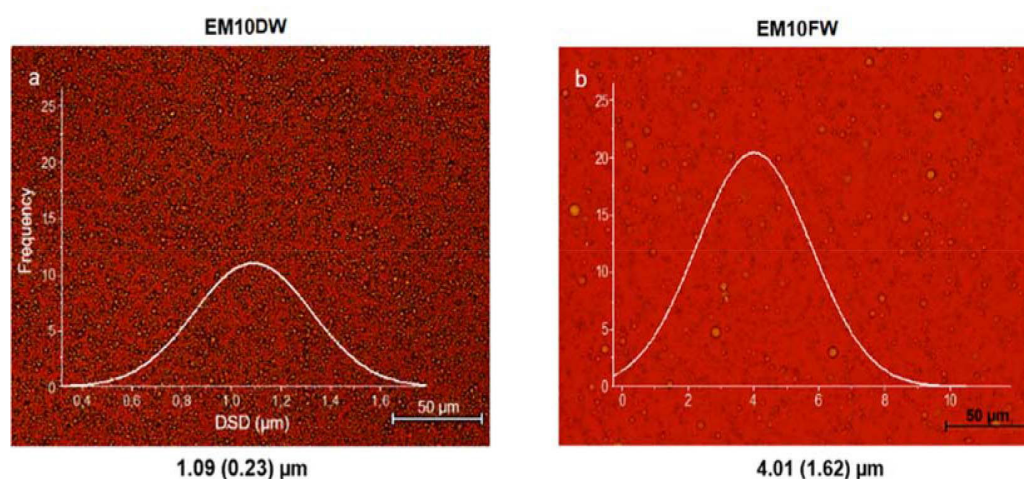

Fig. 6 Photomicrographs of W/O emulsions with 10% w/v: (a) Na$_2$CO$_3$ (S2) and (b) NaHCO$_3$ (S11).

Photomicrographs of these emulsions with a 10% w/v aqueous-phase volume (Fig. 6) showed that slightly larger droplets were found more frequently in EM10S2. These results indicate that emulsions containing a lower ionic strength saline aqueous phase are more resistant against droplet coalescence, which aligns with Moradi et al. [13] and Rayhani et al. [16].

For those prepared with neutral-pH salts—NaCl (S1) and KCl (S4)—the mean DSD ranged from 2.65±1.26 to 4.73±1.21 µm and 2.56±0.71 to 7.37±1.63 µm, respectively, which can also be considered stable. It was observed that, among these, the emulsions prepared with aqueous-phase contents of 10, 20, and 30% w/v KCl (S4) produced higher DSDs than the emulsions with NaCl (S1) for the same contents. This finding may be related to the nature of the cations, since Na^+ and K^+ have different sizes. In addition, the influence of these same ionic species on the DSD of oil W/O emulsions, determining a similar trend to that found in the present study, was evaluated by Muñoz and Solling [18]. Emulsions containing aqueous phases with KCl showed larger DSDs than those prepared with NaCl, as shown in the photomicrographs in Fig. 7. This suggests that the different spheres of solvation of these cations induced different droplet sizes. Furthermore, the average DSDs of the emulsions considered stable, containing neutral and basic salts, correlate with the results of the gravitational separation test, in which none of these coalesced with the water–oil-phase separation, even when subjected to heating. In general, the correlation between the average DSD results and the gravitational test shows that ionic strength also influences the stability of emulsions since, for this particular group of salts, the low ionic strength values may have hindered coalescence.

Concerning the emulsions with acid pH solutions and high ionic strength —the saturated saline solutions S3 and S5–S10—the average DSD ranged from 1.67±0.36 µm for EM01S9 to 9.03±2.61 µm for EM20S10 (Table A1 and Fig. 8). It is worth noting that the largest average DSDs were observed in this group of emulsions. In addition, despite having a DSD of under 10 µm, the gravitational separation test showed that some of these were unstable, with water–oil-phase separation occurring a few days after preparation. These emulsions included EM20S8, EM20S9, EM30S9, and EM10–EM30S10. These results suggest that, despite the small droplets (<10 µm), they likely had insufficiently strong interfacial films to maintain stability over time. It is possible that the salts in these emulsions did not interact well enough with the 32 wt.% resins and 7 wt% asphaltenes to guarantee the stability of the films formed around the droplets. As previously mentioned, the salting-out phenomenon may have occurred in these cases, where the interfacial film is destabilized at high saline concentrations by the migration of polar compounds to the oil phase [50].
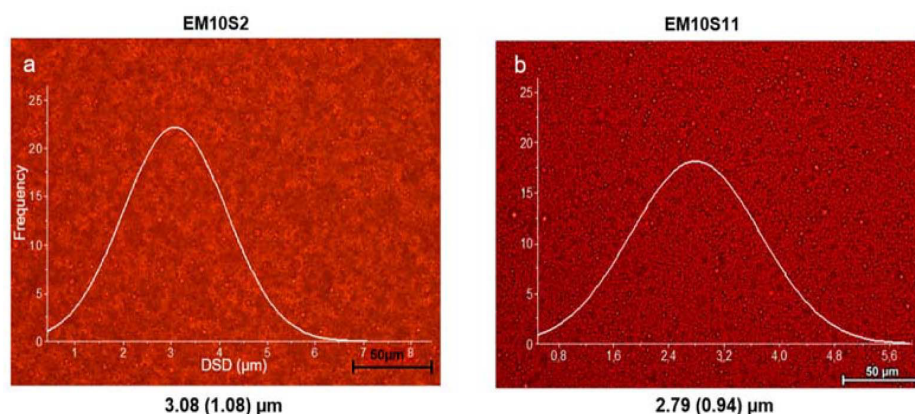

Fig. 6 Photomicrographs of W/O emulsions with 10% w/v: (a) Na_2CO_3 (S2) and (b) $NaHCO_3$ (S11).
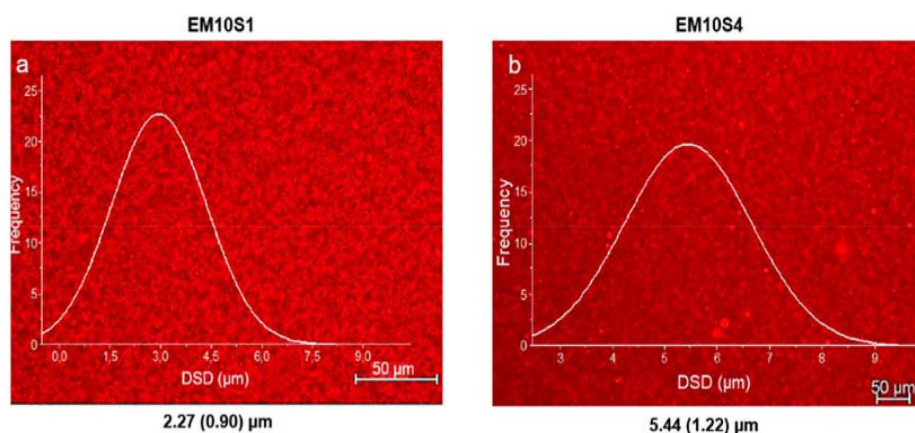

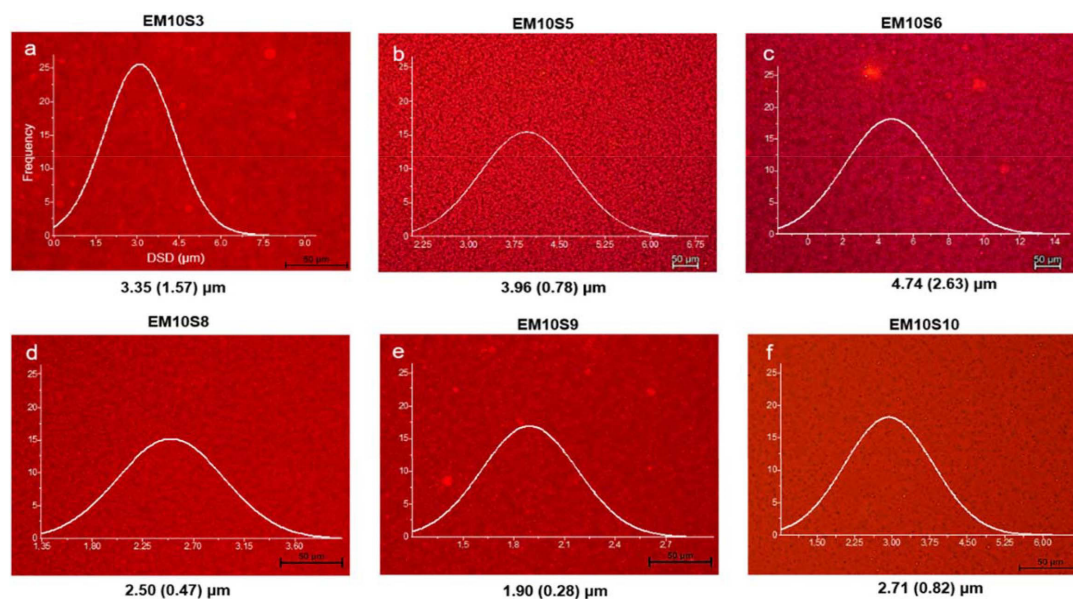**Fig. 7** Photomicrographs of W/O emulsions with 10% w/v: (a) NaCl (S1) and (b) KCl (S4).

Fig. 8 Photomicrographs of W/O emulsions with 10% w/v: (a) NH_4Cl (S3); (b) $CaCl_2$ (S5); (c) $MgCl_2$ (S6); (d) $MnCl_2$ (S8); (e) $Ni(NO_3)_2$ (S9); and (f) $SrCl_2$ (S10). All scales = 50 μm..

The salt solutions discussed in the previous paragraph—S5, S6, and S10 with acidic pH values—were composed of divalent cations of Family 2A (i.e., alkaline earth metals) of the Mendeleev periodic table. The atomic radii of these cations have the size order Mg^{2+} (S6) < Ca^{2+} (S5) < Sr^{2+} (S10), with the charge density also increasing in the same direction. According to Kazemzadeh et al. [7] and Rayhani et al.[16], the Mg^{2+} cation tends to form stronger bonds with the polar components of petroleum. Therefore, the W/O emulsions formed with this cation would likely be more stable, producing smaller DSDs when compared to the other cations of the same group. In this study, it was observed that, generally speaking, the average DSDs of emulsions with an increase in contents of aqueous phases containing these salts followed the increasing size order S6 (3.10 μm) < S5 (4.24 μm) < S10 (4.79 μm). In addition, it is worth noting that the emulsions containing S10 produced the largest average DSDs compared to the rest and were unstable during the gravitational test without heating. These findings demonstrate that the cation size in the aqueous phase influences the droplet size and the stability of the W/O emulsion.

Furthermore, the dispersion of the average DSD values as a function of the added aqueous-phase content for the different types of salts is summarized in Fig. 9. As previously mentioned, results varied between emulsions as a function of salt type and aqueous phase content. Despite these variations, all of the emulsions evaluated ranged between 1–10 μm.

In general, it was observed that the mean DSD values rose by increasing aqueous phase content. Among all of the emulsions, EM20S10 stood out, which presented the highest average DSD value (Fig. 9). However, a lower average DSD was found for the emulsion of the same salt with a higher content of aqueous phase (EM30S10). It may have occurred as, during the preparation of this emulsion, it was necessary to increase the stirring time from 3 to 6 minutes (per subsection of "Preparation of W/O emulsion" in "Results and Discussion"). Indeed, it is possible that the longer stirring time led to a greater dispersion of the droplets and, consequently, a lower mean DSD resulting.
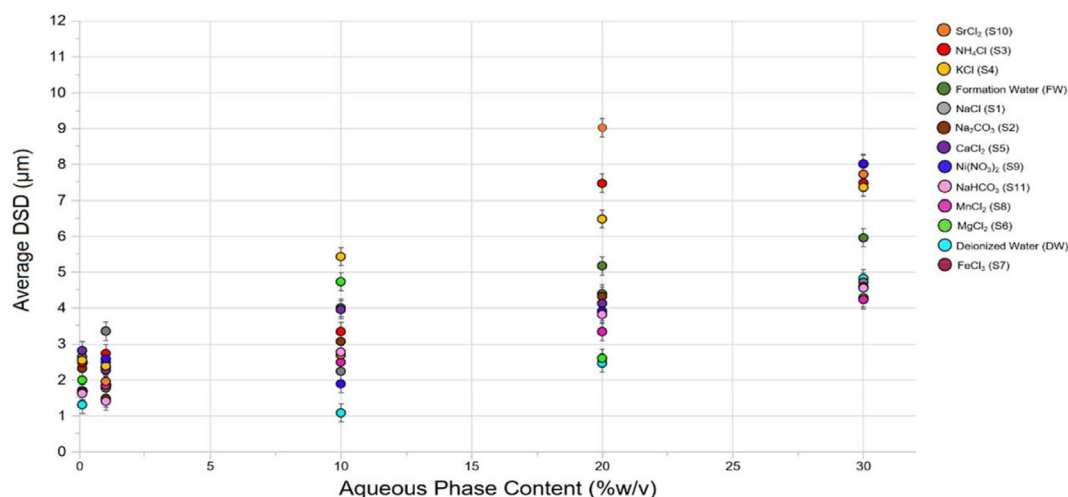

Fig. 9 Average DSD variation with aqueous phase content for different salts.

Finally, to briefly evaluate the influence of different types of aqueous phase on the average DSDs of the W/O emulsions, a graph was constructed to evaluate the average DSD as a function of the type of salt and its physicochemical characteristics, such as conductivity and pH (Fig. 10). The points shown in this graph present the averages of the DSD values found for all aqueous-phase contents (0.1, 1.0, 10, 20, and 30% w/v). Thus, the DSDs represent a single value obtained by averaging the five values for each aqueous phase. The emulsion containing $FeCl_3$ (S7) (pH 1.99, conductivity 59.67 $\mu S \cdot cm^{-1}$) had a small mean DSD value because, for this salt, it was only possible to see droplets of the emulsion at a concentration of 1.0% w/v (as previously noted). Thus, the average DSD value was relatively small compared to the others because it was only possible to obtain droplet size value from an emulsion.

Concerning the pH values of the different types of aqueous phases, it was generally observed that the largest droplet sizes were found in emulsions with acidic pH values and the smallest in those with DW. The neutral- (S1 and S4) and basic-pH emulsions had DSDs intermediate to the others (Fig. 10). These results correlate with those obtained from the gravitational-separation stability test, with most of the emulsions that showed instability with W/O phase separation being those with an acidic aqueous phase. It should be noted that the pH of the FW was neutral, although the DSDs of its emulsions did not behave similarly to those containing neutral pH salts, composed only of one type of monovalent salt. It suggests that the chemical composition of the FW comprised a mixture of monovalent, divalent, and trivalent salts, which influenced both its DSD and pH.

Regarding conductivity, the larger mean DSDs were correlated with high conductivity values (126.8–136.9 $mS \cdot cm^{-1}$). In general, the acidic saline solutions were shown to have higher conductivity values than the basic saline solutions (subsection of "Conductivity, pH, and ionic strength of the water and saturated saline solutions" in "Results and Discussion", (Table 4).

A ternary diagram was constructed to summarize the effect of ionic strength, pH, and aqueous phase content (%) on the average DSD of the emulsions (Fig. 11) to visualize the trends better. A relationship was observed between these properties since higher values of average DSD were found for higher contents of the aqueous phase, high values of ionic strength, and lower pH values.
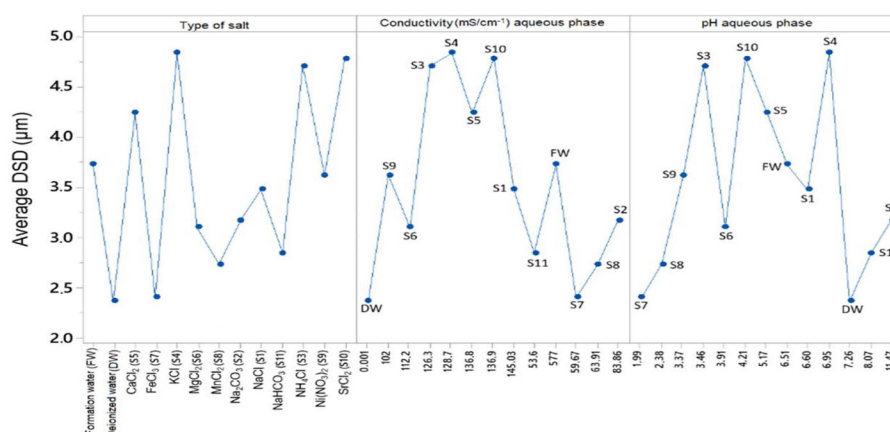

Fig. 10 Effects of salt, conductivity, and pH of the aqueous solutions on the average DSD of the W/O emulsions.
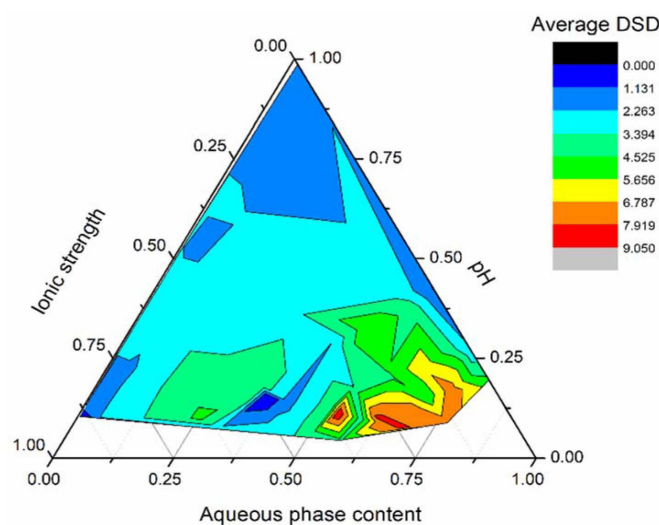

Fig. 11 Ternary diagram of the average DSD as a function of the ionic strength, pH, and aqueous phase content.

Interfacial Tension

The interfacial tension data for the studied oil with the different types of aqueous phases are shown in Figs. 12–13. As mentioned previously, the interfacial tension of the $FeCl_3$ (S7) and $Ni(NO_3)_2$ (S9) salts was not evaluated due to the dark color of those solutions.

Moreover, the average interfacial tension values of the oil with the different types of salts and water are shown in Fig. 12. It can be seen that the mean interfacial tension ranged from <0.01 to 22.37 mN/m. In general, it was noted that the highest values were found for the acidic-pH saturated solutions and the lowest for the basic- (S2 and S11) and neutral-pH (S1 and S4) solutions. The interfacial tension obtained from S2 was below the detection limit of the equipment (<0.01 mN/m), which explains the reported value. Concerning water, the interfacial tension with DW was lower than that of FW.

It has been reported in the literature that, at the oil-water interface, emulsifying agents (asphaltenes, resins, naphthenic acids, and inorganic salts) form a rigid film that provides reduced interfacial tension, contributing to the dispersion of droplets and stabilization of the emulsion [1]. The interfacial tension with DW was one of the lowest for the studied oil (acidic, with a high resin and asphaltene content) (Table 3). It suggests that the compositional characteristics of crude oil contribute to reducing interfacial tension.

The different types of saturated saline solutions evaluated with the studied oil exhibited different behaviors (Fig. 12). It has been established in previous studies that salts can accumulate at the droplet interface and, through ionic interactions with asphaltenes and resins, this can promote a decrease in interfacial tension [56]. However, the results obtained in Fig. 12 show that this reduction did not occur when comparing the interfacial tension value with DW (salt-free), except for the S2 solution (basic). This finding can be attributed to the presence of salt in the aqueous phase shielding the ions, thereby disturbing the interfacial activity of the asphaltenes [12]. Furthermore, the behaviors found for interfacial tension differed due to different ionic strength values. For most salts, it was observed that higher values of interfacial tension were accompanied by greater values of ionic strength—except for basic salts (S2 and S11) and acid (S3).

Comparing the results of the saturated saline solutions shows that lower interfacial tension occurred in those with basic and neutral pH, which presented lower ionic strength values (Table 4). To understand this more fully, Fig. 13 illustrates the effect of pH and the ionic strength of DW, FW, and saturated saline solutions on the mean interfacial tension.
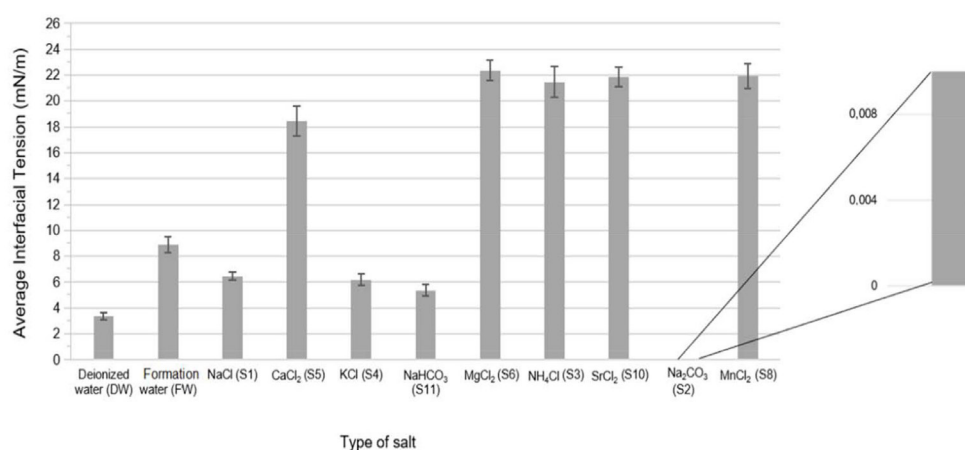

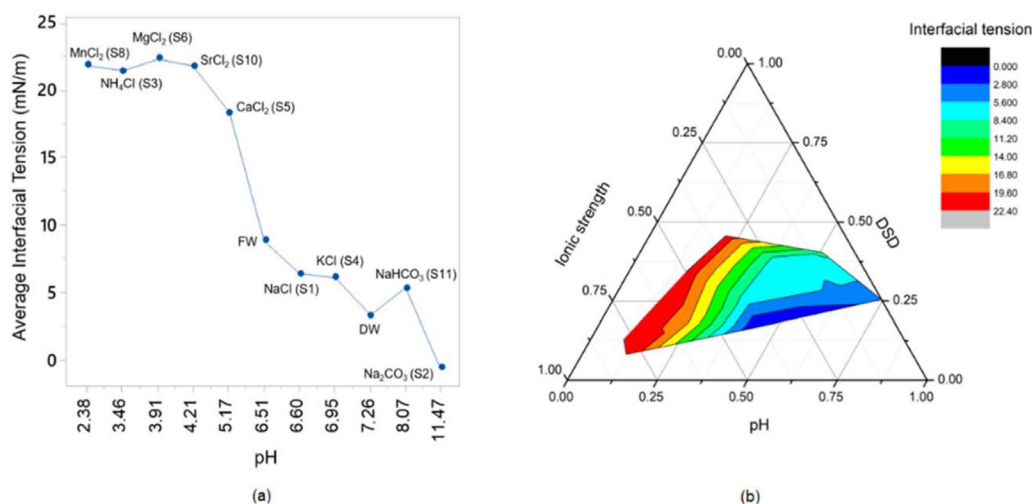**Fig. 12** The average interfacial tension as a function of salt type.

Fig. 13 (a) Effect of DW, FW, and saturated saline solution (S1–S11) pH on the mean interfacial tension. (b) Ternary diagram of the average interfacial tension as a function of the DSD of the 20% w/v emulsions, pH, and ionic strength of the aqueous phases.

65

da Silva M. et al.   Journal of Petroleum Science and Technology 13(4): 40, 2023, Pages 53-71

Lower tension values were found for saline solutions with pH values of 6.51 and upwards, the lowest for the most basic pH (11.47) and the highest for the most acidic (2.38). It suggests that the interfacial tension values depended on the saline solution's pH.

Previous discussions have been about the pH of the aqueous phase and the TAN of crude oil effect on the oil-water interface [20–22]. These studies reported a significant decrease in the interfacial tension of acidic, heavy oils due to the presence of basic species, such as NaOH and Na_2CO_3. It was reported by Palizdan et al. [57] that, considering the acidity of petroleum, an alkaline solution of Na_2CO_3 could react with oil and form natural surfactants, considerably reducing interfacial tension. According to the authors, the interaction between the alkaline aqueous phase would be increased by the ionization of the polar components of the oil. It occurs at basic pH values due to the acids' dissociation in the oil, decreasing the interfacial tension values. The findings of the present study agree with the literature, with a significant decrease in interfacial tension observed in saturated saline solutions with basic pH values. It is likely that the acid molecules present in the studied oil (TAN 1.209 mg·KOH·g⁻¹) (Table 3) dissociated at high pH values, causing a significant decrease in interfacial tension (Figs. 12–13). As previously mentioned, emulsifying agents form a rigid interfacial film around the water droplets, decreasing interfacial tension and stabilizing the emulsion [1]. A stable emulsion tends to contain droplets with diameters of less than 10 μm [2]. Therefore, the interfacial tension can be evaluated as a function of the DSD, as per Plasencia et al. [58]. The authors correlated the drop sizes of saline emulsions of flowing oils with interfacial tension and observed that higher stress values prevent the formation of smaller drops.

Fig. 13.b shows a ternary diagram of the average interfacial tension as a function of the average DSD of the emulsions with 20% w/v, pH, and ionic strength of the aqueous phase. To evaluate the interfacial tension as a function of the average DSD of the emulsions, is was necessary to select a volume of aqueous phase (20% w/v) to construct this diagram. It was done because the interfacial tension evaluated was independent of the amount of aqueous phase added to the oil during the preparation of the emulsions. It is worth noting that, in the present study, the concentration of saline solutions was not varied. All were saturated, with the concentration of the solutions according to the solubility of each salt. Thus, what varied was the volume of solution added to the oil (0.1, 1.0, 10, 20, and 30% (w/v), not the saline concentration.

No correlation was observed between the average DSD of the emulsions and the interfacial tension evaluated between the oil and the respective aqueous phases (Fig. 13.b). Ionic strength has little correlation with interfacial tension. It can be seen in the ternary diagram, where the entire range of interfacial tension values and the ionic strength remained in the same range. The only property that showed correlation and variation with the interfacial tension values was pH (Fig. 13). Both in the graph and in the ternary diagram, a clear trend emerges showing that higher pH values come in tandem with lower interfacial tension values, and vice versa. Of the emulsions that showed phase separation, all were formed by a saturated saline solution of acid pH (subsection of "Stability

by Gravitational Separation" in "Results and Discussion). These emulsions showed kinetic instability, with 3.33 to 29.17% of the aqueous phase separated after 15–25 days of preparation. It may suggest that high interfacial tensions between the aqueous (with acidic pH) and oily phases that make up the emulsions indicate their instability.

It is important to remember that all the emulsions prepared with aqueous phase of neutral and basic pH were stable in the gravitational test, even 30 days after preparation and after having been subjected to heating to 80 °C. These results show pH's strong influence on emulsion stability and interfacial tension.

Analyzing the results of Fig. 13 regarding Hofmeister-type ionic effects, a trend emerges about lower or greater ion-water interaction. According to the Hofmeister series, Na_2CO_3 salt composed of cosmotropic ions (heavily hydrated by water) should cause the salting-out effect on the water-oil interface [45]. As presented, the interfacial tension of the oil with this salt was the lowest obtained (Fig. 13), which seems to contradict Hofmeister's ionic effect. In this case, the pH parameter and interaction with the carboxylic acids of petroleum may most likely explain the reduction of interfacial tension.

Regarding the other salts evaluated, Hofmeister's ion-water interaction's effects may explain the interfacial tension results. According to Robinson et al. [59], the Jones-Dole viscosity B coefficient is a direct measure of the forces of normalized ion-water interactions for the strength of water-water interactions (Table 6).

Table 6 Jones Dole viscosity coefficients for the evaluated ions. Source: Adapted from Collins [60].

Ions	B
Mg^{2+}	0.385
Ca^{2+}	0.285
Na^+	0.086
K^+	-0.007
NH_4^+	-0.007

Positive B coefficients indicate strongly-hydrated (cosmotropic) and negative ions for weakly-hydrated ions (chaotropic). Considering the ions presented in Table 6, there is a tendency to decrease interfacial tension (Fig. 12) with the decrease in B value, or ion-water interaction, reaching negative values. Lower interfacial tension values are presented by salts with cations with lower interaction with water, such as Na^+ and K^+, while the salts of Mg^{2+} and Ca^{2+} present higher values.

The results suggest that lower B coefficient values may induce lower values of interfacial tension since, in these cases, the salting-in effect predominates. In salting-in, water molecules become more available for hydrogen bonds with natural surfactants, keeping them at the interface. Consequently, the interfacial tension decreases for the Na^+ and K^+ (Fig. 13). The interfacial tension of the oil with the NH_4Cl salt did not follow the trend discussed above, where it should provoke the salting-in effect due to the negative value of the coefficient B of the NH_4^+ and Cl^- ions (Table 6). In this case, the acid character of NH_4Cl may instead have followed the trend

about the saline solution's pH, not Hofmeister's water-ion interactions.

Conclusions

The study shows that the presence of polar compounds (asphaltenes and resins) in heavy oil favors the formation of stable emulsions. However, there was no emulsification in the largest volume of added aqueous phase (30% w/v) for some of the salt types tested—especially those with divalent cations. Another occurrence was the influence of pH on the stability of emulsions, verified by gravitational separation at room temperature, where acidic aqueous phase emulsions with high ionic strength were unstable;

The stability analysis by optical microscopy showed that the W/O emulsions could be considered stable, as they presented DSDs of between 1 and 10 μm. Regarding the saline effect, larger drops were observed in the presence of acid pH salts. Thus, the size of the droplets in W/O emulsions can also be related to the properties of the salt solution, such as pH, valence, ionic strength, and size of the cation radius.

The interaction of the polar compounds in petroleum with neutral and acidic salts increased interfacial tension. However, the interfacial tension was significantly reduced in saturated saline solutions with basic pH values, such as Na_2CO_3. Therefore, the pH of the aqueous phase influenced the interfacial tension evaluated. Furthermore, it was observed that increasing the ionic strength of the solutions increased the interfacial tension.

In summary, for the type of petroleum studied, the presence of acid pH salts, high ionic force, and cosmotropic ions of the Hofmeister series may have caused salting-out in w/o emulsions. Due to this, gravitational instability behavior, higher mean DSD, and higher interfacial tension values were observed.

The study is limited to W/O emulsions of heavy oils. Due to the specificity of medium, light, and extra heavy oils, the conclusions obtained in the present study would probably be different for W/O emulsions prepared with other types of oils. Furthermore, the saline solutions used to prepare the W/O emulsions were saturated. In other conditions of saline concentration, the emulsions could present different behaviors concerning the evaluated properties.

Supporting Information

Table of the average droplet size distribution (DSD) of the emulsions W/O and a figure of the gravitational separation test (DOC).

Acknowledgments

Nomenclatures

ASTM: American Society for Testing and Materials
ICP OES: Inductively Coupled Plasma Optical Emission Spectrometry
DSD: droplet size distribution
DW: deionized water
FW: formation water
W/O: water-in-oil
TAN: total acid number
SARA: saturates, aromatics, resins and asphaltenes
K: cell constant
[A]: molar concentration of ion A
[B]: molar concentration of ion B
[C]: molar concentration of ion C
ZA: charge ionic of ion A
ZB: charge ionic of ion B
ZC: charge ionic of ion C
S1: NaCl
S2: Na2CO3
S3: NH4Cl
S4: KCl
S5: CaCl2
S6: MgCl2
S7: FeCl3
S8: MnCl2
S9: Ni(NO3)2
S10: SrCl2
S11: NaHCO3
EM: emulsion
Δp: pressure variation between the surfaces
γ: the surface tension
R: perpendicular radii of curvature
$\Delta\rho$: density difference
g: acceleration of gravity
DE: equatorial diameter of the drop
H: correction factor of the DS/DE determination
As/R: asphaltene/resin

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Appendix

Table A1 Droplet size distribution (DSD) of emulsions prepared with deionized water (DW), formation water (FW) and different saturated saline solutions (S1 to S11).

Emulsion	Type of salt/water	Water content (w/v%)	Average DSD (µm)	Standard deviation (µm)
EM01DW	Deionized water	0.1	1.32	0.29
EM1DW	Deionized water	1	2.50	0.96
EM10DW	Deionized water	10	1.09	0.23
EM20DW	Deionized water	20	2.48	1.43
EM30DW	Deionized water	30	4.83	1.06
EM01FW	Formation water	0.1	1.70	0.51
EM1FW	Formation water	1	1.77	0.66
EM10FW	Formation water	10	4.01	1.62
EM20FW	Formation water	20	5.18	1.34
EM30FW	Formation water	30	5.97	2.44
EM01S1	NaCl	0.1	2.65	1.26
EM1S1	NaCl	1	3.36	1.23
EM10S1	NaCl	10	2.27	0.90
EM20S1	NaCl	20	4.40	1.55
EM30S1	NaCl	30	4.73	1.21
EM01S2	Na_2CO_3	0.1	2.33	0.85
EM1S2	Na_2CO_3	1	1.49	0.47
EM10S2	Na_2CO_3	10	3.08	1.08
EM20S32	Na_2CO_3	20	4.33	1.66
EM30S2	Na_2CO_3	30	4.60	2.26
EM01S3	NH_4Cl	0.1	2.49	0.88
EM1S3	NH_4Cl	1	2.74	0.79
EM10S3	NH_4Cl	10	3.35	1.57
EM20S3	NH_4Cl	20	7.48	1.81
EM30S3	NH_4Cl	30	7.49	2.70
EM01S4	KCl	0.1	2.56	0.71
EM1S4	KCl	1	2.35	0.48
EM10S4	KCl	10	5.44	1.22
EM20S4	KCl	20	6.49	1.23
EM30S4	KCl	30	7.37	1.63
EM01S5	$CaCl_2$	0.1	2.82	0.77
EM1S5	$CaCl_2$	1	2.28	0.46
EM10S5	$CaCl_2$	10	3.96	0.78
EM20S5	$CaCl_2$	20	4.14	1.63
EM30S5	$CaCl_2$	30	8.01	2.12
EM01S6	$MgCl_2$	0.1	2.01	0.85
EM1S6	$MgCl_2$	1	1.86	0.45
EM10S6	$MgCl_2$	10	4.74	2.63
EM20S6	$MgCl_2$	20	2.61	0.80
EM30S6	$MgCl_2$	30	4.29	1.60
EM1S7	$FeCl_3$	1	2.40	0.59
EM01S8	$MnCl_2$	0.1	1.71	0.32
EM1S8	$MnCl_2$	1	1.85	0.61
EM10S8	$MnCl_2$	10	2.50	0.47
EM20S8	$MnCl_2$	20	3.36	1.13

Continued

Table A1 Droplet size distribution (DSD) of emulsions prepared with deionized water (DW), formation water (FW) and different saturated saline solutions (S1 to S11).

EM30S8	$MnCl_2$	30	4.24	1.38
EM01S9	$Ni(NO_3)_2$	0.1	1.67	0.36
EM1S9	$Ni(NO_3)_2$	1	2.60	0.42
EM10S9	$Ni(NO_3)_2$	10	1.90	0.28
EM20S9	$Ni(NO_3)_2$	20	3.91	1.78
EM30S9	$Ni(NO_3)_2$	30	8.03	1.50
EM01S10	$SrCl_2$	0.1	2.50	0.43
EM1S10	$SrCl_2$	1	1.96	0.55
EM10S10	$SrCl_2$	10	2.71	0.82
EM20S10	$SrCl_2$	20	9.03	2.61
EM30S10	$SrCl_2$	30	7.73	2.31
EM01S11	$NaHCO_3$	0.1	1.63	0.62
EM1S11	$NaHCO_3$	1	1.42	0.43
EM10S11	$NaHCO_3$	10	2.79	0.94
EM20S11	$NaHCO_3$	20	3.82	2.23
EM30S11	$NaHCO_3$	30	4.56	1.58
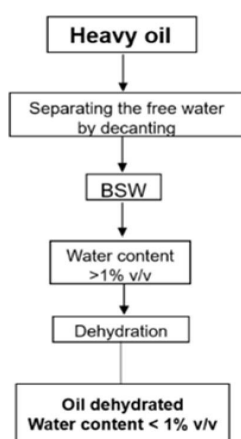
Fig. A1 Flowchart of the oil treatment procedure.
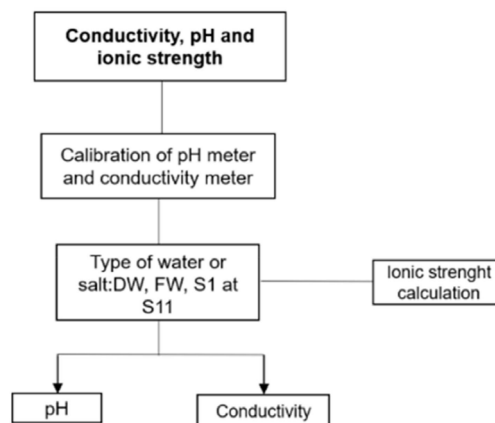
Fig. A3 Flowchart of the procedure for characterizing the aqueous phases used to prepare the emulsions.
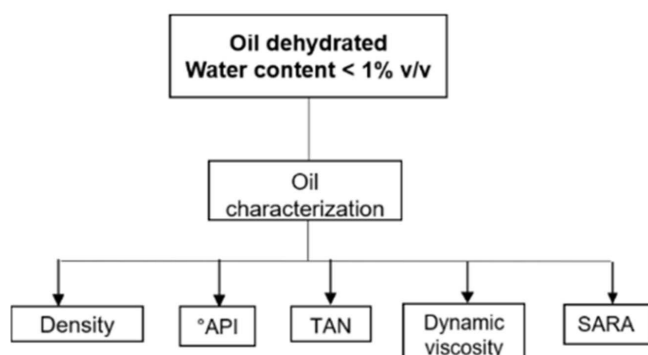
Fig. A2 Flowchart of the petroleum physicochemical characterization procedure.
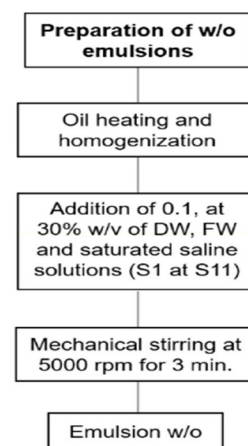
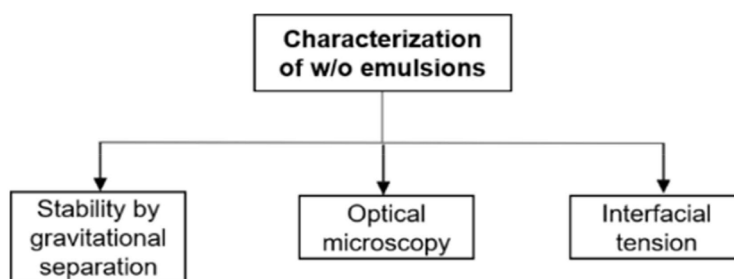**Fig. A4** Flowchart of the W/O emulsion preparation procedure.

Fig. A5 Flowchart of the W/O emulsion characterization procedure.
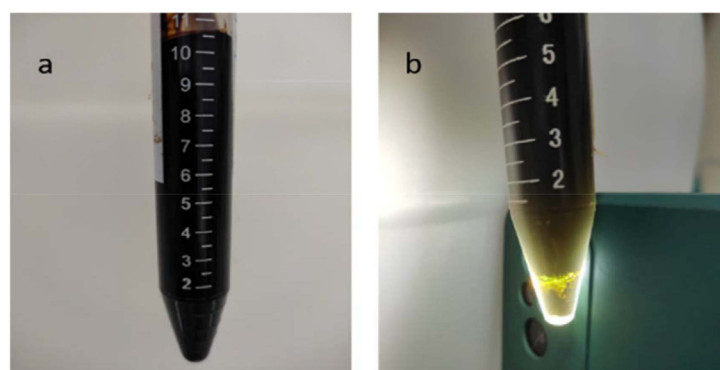

Fig. A6 Example of (a) stable and (b) unstable emulsion with aqueous phase separation.