



## Effect of CO<sub>2</sub> on the dynamic and equilibrium interfacial tension between crude oil and formation brine for a deepwater Pre-salt field

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### ABSTRACT

Interfacial tension (IFT) between oil and brine is key to determine the Capillary Number, which governs capillary forces in the porous medium. As a result, changes in IFT affect the displacement efficiency and the residual oil saturation having direct impact on the Recovery Factor. Fluids in Pre-salt fields (offshore Brazil) have particular characteristics, such as high salinity in the brines, elevated content of asphaltenes and resins in the oils and high CO<sub>2</sub> content in the produced gas for some fields. The effect of CO<sub>2</sub> on the IFT depends on complex electrostatic and acid-base equilibria, and cannot be predicted by a single fluid property. This work presents the experimental study of the effect of CO<sub>2</sub> dissolution on the IFT between a Pre-salt oil with a high total base number (TBN) and non-negligible total acid number (TAN) and a high salinity brine using the pendant drop technique. The oil and its asphaltenic fraction were characterized by Fourier-transform infrared spectroscopy, nuclear magnetic resonance spectroscopy, and elemental analysis identifying characteristic functional groups and indicating both acidic and basic polar functional groups. CO<sub>2</sub> dissolution resulted in an IFT increase of 56% evidencing that, despite the high TBN of this oil, basic groups have low surface-activity. Moreover, a study of IFT as a function of pH showed that the maximum IFT was found in strongly acidic environments, but constant IFT values were obtained at neutral and basic pH values. Thus, the interfacial activity is governed by asphaltenes and resins with polar groups of varying acid/base behavior. The presence of CO<sub>2</sub> also accelerated the dynamic behavior of IFT reducing the equilibrium time by 70%. This is caused by the reduction of oil viscosity, which impacts the relaxation time and enhances the diffusion of surface-active species towards the interface. The results in this work evidence that the CO<sub>2</sub> content should be considered when modeling fluid properties for this type of reservoirs, as it affects the oil-brine IFT. In addition, for this oil with high content of surface-active compounds and non-negligible TAN and TBN, CO<sub>2</sub> flooding does not contribute to reduce the IFT. Therefore, the efficiency of this Enhanced Oil Recovery technique in this type of field relies on viscosity reduction, miscible displacement and wettability alteration rather than IFT reduction.

### 1. Introduction

Offshore Pre-salt fields in Brazil have been among the most important assets in the Oil and Gas Industry for the last ten years reaching productions over 1.5 million barrels per day (Mejia Sanchez et al., 2019). One of the greatest exponents in Santos Basin, Lula Field, has over 6 billion barrels of oil equivalent (boe) reserves (Henriques et al., 2012). Initial characterization of its fluids rendered light oil (28° API) and gas to oil ratio (GOR) up to 230 m<sup>3</sup>/m<sup>3</sup>, with up to 12% volume of CO<sub>2</sub> (Nakano et al., 2009). However, further publications reported GOR values up to 350 m<sup>3</sup>/m<sup>3</sup> with CO<sub>2</sub> contents of up to 20% (Tadeu et al., 2015). Ultra-deep waters result in high pressures (over 8000 psi);

however, temperatures were found to be moderate between 60 and 70 °C (Cezar et al., 2015; Henriques et al., 2012).

Transportation of fluids from production platforms is challenging due to the large distances of over 200 km to the coast (Filho et al., 2015). The application of CO<sub>2</sub> and water alternated with gas (WAG) injection in Lula Field is aimed as an Enhanced Oil Recovery (EOR) method that simultaneously reduces the emissions of this greenhouse gas. In this regard, gas flooding and WAG were taken into consideration since the early days of the development of Lula Field (Hauville et al., 2014). The first pilot for the injection of CO<sub>2</sub>-enriched natural gas in Lula field was reported in 2011 (Pizarro and Branco, 2012). In this pilot test, CO<sub>2</sub> enrichments up to 50% were applied obtaining successful results in

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terms of connectivity of the reservoir and sustained well productivity.

CO<sub>2</sub> flooding is a mature EOR technique which has been applied for over 60 years. The main mechanisms for incremental oil production in miscible flooding are viscosity reduction and oil swelling (Lake, 1989). Stalkup discussed the physical properties that affect sweeping and displacement efficiencies in immiscible gas flooding (Stalkup, 1978). At high pressures and moderate temperatures, CO<sub>2</sub> density is in the same order of magnitude than that of average oils reducing the effects of gravity segregation. However, the viscosity ratio between CO<sub>2</sub> and oil is unfavorable (i.e. much lower than 1), giving place to WAG to improve mobility ratio increasing the sweeping efficiency.

The most relevant operational parameters including common problems in WAG projects, such as poor injectivity and corrosion among others, were reviewed elsewhere (Christensen et al., 2001). A more recent publication presented a sensitivity analysis of key aspects of WAG and gas flooding, i.e. gas and water injected volumes and well pattern design (Perera et al., 2016). One key variable for modeling reservoir scenarios is interfacial tension (IFT), as it is directly related to the Capillary Number which represents the ratio between viscous and capillary forces (Sheng, 2010). Nevertheless, there is no straightforward relationship between CO<sub>2</sub> mole fraction and oil-brine interfacial tension, since this physical property depends on complex intermolecular forces including electrostatic, acid-base and other interactions.

Several studies presented the effect of CO<sub>2</sub> dissolution on the interfacial tension between oil and water phases. For systems with low concentration of surface-active components (i.e. decane and water), the increment in CO<sub>2</sub> mole fraction results in lower IFT values (Georgiadis et al., 2011). Another work (Sun and Chen, 2005) obtained the same trend for live oil and brine (salinity of 2969 ppm) obtaining a decrease of 30% from the initial IFT for a CO<sub>2</sub> mole fraction of 65% in the oil phase.

Compounds containing polar functional groups in the oil such as alcohols (Moradi et al., 2014) and carboxylic acids (Hoeiland et al., 2001; Sayed et al., 2019) have effect on the IFT. Most of the components with interfacial activity concentrate in the asphaltene and resin fractions of the oil (Buckley et al., 1998). The capability of asphaltene and resins in crude oil to decrease interfacial tension with the aqueous phase was thoroughly discussed elsewhere (Lashkarbolooki et al., 2016; Lashkarbolooki and Ayatollahi, 2016; Schorling et al., 1999). The composition of the asphaltenes has a greater effect on their surface activity than their overall concentration (Yang et al., 2014). In addition, the efficiency of these polar compounds as surfactants is affected by the other components in the oil phase, such as the composition and concentration of paraffin fractions and the presence of light fractions such as dissolved gas (Doryani et al., 2015). Also, properties of the aqueous phase such as ionic composition (Buckley and Fan, 2007; Kakati and Sangwai, 2017; Lashkarbolooki et al., 2016; Mahmoudvand et al., 2019; Tichelkamp et al., 2015) and pH (Ashrafizadeh et al., 2012; Hutin et al., 2016; Hyde et al., 2018; Ramakrishnan and Wasan, 1983) are of paramount importance to determine the activity of these amphiphilic compounds and, thus, the IFT between oil and brine. Buckley and Fan (2007) identified the concentration of asphaltenes, total acid number (TAN), total basic number (TBN) and oil viscosity as the most relevant parameters to influence oil-brine IFT. The contribution of each one of them depends on the pH of the aqueous phase. Particularly, while TAN has an effect at basic conditions, TBN is significant in acid environments. Ultra-low IFT was achieved for oils with TAN over 0.1 at pH values greater than 10 indicating the increased surface activity of acid compounds in basic environments.

CO<sub>2</sub> dissolution in the brine phase decreases the pH due to the equilibrium of carbonic acid (Bhatt et al., 2019). For oils with acidic or basic surface-active compounds, this shift of pH has a strong influence on the ability of these compounds to reduce IFT (Lashkarbolooki and Ayatollahi, 2018). Asphaltenes and resins forming acids (i.e. sulphonic or carboxylic acids) will be ionized in basic environments showing greater interfacial activity at high pH. On the other hand, compounds with basic groups (i.e. amines) are more active at low pH solutions

where they are positively charged.

Lashkarbolooki et al. studied the effect of CO<sub>2</sub> dissolution in brine on the IFT for oils with different concentrations of acid groups and found that carbonated brine resulted in higher interfacial tension for more acidic oils. They also reported that the hydrophobicity of the native surfactants in the crude oil sample increased when CO<sub>2</sub> was dissolved in the brine. In addition, they studied the dynamic behavior of IFT concluding that the mass transfer and surface orientation of native surfactants is affected by CO<sub>2</sub> diffusion in the oil phase (Lashkarbolooki et al., 2017). In posterior research (Lashkarbolooki et al., 2018), the authors investigated the dynamic IFT between different oils and brines at elevated pressures and temperatures. They found that the key factors controlling the change of IFT are the concentration and nature of acid and basic compounds and the pH of the aqueous phase. In contrast, pressure and temperature did not show a critical effect. Also, their results supported the idea that CO<sub>2</sub> diffusion in crude oil acts as a mass transfer barrier for the efficient packing of the surface-active components. This diffusion has a contrary effect to that of the ionization of basic compounds in acid environments. As a result, the IFT will depend on which of these phenomena overcomes.

Another work by the same group (Lashkarbolooki and Ayatollahi, 2018) analyzed the IFT between oils with different total acid numbers (TAN) and asphaltene and resin contents and brines with different salinities and pH values. Their experiments showed that the TAN alone is not enough to define the interfacial activity of different crude oils. The distribution of functional groups (such as those containing Sulfur, Nitrogen and Oxygen) in the oil and the pH of the aqueous phase proved to be determinant in the resulting IFT. Moreover, both seawater and deionized water showed the same trends for the variation of IFT with pH.

The cited bibliography evidences that the effect of CO<sub>2</sub> dissolution on IFT involves the contribution of complex phenomena and is dependent on the specific composition of the aqueous and oil phase. Given the characteristic of the Pre-salt scenario, the investigation of the effect of CO<sub>2</sub> on IFT is of great relevance to study fluid-fluid interactions in these reservoirs either for reservoir characterization or EOR research purposes. This work proposes an experimental investigation of the effect of CO<sub>2</sub> dissolution on the dynamic and equilibrium interfacial tension between a crude oil and brine characteristics of Pre-salt reservoirs. Its main objective is to understand the variation of IFT as CO<sub>2</sub> is introduced in the system, in correlation with the properties of the fluids in this challenging reservoir environment.

## 2. Materials and methods

Formation brine was reproduced in laboratory following the composition of the formation water from a Brazilian Pre-salt field reported by Shell Brasil (Table 1). The operator also provided a sample of crude oil (Oil B) from the same field. In addition, a synthetic oil (Oil M, 71.1 wt% n-C16 and 28.9 wt% toluene) was prepared matching the ratio between asphaltenes and saturates from the Pre-Salt oil sample. The reagents were acquired from Sigma-Aldrich with a purity of 99.9%.

Fluids were characterized using the following procedures. Formation

**Table 1**  
Pre-Salt formation brine composition.

Ions	Concentration [ppm]
Na <sup>+</sup>	57580
Ca <sup>2+</sup>	24250
Mg <sup>2+</sup>	2120
K <sup>+</sup>	1200
Ba <sup>2+</sup>	24
Sr <sup>2+</sup>	1260
SO <sub>4</sub> <sup>2-</sup>	54
Cl <sup>-</sup>	139900
TDS	226388

brine conductivity and pH were measured using a Mettler Toledo SevenExcellence meter. SARA analysis was performed by IP 143 n-heptane precipitation method (asphaltenes) and medium pressure liquid chromatography (saturates, resins and aromatics). In addition, total acid number (TAN) and total base number (TBN) were calculated using the ASTM D664 procedures, and gas chromatography (GC) was performed in an Agilent HP7890B with a DB-Petro column. Finally, the API gravity was measured in a Mettler Toledo DM40 density meter, and dead oil viscosity was measured in an Anton Paar SVM 3000.

The asphaltene fraction of the crude oil was separated using n-heptane following the procedure by Franco et al. (2013). The characterization was made by Fourier-transform infrared spectroscopy (FTIR) with a Nicolet 6700 spectrometer (Thermo Scientific) using a DTGS KBr detector and nuclear magnetic resonance (NMR) with a Bruker AV400 using 16 scans. Carbon, hydrogen, nitrogen and sulfur contents were obtained for both crude oil and asphaltenes by elemental analysis using the procedures in ASTM D5291 performing triplicate analysis of all samples with a maximum standard deviation of 0.81 wt%.

IFT measurements were made at 60 °C and 1000 psi using a high-pressure high-temperature (HPHT) Drop Shape Analyzer (DSA) apparatus designed by Kruss and Eurotechnica. Fig. 1 shows the scheme for the experimental setup used for the tests. Different tests were made to analyze the effect of both the CO<sub>2</sub> dissolution in the fluids and the pH of the aqueous phase.

For experiments with dead fluids (no CO<sub>2</sub>), the DSA chamber was first filled with brine and then all lines were bled. The pressure and temperature were raised to reach stabilized experiment conditions. Then, the drop of oil was injected into the chamber using a u-shaped line giving start to the experimental run. Measurements were taken every 30 s.

Recombination of dead oils and brines with CO<sub>2</sub> was carried out following the procedures detailed elsewhere (Drexler et al., 2019). In the experiments containing CO<sub>2</sub>-saturated fluids, degassed brine was first pumped into the chamber, all lines were bled, and test conditions were set. Then, the CO<sub>2</sub>-saturated brine was pumped towards the chamber, pushing the degassed brine back to a piston cell. After injecting at least three times the total volume of the system, the drop of oil saturated in CO<sub>2</sub> was formed and the experiment began. After all experiments, the cleaning routine consisted of flowing toluene and pure water through the oil and brine lines, respectively. Then, methanol was used to flush

the system, and finally nitrogen was used to dry it.

Density and viscosity of dead and recombined fluids were calculated with commercial software. For oil phases, PVTsim Nova 3.3, (Calsep) with the Soave-Redlich-Kwong equation of state (EOS) and the Peneloux volume correction was used. Brine properties were calculated with OLI studio 9.6 (OLI Systems Inc.) with the Mixed Solvent Electrolytes + Soave-Redlich-Kwong EOS.

IFT measurements are time-dependent, mostly due to the diffusion process of surface-active species to the interface (Georgiadis et al., 2011). This dynamic behavior introduces uncertainties when analyzing the data because the equilibration process can take several hours. A logarithmic function was used to model the data set for each experiment. Since this function is not asymptotic, a threshold value of 0.01 mNm<sup>-1</sup>h<sup>-1</sup> was taken as the stabilization limit derivative. Using this threshold value to calculate the stabilization time for each data set made it possible to calculate the equilibrium IFT with the fitting logarithmic function.

The numerical procedures involved in the calculation of the IFT value from the drop profile were already discussed in the literature (Anastasiadis et al., 1987; Song and Springer, 1996). Finally, all experiments were repeated 3 times, and the results shown in this work are the mean values, with the error bars representing the standard error of the mean.

### 3. Results and discussions

#### 3.1. Fluid characterization

The gas chromatography (GC) analysis of crude Oil B is shown in Table 2, and the SARA composition, total acid and basic numbers (TAN and TBN) are presented in Table 3. It can be observed that although the TAN/TBN ratio is lower than one indicating a more basic behavior; both TAN and TBN have non-negligible values, indicating the presence of both acid and basic groups in Oil B. In addition, the resin and asphaltene contents suggest that Oil B has a considerable concentration of interfacial-active components.

Elemental analysis characterization of Oil B and its asphaltene fraction is reported in Table 4. The relative strength of each of these contributions is yet to be assessed. As expected, the asphaltenes have a lower H/C ratio than the crude oil due to their higher degree of



Fig. 1. DSA apparatus experimental setup for IFT measurements at HPHT.

**Table 2**  
Pre-salt oil chromatography.

Component	wt%	Component	wt%
C3	0.00	C12	2.68
iC4	0.01	C13	3.12
nC4	0.01	C14	3.03
iC5	0.12	C15	3.29
nC5	0.18	C16	2.90
C6	0.48	C17	2.85
Mcylo-C5	0.21	C18	3.15
Benzene	0.00	C19	2.89
Cyclo-C6	0.19	C20	2.62
C7	0.94	C21	2.54
Mcylo-C6	0.48	C22	2.47
Toluene	0.03	C23	2.39
C8	1.72	C24	2.38
C2-Benzene	0.08	C25	2.31
m&p-Xylene	0.09	C26	2.33
o-Xylene	0.05	C27	2.37
C9	2.11	C28	2.39
C10	2.61	C29	2.45
C11	2.56	C30+	39.97

**Table 3**  
SARA analysis and total acid and base numbers of Pre-salt crude oil.

Pre-salt Oil	
Saturates (wt%)	64.06
Aromatics (wt%)	25.98
Resins (wt%)	8.46
Asphaltenes (wt%)	1.50
TAN (mg KOH/g)	0.37
TBN (mg KOH/g)	4.00

**Table 4**  
Mass percent elemental analysis for Oil B and its asphaltene fraction.

	N %	C %	H %	S %	H/C
Oil	0.48	83.5	11.31	0.216	1.35
Asphaltene	1.78	81.1	9.03	1.30	1.11

unsaturation and higher concentration of heteroatoms. The presence of sulfur may indicate the existence of acid groups, whereas nitrogen suggests the presence of basic functional groups. In agreement with TAN and TBN measurements, this indicates that this crude oil may have both acid and basic functional groups in the polar fractions, which contribute to interfacial interactions.

The functional groups in the asphaltene fraction were identified by Fourier transform infrared spectroscopy (FTIR) using data in the literature (Silverstein et al., 2014; Wilt et al., 1998) to identify wave numbers of characteristic groups in the asphaltene fraction of crude oils (Table 5). The identified hydroxyl group may be bonded to a molecule of the sample or could represent residual water in the sample. Nonetheless,

**Table 5**  
Functional groups identified in the asphaltene fraction by FTIR spectroscopy.

Wave number (cm <sup>-1</sup> )	Functional group
3403	OH <sup>-</sup>
2920	CH <sub>2</sub> + CH <sub>3</sub>
2850	CH <sub>2</sub> + CH <sub>3</sub>
1697	C=O
1604	C=C aromatic
1461	CH <sub>2</sub> + CH <sub>3</sub>
1376	CH <sub>3</sub>
1306	C-O
1031	C-O
872-719	CH aromatic

according to Silverstein et al. (2014), free OH<sup>-</sup> occurs in the 3700-3450 cm<sup>-1</sup> range, whereas intermolecular bonds of OH<sup>-</sup> occur between 3550 and 3200 cm<sup>-1</sup>, which actually includes the identified peak. This may indicate that OH<sup>-</sup> exists bonded to the asphaltene molecules, thus contributing to their acidity. Furthermore, the identification of both C=O and C-O groups in these ranges can indicate the presence of esters in the sample.

Proton nuclear magnetic resonance (NMR) characterization of the asphaltene fraction using the work by Silverstein et al. (2014) to identify the functional groups is reported in Table 6. The results agree with the FTIR characterization, confirming the presence of aliphatic and aromatic carbon-hydrogen bonds and hydroxyl groups.

The impact of CO<sub>2</sub> dissolution on density and viscosity for crude Oil B and synthetic Oil M were assessed using the procedure described in the previous section. The results in Fig. 2 show that CO<sub>2</sub> has low (below 1.5%) impact in density for both oils, which is an input variable for density calculation using the Drop Shape Analysis (DSA) technique. On the other hand, viscosity was significantly affected by CO<sub>2</sub> dissolution, resulting in a decrease of over 80% of its initial value for crude Oil B. This affects the dynamic behavior of the IFT measurements, as discussed in the following section.

### 3.2. Interfacial tension measurement

As stated before, pendant drop IFT measurements are characterized by a decrease in IFT with time before reaching an equilibrium state. Fig. 3 shows the dynamic behavior for the four systems of this work. The diamond marks indicate the equilibrium time for each system. It is possible to notice that the presence of CO<sub>2</sub> results in a decrease in the stabilization time for systems. For Oil M, the equilibrium time decreased by 1 h. On the other hand, Oil B had a greater reduction (about 6 h). This may be related to the reduction in the viscosity of both oil phases due to the CO<sub>2</sub> dissolution. Rahman et al. related the viscosity of the fluid to the relaxation time of the interfacial tension experiments. As the viscosity depends directly on the molecular interactions within a fluid, it has a critical role in the diffusion of active components from the bulk to the interface (Rahman et al., 2019). Therefore, a reduction in the equilibrium time is expected if the bulk viscosity is decreased with the presence of CO<sub>2</sub>. Oil B has an elevated viscosity in the absence of CO<sub>2</sub>, and the dissolution of this gas reduces its viscosity over five times (Fig. 2). This impacts the equilibrium time, obtaining a 70% reduction to the value calculated for the dead crude oil. In contrast, while CO<sub>2</sub> reduced the viscosity of Oil M three times, the viscosity of this synthetic oil is an order of magnitude lower than that of the crude oil. As a result, the dissolution of CO<sub>2</sub> does not affect the equilibration time of Oil M significantly. This indicates that the long time required for its stabilization may be due to another factor beyond our scope and needs further investigations.

Equilibrium oil-brine IFT was plotted for dead and CO<sub>2</sub>-saturated oils B and M in Fig. 4. Comparing both dead oils (with no dissolved CO<sub>2</sub>), crude Oil B has an IFT over 20 mN/m lower than synthetic Oil M. This evidences the interfacial activity of asphaltene and resins in this crude oil, which results in an IFT of 10.5 mN/m with the brine. In addition, saturating the fluids with CO<sub>2</sub> decreased the IFT between Oil M and brine over 20% from the value obtained without CO<sub>2</sub> dissolution. This is in agreement with trends found for oils with light or intermediate alkanes as major components in which CO<sub>2</sub> partitioning contributes to increase the interaction between the oil and aqueous phase (Georgiadis

**Table 6**  
Functional groups identified through Proton NMR.

Domain in ppm	Functional group
7.271	CH aromatic
2.544	OH <sup>-</sup>
0.882-1.280	CH <sub>2</sub> + CH <sub>3</sub>

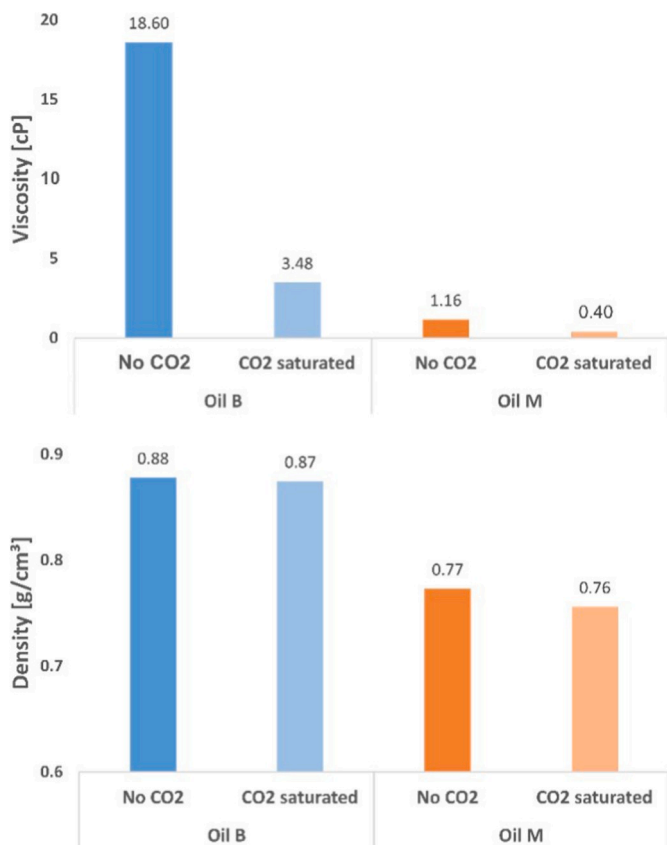


Fig. 2. Viscosity (top) and density (bottom) of dead and CO<sub>2</sub>-saturated oils B and M at 60 °C and 1000 psi.

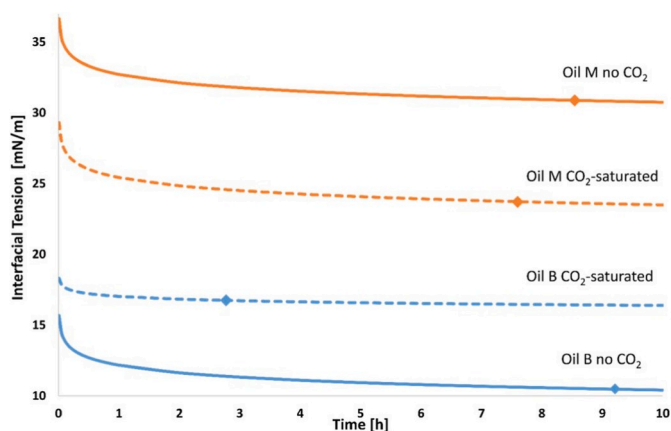


Fig. 3. Dynamic behavior of interfacial tension for oils M and B in the presence and absence of CO<sub>2</sub> at 60 °C and 1000 psi. The diamonds indicate the stabilization time. The full lines represent oil with no CO<sub>2</sub> and the dashed lines represent CO<sub>2</sub>-saturated oil. Orange lines stand for Oil M and blue lines for Oil B. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

et al., 2011; Honarvar et al., 2017).

In contrast, CO<sub>2</sub> dissolution had the opposite effect for Oil B obtaining an increase on the IFT of 56% for CO<sub>2</sub>-saturated fluids compared to the experiments with dead oil and brine. This indicates that IFT is pH-sensitive for this crude oil with considerable TAN and TBN and high content of asphaltenes and resins. As cited in the introduction of this work, Lashkarbolooki and Ayatollahi (2018) discussed the effect of pH on IFT for oils with different TAN, asphaltene and resin fractions.

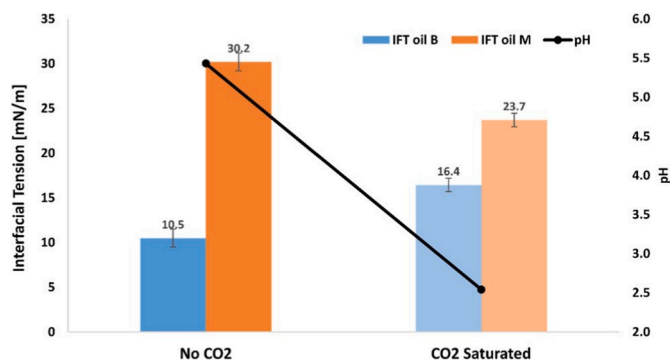


Fig. 4. Equilibrium interfacial tension of oils M and B in the presence and absence of CO<sub>2</sub> at 60 °C and 1000 psi. The full line indicates the brine pH for each condition.

They reported that, although oils with high TAN tend to have higher IFT in acid environments in which acid compounds show lower surface activity, the IFT behavior with pH does not depend only on the absolute TAN. The functional groups on acid and basic compounds in the crude oil will be more important in determining their surface activities at different pH values. In oils with basic compounds that show high interfacial activity when ionized, CO<sub>2</sub> injection reduces the interfacial tension due to the reduced pH of the carbonated brine (Lashkarbolooki et al., 2018).

In the previous section, Oil B was evidenced to have a distribution of acid and basic compounds. Following the discussion of the last paragraph, CO<sub>2</sub> injection reduced the pH of the aqueous phase from 5.4 to 2.4. Therefore, the increase of IFT with pH found for Oil B indicates that, even though its TAN/TBN ratio is lower than 1, basic compounds are not the main surface-active agents in this oil. The relatively low IFT value obtained for dead Oil B may be the results of amphiphilic compounds that are more active at slightly acid or even neutral or basic environments, such as those containing acid groups. This set of results supports the idea that measurement of acid and basic numbers is not sufficient to predict the effect of pH on the IFT between crude oil and brine. For this Pre-Salt crude with high TBN, acid compounds showed to be more efficient in decreasing IFT than their basic counterparts.

To further investigate the effect of pH on IFT between oil B and the formation brine, 0.1 M NaOH and HCl solutions were used to adjust the aqueous phase pH in a range between 3 and 9.5. IFT between Pre-salt oil and each of these aqueous solutions was measured at 60 °C and atmospheric pressure, and the results were represented as a function of pH in Fig. 5. In agreement with the previous discussion, the results show that the acidic pH (3) corresponds to the minimum activity of the surface-active compounds leading to a greater IFT. For the slightly acidic conditions that correspond to the range of the degassed Pre-salt formation brine, a decrease in IFT was observed. However, with further increase in pH to neutral and basic conditions the IFT plateaus. Thus, for this oil

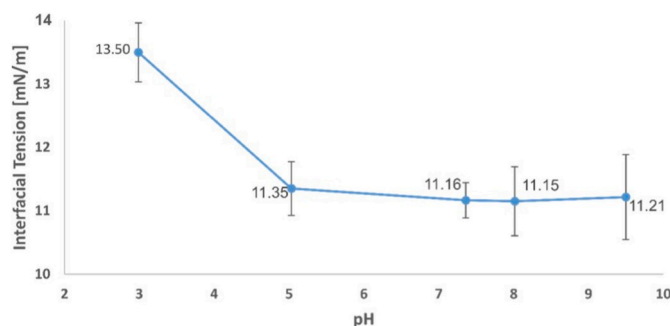


Fig. 5. Interfacial tension between Pre-salt oil and brine as a function of pH (adjusted with 0.1 M HCl and NaOH) at 60 °C and atmospheric pressure.

with non-negligible TAN and TBN, there is no increase in surface activity of the polar compounds at basic pH.

Previous investigations of the effect of pH on IFT for different types of crudes evidenced that, given the complex composition of both phases, there is no general trend based on a single property of the oil. Al-Rossies et al. (2010) obtained a maximum IFT for the neutral pH range for three different crudes, but there was no quantification of the acidity of their polar compounds. Lashkarbolooki and Ayatollahi (2018) found a decrease of IFT with pH for a heavy oil with TAN greater than 1, and a maximum IFT at neutral pH for the lighter oils with TAN lower than 1. In their article, the TBN was not reported and the salinity is over five times lower than the one used in our experiments. They concluded that the sole measurement of the TAN is not sufficient to predict the effect of pH on IFT, and the different polar functional groups in the oil must be considered.

The scenario presented in this work consists of a high salinity aqueous phase and an oil with a TAN/TBN ratio lower than 0.1. Evidence of acid functional groups was found in the characterization of the oil and the asphaltene fractions. The results in Fig. 5 indicate a very low activity of strong polar basic compounds, and a greater interaction of neutral and acid components. However, given the plateau of the curve at high pH values, the surface activity of this crude oil is not governed by components with strong acid behavior. A combination of compounds with different ranges of acidity and basicity, whose activity was only hindered at strongly acidic pH, may be responsible for the low IFT values found for this oil. These results support recent research (Drexler et al., 2019) that evidenced the low activity of basic components of the same crude with high TBN in rock-fluid interactions.

#### 4. Conclusions

This work studies the effect of CO<sub>2</sub> dissolution on the dynamic and equilibrium behavior of the interfacial tension (IFT) between crude oil and brine characteristic of a Pre-salt field. The aqueous phase has slightly acidic pH, high salinity and hardness. In addition, the oil phase has high basic number (TBN), a non-negligible acid number (TAN) and a considerable content of asphaltenes and resins.

In this scenario, the dead fluids presented a low equilibrium interfacial tension (i.e. 10.5 mN/m). Addition of CO<sub>2</sub>, which lowers the pH, increased the IFT by 56%. This shows that the TAN/TBN ratio alone is not sufficient to predict the activity of surface-active compounds, in agreement with recent findings in the literature cited in the Introduction of this paper. For a synthetic oil with no asphaltenes or resins, CO<sub>2</sub> dissolution reduced the IFT by 21% following the behavior previously reported for paraffinic oils.

The addition of CO<sub>2</sub> also decreased the time to achieve the equilibrium IFT by 70%. This is caused by the reduction of viscosity, which accelerates the diffusion of surface-active components towards the interface. Also, the reduced activity of the surface-active components at low pH may contribute to this decreased reduction of IFT with time.

The variation of IFT with the pH was analyzed, and the maximum IFT was found for strongly acid conditions. For pH values from slightly acid to neutral and basic, the IFT did not change. Therefore, for this oil, which contains a TAN/TBN ratio lower than 0.1, a combination of polar compounds with different acid strength govern the surface activity. Acid polar groups were identified in the characterization of the oil and asphaltene phases. However, further investigation is required to identify the distribution of polar groups which are responsible for this behavior.

The results of this research have implications on the characterization of fluid-fluid interactions for this Pre-salt field. From a Reservoir Engineering point of view, the CO<sub>2</sub> content in the dissolved gas needs to be accounted for, as it affects the pH and oil-water IFT. Moreover, for EOR operations (i.e. WAG injection), the injection of CO<sub>2</sub> is not expected to contribute to increase the Capillary Number in this particular scenario. On the contrary, an increase of IFT was found and should be taken into consideration.

#### Declaration of competing interest

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

#### CRediT authorship contribution statement

**Santiago Drexler:** Conceptualization, Methodology, Investigation, Writing - original draft, Supervision, Project administration. **Elton L. Correia:** Investigation, Validation, Writing - review & editing. **Ana Carolina Jerdy:** Software, Writing - review & editing. **Leandro A. Cavadas:** Investigation. **Paulo Couto:** Project administration, Funding acquisition.

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