Study of the Influence of Salinity on the Formation and Characterization of the Interfacial Material of Water-in-Oil Emulsion

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Abstract. This study addressed the stability of water-in-oil (W/O) emulsions of crude oil. Emulsion stability is influenced by various factors, including the interaction of colloidal particles, surfactants, polymers, salts, and pH. The study utilized a sample of petroleum and evaluated the effect of salinity on the stabilization of W/O emulsions. Four emulsions with different water and saline solution contents were prepared and characterized in terms of density, API gravity, emulsion stability by measuring droplet size distribution (DSD), and interfacial tension (IFT). The results showed that the petroleum could be classified as medium oil in terms of density and API gravity. The emulsions remained stable during gravitational separation monitoring, suggesting that the presence of an aqueous phase with low ionic strength favored more robust emulsions. Water content affected the average droplet size. The addition of saline solution reduced interfacial tension, promoting emulsion stabilization. Photomicrographs of the emulsions showed differences in the size and quantity of droplets among samples with different water and saline solution contents. Overall, the study indicated the importance of salinity in the stabilization of water/oil emulsions in the petroleum industry and how different factors influence their properties.

Keywords. IFT, ESI(+)Orbitrap MS, Emulsion, Petroleum, Salinity.

1. Introduction

The Brazilian energy matrix consists of 34.4% of oil and its derivatives. The oil production in January 2024 was 3.519 million bbl/d (million barrels per day), showing a variation of -1.8% compared to the previous month and 7.5% compared to the same month in the previous year, with 97.5% of this production occurring in offshore fields [1].

Throughout the journey from the reservoir to the surface, both oil and formation water are exposed to intense agitation. This environment, along with heat, pressure, and natural surfactants present in the chemical composition of the oil, promotes the formation of stable emulsions [2]. In the oil industry, the immiscible liquids are typically oil and water, both with high salinity [3,4]. Regarding emulsifying agents, consideration should be given to those present in both formation water and oil.

The presence of amphiphilic compounds in oil, such as asphaltenes, resins, and naphthenic acids, favors the stability of these emulsions. These compounds have hydrophilic groups in their molecules, which causes them to concentrate at the oil-water interface and form a rigid film around the droplets. This helps reduce interfacial tension and disperse the water droplets in the continuous phase of the oil [5]. Additionally, salts present in the formation water can be found at the interface due to ionic interactions with the natural emulsifiers [5].

Water-in-oil (W/O) emulsions can pose various challenges across all stages of the oil production chain, from their formation to refining and transportation. This is due to the relatively high saline content of the water present in the emulsions, which can lead to issues such as corrosion, hydrate formation, and salt deposition [3]. Their characteristics are determined by the saturation and concentration of dissolved salts and their composition. Additionally, emulsions exhibit higher viscosity compared to dehydrated oil, making their

flow and transportation more difficult. These challenges can result in damage to oil processing units, increased costs, and reduced efficiency throughout the production chain [3]. The objective of this study was to assess the effective influence of salinity on the formation and characterization of the interfacial material of water-in-oil emulsions.

1.1 Materials and Methods

1.2 Preparation of W/O Emulsions

A sample of petroleum from the Brazilian coast, originating from an onshore field, was selected. This sample underwent a prior dehydration process, resulting in a water content below 1% (v/v) [4]. The emulsions were prepared by adding the aqueous phase to the oil, and this mixture was subjected to shearing at 8000 rpm for three minutes at a temperature of 60°C using a mechanical homogenizer, model IKA T25 Digital Ultra Turrax. Two W/O emulsions were prepared containing deionized water (0.5% and 10%), and two were prepared with saline solution (NaCl) at 50 g.L-1 (0.5% and 10%).

1.3 Gravity Separation

To analyze the stability of the emulsions, a water-in-oil (A/O) phase separation test was conducted through gravitational separation at room temperature (25±3) ºC for 72 hours. The procedure involved separating aliquots of approximately 10 mL from each A/O emulsion into Falcon tubes and monitoring them at 24-hour intervals over a total of 3 days. During this period, the occurrence of A/O phase separation was observed, and the percentage of separated aqueous phase was quantified. Emulsions that did not undergo phase separation were considered stable.

1.4 Optical Microscopy

To evaluate the homogeneity and stability of the prepared W/O emulsions, microscopic techniques were used to analyze the size, shape, and coalescence of the droplets present. Four glass slides were prepared, each with a drop of the emulsion to be analyzed.

Images were acquired using a Nikon Eclipse LV100POL polarized light optical microscope equipped with a LV100's CFI LU Plan Fluor EPI P 50x objective and a DS-Fi1 digital camera attached. The slide containing the emulsion was placed on the microscope stage, and the 50x objective was used to magnify the sample image. The obtained photomicrographs were analyzed using NIS-Elements D software version 3.2 to determine the droplet size distribution (DSD) in terms of D [1,0], as well as to verify the shape of the droplets.

1.5 Interfacial Tension

Tensiometric analyses measure interfacial tension at the oil-water interface between two fluids of different specific masses. For the interfacial tension analysis, a Surface Electro Optics (SEO) tensiometer,

model Phoenix MT (M), employing the pendant drop method was used. A plastic syringe with a 'U'-shaped needle filled with the oil was utilized. The syringe-needle-oil assembly was placed on the manual piston of the equipment and immersed in a transparent container containing deionized water and saline solution (aqueous phase). After calibrating the needle diameter, a drop was dispensed and recorded. This procedure was conducted in triplicate at room temperature.

1.6 Density and API Gravity

To determine the density of the petroleum, ASTM D5002 standard [7] was followed using a viscometer with a digital densitometer, Anton Paar Stabinger SVM 3000 model, with a detection limit of 0.0002 g·cm-3 at 20°C. For the analysis, approximately 5 mL of the samples were injected into the viscometer's measurement cell after being preheated to the same test temperature. The analysis was performed in duplicate at temperatures of 40 and 50°C.

To determine the API gravity of the oil, ASTM D1250 [8] and ISO 12185 [9] standards were followed. The densities measured previously at temperatures of 40 and 50°C were converted to their equivalent value at 20°C for the calculation of API gravity.

1.7 Extraction of Interfacial Material

For the extraction of interfacial material, the methodology developed by Jarvis et al. [10], which was later adapted by Norrman et al. [11] for a 15 g scale, was utilized to obtain a larger quantity of material. The procedure began with the preparation of hydrated silica, which involved the controlled addition of 20 mL of water to 30 g of activated silica gel (70-230 mesh). This mixture was repeatedly agitated until a uniform free-flowing powder without lumps was formed. Subsequently, approximately 15 g of hydrated silica was dissolved in 15 g of oil sample using a solution of 250 mL of heptol (1:1 heptane/toluene), and the material was gently stirred and allowed to rest for 24 hours.

After the resting period, a glass column was assembled, with glass wool used at the base to filter the solution. Initially, all the material was passed through the column to separate the liquid part from the silica, followed by the transfer of the heptol through the column until the solution flowed colorlessly, producing the cleaning fraction (FL), which contains species that are not part of the scope of this work. Subsequently, a solution of 10:25 methanol/toluene (v/v) was used to wash the silica until it was completely clean, producing the fraction of interest corresponding to the interfacial material (MI). The resulting material from the column was then collected and subjected to evaporation in a fume hood.

1.8 ESI(+) Orbitrap MS

The ESI(+)Orbitrap MS data were obtained using a Q-Exactive Hybrid Quadrupole-Orbitrap mass spectrometer (Thermo Scientific, Bremen, Germany).

The samples were diluted in toluene/methanol (1:1) containing 0.1% v/v formic acid. The resulting solutions were injected into the ESI(+) source under the following operating conditions: spray voltage 3.5 kV, mass range m/z 100 to 1000; Sheath gas 10; S-lens 50; capillary temperature 350°C.

The obtained spectra were recalibrated using Xcalibur software (Thermo Scientific, Bremen, Germany), and the data were processed using Composer software (Sierra Analytics, Pasadena, CA, USA). The elemental compositions were determined based on m/z values.

The degree of unsaturation of each molecule can be directly deduced from its number of double bond equivalents (DBE) according to Equation 1:

$$DBE = c - \frac{h}{2} + \frac{n}{2} + 1 \qquad (1)$$

Where C, H, and N are equivalent to the number of carbon, hydrogen, and nitrogen atoms, respectively, in the molecular formula.

2. Results and Discussion

According to **Table 1**, the results obtained for the stability analysis of the W/O emulsions through gravitational separation demonstrated stability over 72 hours, with no phase separation occurring between water and oil. These results suggest that, in the specific case of the oil used, the presence of an aqueous phase with low ionic strength favors the formation of more stable emulsions. Regarding DSD, it was observed that the means ranged from 5 to 11 µm, indicating the stability of the emulsions [13]. There was a slight increase in the mean DSD as the content of the aqueous phase increased (from 0.5 to 10% w/v), except for the sample with 10% saline solution, which was smaller than that of 0.5%. The high standard deviation indicates that the emulsions are heterogeneous, with the droplet size varying considerably.

According to **Table 1**, the density value ranged from (0.87 < Υ ≤ 0.92) and the API gravity ranged from (22.3 ≤ °API < 31.1) for the oil. According to ANP [12], the crude oil is classified as medium, and its W/O emulsions increase the density and decrease the API gravity.

Table 1. Results of the physicochemical analyses of the petroleum and W/O emulsions obtained.

Sample	Grav. Sep 72h % v/v	DSD (µm)	Water Content % (v/v)	Density (g.cm⁻³)	°API
Reference Oil	0,0	0,0	0,0	0,86820 (±0,00005)	30,72 (±0,01)
0.5% Deionized Water	Stable	6,94 (±5,71)	0,5	0,87535 (±0,00021)	29,31 (±0,05)
10% Deionized Water	Stable	7,74 (±6,47)	10	0,88245 (±0,00007)	28,13 (±0,03)
0.5% Saline Solution 50 g.L⁻¹	Stable	10,42 (±6,95)	0,5	0,87590 (±0,00006)	29,33 (±0,02)
10% Saline Solution 50 g.L⁻¹	Stable	8,40 (±4,75)	10	0,88450 (±0,00005)	29,74 (±0,02)

The emulsifying agents, such as asphaltenes, resins, naphthenic acids, waxes, etc., organize into a rigid layer, while inorganic salts affect the emulsion stability, resulting in a reduction of interfacial tension. This, in turn, promotes droplet dispersion and emulsion stabilization [5]. In **Table 2**, it is possible to observe a reduction in the interfacial tension value compared to crude oil, with this reduction being smaller in the saline emulsion, suggesting that salinity contributes to the decrease in interfacial tension.

Table 2. Results of the interfacial tension analysis between oil and aqueous phases.

Sample	IFT
Oil + Deionized Water	27,76(±0,94)
Oil + Saline Solution 50 g.L⁻¹	22,45(±0,37)

The visual analysis between Figure 1.A and 1.B reveals the presence of droplets with similar dimensions and close quantities. In Figures 1.C and 1.D, a notable disparity between the samples regarding the size and quantity of droplets is observed. The droplets exhibit polydispersity among them. A prominent film around the droplets can be observed.
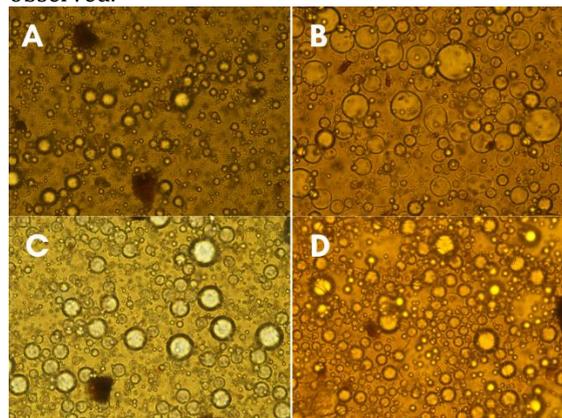

Figure 1. Photomicrographs at 50x magnification of W/O emulsions with 0.5% w/v of (A) deionized water and (B) saline solution, and 10% w/v of (C) deionized water and (D) saline solution.

The Figure 2 displays the ESI(+)Orbitrap MS spectra for the reference oil (Figure 2a) used in the study and their respective cleaning fraction, FL (Figure 2b), and interfacial material, MI (Figure 2e) obtained by wet silica [11, 12]. It is possible to observe that the mass spectra of the oil (Figure 2a) and FL (Figure 2b) showed Gaussian profiles with distinct m/z 200 – 800 values from the spectral profile of MI (Figure 2e).

Figure 2 also shows the FL and MI fractions obtained from the emulsions: 10% deionized water (deionized water emulsion) and 10% saline solution (saline solution emulsion). It is noted that the spectra of the FL fractions of the 10% deionized water emulsion (Figure 2c) and 10% saline solution emulsion (Figure 2d) presented different Gaussian profiles from each other, with values of m/z 200 – 600 and 200-800, respectively. However, the spectrum corresponding to the MI of the 10% deionized water emulsion

(Figure 2f) exhibited a profile with four different Gaussian peaks, while the spectrum of the MI corresponding to the 10% saline solution (**Figure 2g**) showed a profile with three Gaussian peaks. In both cases, this can be attributed to the resulting solution injected into the ESI source, which was too concentrated for measurement in the Orbitrap MS.

Figure 3 presents the compound class plot obtained from the processing of ESI(+)Orbitrap MS spectra of the reference oil and the MI of the oil and the deionized water (DW) and saline solution (SS) emulsions. The data reveal the predominant presence of class N (analogous to pyridines) for the reference oil and the MI obtained from it. However, it is noticeable that, in addition to the pyridines class, classes N_2 and O_2S stand out for the MI of the DW and SS emulsions.
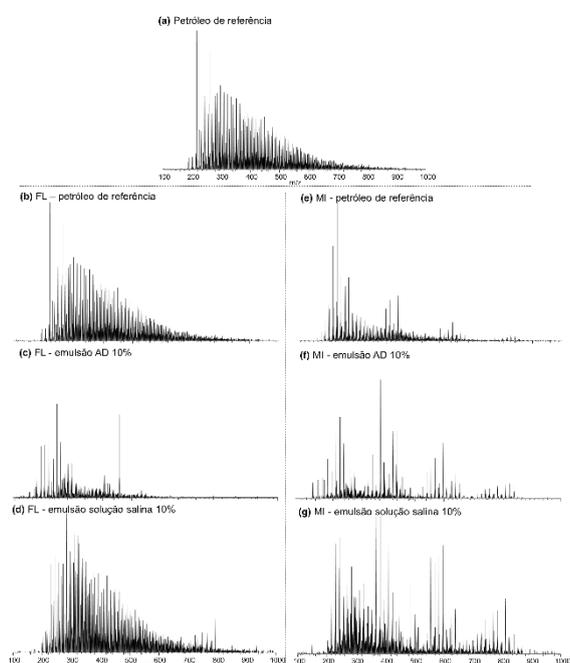

Figure 2. ESI(+)Orbitrap MS spectra of fractions obtained by the wet silica method from the reference oil **(a)**, the cleaning stage, FL, **(b, c, d)**, and the interfacial materials, MI, from the oil, emulsions with deionized water, DW, and 10% saline solution **(e, f, g)**.
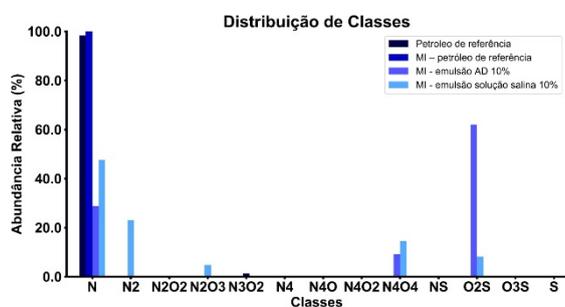

Figure 3. Heteroatom-containing compound class distribution of the compounds present in the reference oil and the MI of the reference oil and the deionized water emulsions (10% DW emulsion) and 10% saline solution identified by ESI(+)Orbitrap MS.

Figure 4 presents the DBE versus the number of carbons (NC) graphs of the highlighted classes when processing the ESI(+)Orbitrap mass data. It is possible to observe a wide range of compounds in class N for the reference oil (**Figure 4a**, DBE = 4-15 and NC = 15-50), which is significantly reduced in the MI compounds. However, the N class of the MI for the saline solution emulsion (**Figure 4d**, DBE = 1-10 and NC = 25) indicated a greater range compared to the MI of the reference oil (**Figure 4b**, DBE = 5-10 and NC = 15-25) and the DW emulsion (**Figure 4c**, DBE = 5 and NC = 15-18). This highlights that salinity contributed to the ionization of a wider range of molecules with lower DBE.
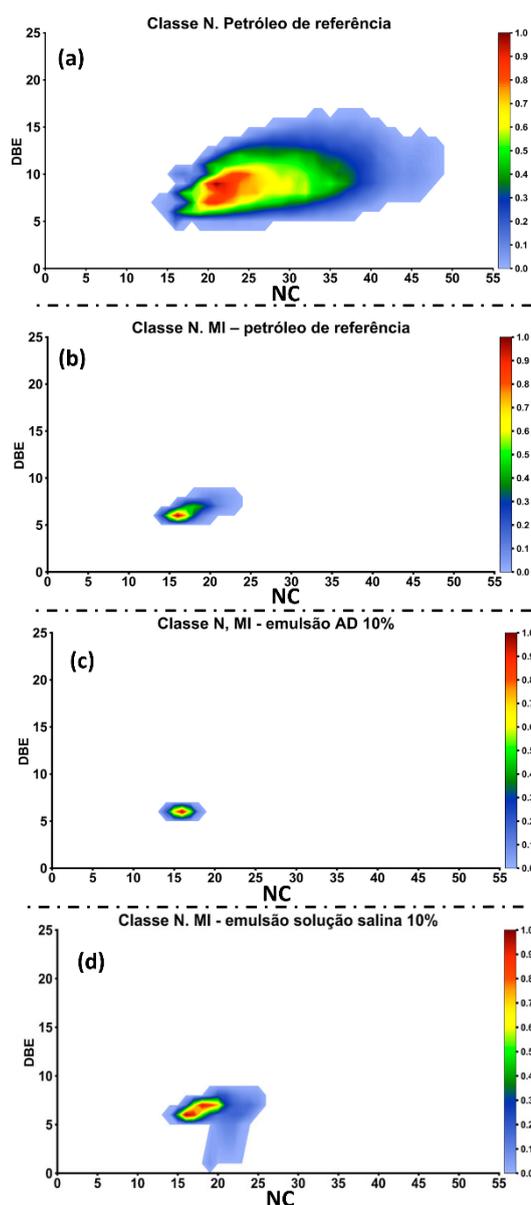

Figure 4. DBE versus number of carbons (NC) graphs of class N for the reference oil **(a)**; the MI of the reference oil **(b)**; the MI of the deionized water emulsions (10% DW emulsion) **(c)**; and 10% saline solution **(d)** identified by ESI(+)Orbitrap MS.

3. Conclusion

During the study, it was observed that the emulsions

prepared from the reference oil exhibited stability for more than 72 hours due to the saline effects, which was also evidenced by the average DTG, and there was also a decrease in the interfacial tension of the droplets, as observed through the pendant drop method.

The ESI(+)Orbitrap MS data showed different spectral profiles between the original oil and the fractions obtained by wet silica from the 10% deionized water and 10% saline solution emulsions. However, the spectral profiles of the MI of the emulsions revealed multiple Gaussians, indicating the need for the preparation of more diluted solutions for analysis, requiring further study at different concentrations.

The ESI(+)Orbitrap MS data revealed the predominance of class N for the reference oil and the MI obtained from it. On the other hand, classes N2 and O2S stood out for the MI of the deionized water and saline solution emulsions.

The results also demonstrated that salinity contributed to the ionization of a wider range of molecules with lower DBE.

4. Acknowledgments

5. References

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