Journal of Petroleum Science and Technology 10 (2020) 20-29
DOI:10.22078/jpst.2020.4042.1645

Journal of Petroleum Science and Technology

https:///jpst.ripi.ir/

Experimental Data of Interfacial Tension and Contact Angle at Reservoir Condition: Influence of Tuned Water

Nilo Ricardo Kim[1]*, Alessandra Winter[1], Euclides José Bonet[1], Gabriel Soares Bassani[2], Rafael Valladares Almeida[2]

[1] *Center for Petroleum Studies (CEPETRO), Universidade Estadual de Campinas (UNICAMP), São Paulo, Brazil*

[2] *Repsol Sinopec Brasil*

Abstract

Tuned water (brine with designed compositions) has proved to influence the oil recovery factor. One of the hypotheses supported to understand this technique involves decreasing the oil-water interfacial tension (IFT) and the rock's wettability alteration, indicated by contact angle (CA) measurements. The literature lacks experimental data regarding the interfacial tension in oil-brine and contact angle in oil-brine-carbonate systems at reservoir conditions considering pressure and temperature, and reservoir rocks. The objective of this study is to obtain new data, at 5,000 psi and 63 °C, on brines with different concentrations. The experiments were carried out in three steps. First, the concentration of sodium chloride was varied 0, 0.25, 0.5, 0.75, and 1 times which is the quantity in a seawater sample. After identifying the best concentration of NaCl (75% of NaCl in original seawater), steps were taken to modify the amount of magnesium 0, 0.5, 1, 2, and 4 times, in the brine. Finally, the same proportions of sulfate were tested. The behavior of IFT and CA towards the function of these various concentrations was also investigated and discussed. Furthermore, the results reveal that the behavior of IFT was not predictable, as the salinity increases at times and decreases at others. This property probably depends more on the compounds in the brine than on the total salinity. Also, the images used to gauge the CA show a greater tendency toward water-wet conditions when the sulfate concentration decreases,and when the magnesium concentration decreases, the images present the opposite effect .

Key words: Tuned water, Interfacial tension, Contact angle, Carbonate, Reservoir condition.

Introduction

Control of the salinity and composition of the injected water has become an enhanced oil recovery technique. Seawater is often used to maintain the pressure and displace the oil from reservoirs. Changing the water content has been environmentally friendly and cheaper in comparison with other approaches, such as the use of polymer additives.

A literature review and laboratory tests pointed out that for water injected into the reservoir, modifying the concentration and/or compounds of the brine could increase the oil recovery in carbonate rocks, as highlighted by Yousef et al in 2011 [1], who tested field connate water, injection seawater, and different dilution versions of seawater, including twice diluted, 10-times diluted, 20-times diluted, and 100-times diluted, core plugs from a carbonate reservoir, and oil gravity of 30°API. Four types of water: (1) injection water that had been used in flooding a reservoir for many years, (2) formation water, (3) seawater, and (4) distilled water were applied by Al-Attar et al in 2013 [2]. The three former water types were also diluted into three different proportions. From one dilution, two other series, varying the concentration of Ca^{2+} and SO_4^{2-}, were prepared. In addition, core samples were tested from a well and reservoir crude oil with a density equal to 0.825 g/ml (at room conditions). To investigate the effects of reducing total salinity of injection water on carbonate plugs under real reservoir conditions, core flooding experiments were performed by Klinger et al. in 2018 [3]. In their experiments, six brines including formation water, seawater, and its dilutions, 2, 10, 50, and 100 times were applied. The fresh crude oil was recombined and used in the laboratory.

There are several possible mechanisms to explain differences in oil recovery in core flooding tests; among them, researchers studied the decrease of interfacial tension and or wettability alteration toward more water-

*Corresponding author: Nilo Ricardo Kim, *Center for Petroleum Studies (CEPETRO), Universidade Estadual de Campinas (UNICAMP), São Paulo, Brazil*
E-mail addresses: nilokim@unicamp.br
Received 2020-01-14, Received in revised form 2020-07-13, Accepted 2020-08-17, Available online 2020-11-22

wet conditions [4]. Experimental measurements of the interfacial tension and contact angle intend to analyze these aspects. Interfacial tension is a measure of energy per unit area at the interface between two immiscible liquids, while wettability (capacity to spread over a solid surface) is an important characteristic of the reservoir rock because it enables us to understand the interaction between rock and fluid. It cannot be measured directly, but it may be inferred through the contact angle seen at the border of the oil droplet attached to the rock's surface, inside a brine medium, at reservoir conditions.

An experimental study using crude oil with a total acid number equal to 1.46 mg KOH/g was conducted by Lashkarbolooki and Ayatollahi in 2016 [5]. Asphaltene and resins were extracted, and two different solutions of 8 wt/wt % of these components in toluene were prepared. Moreover, the interfacial tension between these three fluids and sulfate salts, including Na_2SO_4, $MgSO_4$, and $CaSO_4$ was measured, and the concentration of each salt ranged from 0 to 45,000 ppm. For IFT reduction, the capability of asphaltene molecules was higher compared with the resin.

The effects of tuned water were studied by several authors. Moreover, it was demonstrated by Honarvar et al. in 2019 that by increasing salt concentration at 80 °C and 14.7 psia, IFT decreased to an optimum concentration for NaCl (10,000 ppm), and then IFT increased again to higher values [6]. Also, the same trend with experiments conducted at ambient conditions was demonstrated by Rostami et al. in 2019 [7]. This behavior was different from the observed behavior in the present work, but this was expected because studies on tuned water mechanisms led to various and contradictory results. The comparison between SARA (Saturate, Aromatic, Resin, Asphaltene) tests, temperature, and pressure, apart from brine composition, and pH could explain these differences. Moreover, it was discussed by Rostami et al. in 2019 [7] that when inorganic salts are added into the aqueous phase, water molecules form a cage-like structure around the salt ions, which migrate to the bulk of the brine and deplete at the oil-water interface, lead to higher IFT, because the Gibbs surface excess of salts becomes negative. Asphaltenes, resins, and waxes have surfactant properties that decrease IFT. Oil-soluble asphaltenes, which are ionized and could be affected by the salt concentration, become more soluble in oil, with a reduced tendency to move to the interface, and increase IFT. When salts are added into the bulk phase, the activity coefficient increases as their concentrations rise, and the salt molecules transfer to the oil phase. In addition, cations tend to move towards the interface, interacting with the polar terminals of the oil. Divalent cations like magnesium will deplete the interface from the surface-active agents, thus increasing IFT. Regarding wettability alteration, crude oil and carbonates are usually oppositely charged, which it provokes electrical double layer attraction and causes the oil-wet situation. Multi ionic exchange is also proposed to explain the wettability modification, as sulfate ion can negatively charge the carbonate, magnesium ion can approach the rock surface and substitute the adsorbed carboxylic group; thus, carbonates are become more water-wet.

Cation type and cation concentration in the tuned water can significantly impact the oil recovery, as studied by Nasralla and Nasr-El-Din in 2014 [8]. Therefore, the effects are not only a function of the total dissolved salts in the injected water, but also the composition and ratios of the cations in the brine. By extending the analyses to the effect of monovalent and divalent salts on interfacial tension, the results of experimental tests at ambient conditions were reported by Kakati and Sangwai in 2017 [9]. The authors also proposed a mechanism of IFT variation, discussing Gibb's adsorption isotherm. The surface excess concentration (or superficial density) of a species is defined as the difference between concentration in bulk and that at the interface. Positive surface excess concentration means that a surface excess of the component is present. When surface excess is positive, there is a reduction in interfacial tension. The dissociated cations in brine are preferentially located at or around the oil-water interface, due to the interaction of the cations with the hydrocarbon phase. These cations at the interface induce surface excess increase, and IFT decreases. At a certain concentration of the salt, there is saturation at the interface, and additional amounts increase the bulk concentration. Afterwards, surface excess decreases, and IFT increases. The interaction of cations with the hydrocarbon phase depends on oil compounds. A cation-induced dipole type is presented in the case of alkanes. For aromatic hydrocarbon, cation-π interaction is observed. Despite these discussions, it has been concluded that the mechanism may be more complex, requiring further investigation using molecular-level simulation.

A review of low salinity waterflooding was published by Sheng in 2014 [10]. In the review, some mechanisms are discussed to explain the enhanced oil recovery, as fine mobilization, limited release of mixed-wet particles, pH, multicomponent ion exchange, double layer effect, salt-in effect, osmotic pressure, and wettability alteration.

Pendant drop method was applied to measure interfacial tension between heavy oil and brines, in the research of Moeini et al. in 2014 [11], studying two types of salt, NaCl and CaCl2, using different salinities, from 0 to 200,000 ppm, at 313.15 K and 0.10 MPa. They noted that the optimum salinity ranged from 20,000 to 40,000 ppm and discussed the influence of heavy oil components in this behavior, as well as the effect of cation valence. A second series of tests analyzed the effect of temperature (298.15, 313.15, 343.15 and 363.15 K) at constant pressure of 0.10 MPa and 20,000 ppm. Increasing the temperature reduced the IFT. A third sequence of laboratory experiments was performed to investigate the effect of pressure, at 313.15 K and six different pressures (0.10, 3.44, 6.89, 10.34, 13.78 and 17.23 MPa), with the same solutions used in the temperature tests. Moderately increased IFT values were determined as pressure was increased.

Surfactant produced with sulfonic acid, nonylphenol 10 mol ethoxylated, triethanol amine and isobutanol was used in heavy oil displacement tests and its effect in IFT was pointed out by Dehghan et al. in 2015 [12], through measurements in spinning drop apparatus. Solutions containing 0.05, 0.1, 0.2 and 1 wt% of the surfactant were prepared in the salinity range of 20,000 to 250,000 ppm. Crude oil and water presented interfacial tension equal to 25.5 mN/m. Increasing the surfactant concentration reduced the interfacial tensions to less than 1 mN/m at salinities more than 40,000 ppm. Dehghan et al. in 2017 [13] added sodium metaborate to the surfactant solution. This component reduced the interfacial

tension to ultra-low values and decreased the surfactant emulsion generation capability at higher salinities.

Shojaei et al. in 2015 [14] measured contact angle, showing that wettability of rock slices changed from mixed-wet towards water-wet conditions, after water flooding with 38,000 ppm salinity for 5 hours. Similar results were observed with brine of 3,800 ppm. The sandstone rocks were used after aging with crude oil. Using pendant drop technique, they measured interfacial tension between oil and brine, at three different salt concentrations: 38,000 ppm, 19,000 ppm and 3,800 ppm. The IFT decreased.

Maaref et al. in 2017 [15] used three brines with salinity level low (40 g/L NaCl), intermediate (100 g/L NaCl) and high (140 g/L NaCl). The IFT between crude oil and brine was measured with pendant drop tensiometer at room condition, slightly increasing with higher brine salinity.

The effect of salinity and sulphate ion was studied by Safavi et al. in 2019 [16]. Test brines were of three types: Reservoir Formation Water, Seawater and Managed Water Salinity. They were used to produce 8 water samples, 3 as high salinity water and 5 as low salinity water. Different wetting tendency was related to the concentration of SO_4 ion. By increasing the SO_4 content, the proportion of negative charge on the carbonated rock surface increased, enhancing the amount of water sticking to the surface. It could also cause separation of the carboxylate bond from the surface of the rock. The SO_4 ion could be adsorbed on carbonate surface, which simultaneously captures divalent ions of Ca and Mg on the surface of the rock. This action makes it possible to separate some of the oil compounds from the rock surface, thereby altering the wettability.

More studies are still required to identify the mechanisms that govern interfacial properties, especially at high pressure and temperature.

The experimental equipment devised to present work was prepared to measure the interfacial tension between an oil droplet (just before its release from the needle) and the brine. After the drop detaches the needle and settles on the rock's surface, the contact angle between the drop of oil and the rock immersed in brine could be determined by the equipment. To calibrate the apparatus, IFT was calculated using a droplet of water in the air at ambient conditions. In this case, the interfacial tension, γ, in mN/m, can be estimated using the International Association for the Properties of Water and Steam (IAPWS) report (2014) [17] through the following equation:

$$\gamma = 235.8(1-\frac{T}{T_c})^{1.256}\ [1-0.625(1-\frac{T}{T_c})] \quad (1)$$

where T is temperatures and critical temperature, Tc, is equal to 647.098 K. At 25°C, the interfacial tension between water and air, through this formula, results in 72 mN/m, the value obtained in the present experimental apparatus.

A comprehensive literature review about the pendant drop method was made by Berry et al. in 2015[18]. In addition, the pendant drop method has proved to be a reliable procedure for IFT determination. The technique's accuracy was studied by Yang et al. in 2017 [19].

The purpose of this study is to present experimental data of interfacial tension and contact angle measurements in oil, brine, and rock systems at reservoir temperature and pressure, which in turn, will provide a better understanding of the oil recovery mechanisms.

Materials and Methods

The determination of the interfacial tension between oil and brine by pendant drop technique, as well as the measurement of the contact angle between the oil droplet and the rock, immersed in brine, is based on two factors: (1) the quality of the image and (2) the process of analyzing this image. The first feature depends on the illumination, the lenses used and the capturing of the image by the camera, which must have a high resolution and ensure that the images are collected and transferred to the software without distortion. The applied computer program extracts the drop profile from the stored image, adjusting this curve with the Young-Laplace equation. For this, the Attension Theta software, version 4.1.0, is used.

A modified laboratory device enabled the pressurization of the medium in which the drop of oil was observed. Such equipment, including a digital camera, which connects to a computer program, analyzes the images of the droplet at the moment of its release from the needle, generates a curve with its profile and thus calculates the interfacial tension. After the detachment of the droplet from the needle, it was fixed in the rock surface, enabling the measurement of the contact angle (Figure 1).

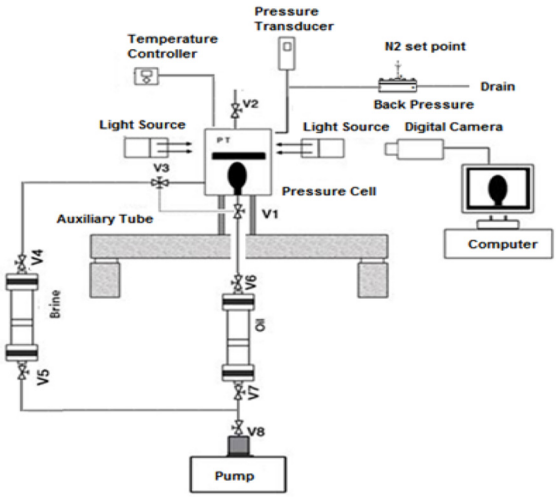

Fig. 1 Experimental set up for interfacial tension and contact angle test.

In the experiment, a clean, evacuated, high-pressure cell maintained at the desired constant temperature was filled with brine, which was stored in a cylinder with a floating piston, by valve V3 until a pressure of 5,000 psi was reached. The oil sample was introduced through the valve V1 with a needle internally connected to the pressurized cell to form the oil droplet. Afterwards, the droplet was released from the needle and attached to the solid surface of the rock.

Throughout this process of drop volume increase, accurate digital images were taken sequentially and stored on the computer. These pictures were processed and analyzed to determine drop volume and interfacial tension at different times, applying computational techniques. When the droplet detached from the needle, it accommodated at the surface of the rock, and thereby the measurement of the contact angle is allowed.

A PVT cell, with observation windows on both sides and a volume of 100 ml, manufactured by Ruska, model 2329-800, for 10,000 psi, was adapted to receive a tube with an external diameter of 1.6 mm and an internal diameter of 0.5 mm, acting as a needle. This visual cell had four openings: one at the base (valve V1), another at the top (V2), and on each of the two sides. A V3 valve was placed at the bottom lateral exit. At the fourth opening, a pressure transducer, Marsh manometer, up to 10,000 psi, was connected to indicate the internal pressure in the cell, along with a back pressure with a nitrogen set point. The digital camera used was a FireWire CCD (Charge-Coupled Device) Monochrome, manufactured by The Imaging Source, model DMK 21AF04, Format 1/4", 60 frames per second, 640x480 pixels. It could be coupled with Pentax lenses, CCTV (Closed Circuit Television), with available modes: C5028-M (focal length: 50 mm), C2514-M (focal length: 25 mm) and C1614-M (focal length: 16 mm), plus a Fujinon lens, model HF35HA-1B (focal length: 35 mm) with Cosmicar/Pentax X2 Extender. The best size of the image in the computer monitor was produced with the Extender connected to the Fujinon lens. Drop illumination, when necessary, could be obtained through a system consisting of Light Emitting Diode (LED) and optical fibers, supplied by Schott, model KL 1500 LED.

The oil flow from the storage bottle, with floating piston to the needle, was controlled by a Schlumberger DBR positive displacement pump, of fluid volume equal to 500 cm^3, capacity up to 15,000 psi. The heating of the cell was adjusted with the aid of flexible thermal tapes OMEGALUX, up to 260 °C, connected to temperature control systems with thermoresistors. A thermal isolation jacket covered the high-pressure cell and the tubes.

Experimental Tests

The crude oil, from a carbonate reservoir, was maintained in a 50-liter metal container. To homogenize it, the vessel was placed in an oven at 70 °C, being removed and shaken every half hour. The total warming time was 6 hours, at the end of which, a half-liter aliquot was withdrawn and stored at 63 °C and 5,000 psi. Oil properties are shown in Table 1.

The basic brine similar to seawater (SW) is representative of the reservoir area, contained cations and anions, and its concentration is seen in Table 2, resulting in Total Dissolved Solids (TDS) equal to 34,390 mg/L.

Table 1 Properties of oil.

Parameter	Value
Saturates (%)	79.7
Aromatics (%)	5.3
Resins (%)	14.4
Asphaltenes (%)	0.6
Acid Number (mg KOH/g)	0.04
Molecular Weight (g/mol)	250
Density @ 63°C, 5000 psi (g/ml)	0.86
API	28

Table 2 Composition of seawater.

Ion	Concentration [mol/L]
Na^+	0.5
Mg^{2+}	0.05
K^+	0.01
Ca^{2+}	0.01
Sr^{2+}	0.0001
Cl^-	0.5
SO_4^{2-}	0.03
HCO_3^-	0.002
TDS [mg/L]	34,390

Distilled water and seven salts were used to produce the brine, i.e. NaCl, KCl, and Na_2SO_4, with a minimum content of 99,0% while hydrated compounds $MgCl_2.6H_2O$, $CaCl_2.2H_2O$, $SrCl_2.6H_2O$, and $NaHCO_3$, presented minimum content of 99,0 – 105,0 %. These chemical products were provided by Synth or Dinâmica, traditional suppliers in Brazil.

The test design was planned to execute a sequence of several types of tuned water, in three series: varying NaCl, Mg^{2+}, and $SO4^{2-}$. The total brine salinity influence in interfacial tension and contact angle can be analyzed by changing NaCl content. The two divalent ions, magnesium, and sulfate are very important in oil recovery, according to the literature review. As the tuned water was obtained using seven salts, these three series were performed altering, respectively, three salts: NaCl, $MgCl_2.6H_2O$, and Na_2SO_4.

In the first series, the planned variation in the concentration of sodium chloride was verified, according to Silva in 2018 [20], maintaining the other components in the same quantity presented by seawater:

- 0.00 NaCl: without sodium chloride.
- 0.25 NaCl: 25% of the amount used in seawater.
- 50 NaCl: 50% of the amount used in seawater.
- 0.75 NaCl: 75% of the amount used in seawater.
- 1.00 NaCl: quantity used in seawater.

The last concentration was exactly the same as seawater.

In the second series, the planned variation in magnesium concentration was observed, with changes to the amount of magnesium salt ($MgCl_2.6H_2O$) in the brine with 75% NaCl concentration (the best result of the first batch of tests):

- 0.0 Mg^{2+}: no magnesium is used.
- 0.5 Mg^{2+}: 50% of the amount used in the water with 75% NaCl concentration.

• 1.0 Mg^{2+}: quantity used in the water with 75% NaCl concentration.
• 2.0 Mg^{2+}: twice the amount used in the water with 75% NaCl concentration.
• 3.0 Mg^{2+}: four times the amount used in the water with 75% NaCl concentration.
The concentration of 1.0 Mg^{2+} was equal to that of the brine with a 75% concentration of NaCl, so it was not necessary to repeat it. It should be noted that the amount of ion Cl- also varied in this step.
In the third series, the planned variation in sulfate concentration was tested, with changes to the amount of sulfate salt (Na_2SO_4) in the brine with the best NaCl concentration (the result of the first series, 75% of NaCl in the seawater):
• 0.0 $SO4^{2-}$: no sulfate is used.
• 0.5 $SO4^{2-}$: 50% of the amount is used in the brine with 75% NaCl concentration.
• 1.0 $SO4^{2-}$: the amount is used in the brine with 75% NaCl concentration.
• 2.0 $SO4^{2-}$: twice the amount is used in the brine with 75% NaCl concentration.
• 4.0 $SO4^{2-}$: four times the amount is used in the brine with 75% NaCl concentration.
The concentration of 1.0 $SO4^{2-}$ was the same as that of the brine with 75% concentration of NaCl. Changing the amount of sulfate also varied the concentration of the ion Na^+.
Following this planning, there were 13 tuned water samples to be tested, whose concentrations are shown in Table 3.

Table 3 Main ion composition of brines.

	Concentration [mol/kg]					
Tuned Water	Na^+	Mg^{2+}	SO_4^{2-}	Cl^-	TDS [mg/L]	ρ(*)[g/cm³]
SW	0.45	0.05	0.03	0.5	34,390	1.018
0 NaCl	0.06	0.05	0.03	0.1	10,900	1.004
0.25 NaCl	0.16	0.05	0.03	0.2	16,780	1.007
0.5 NaCl	0.25	0.05	0.03	0.3	22,650	1.011
0.75NaCl	0.35	0.05	0.03	0.4	28,520	1.015
0 Mg^{2+}	0.36	0	0.03	0.3	23,570	0.999
0.5 Mg^{2+}	0.35	0.03	0.03	0.4	26,050	1.008
2 Mg^{2+}	0.35	0.10	0.03	0.5	33,460	1.021
4 Mg^{2+}	0.35	0.20	0.03	0.7	43,350	1.029
0 SO_4^{2-}	0.30	0.05	0	0.4	24,600	1.012
0.5 SO_4^{2-}	0.33	0.05	0.01	0.4	26,560	1.013
2 SO_4^{2-}	0.41	0.05	0.05	0.4	32,430	1.018
4 SO_4^{2-}	0.51	0.05	0.11	0.4	40,270	1.024

The greatest and the smallest variations in density were detected in the magnesium and sulfate series, respectively. The greatest and the smallest variations in total dissolved solids occurred in sodium chloride and sulfate series.
Reservoir rock plugs were received in the laboratory. They were cut into cylinders with 2.54 mm diameter and 8 mm height, and then they were polished until surface roughness of 31.3 µm was obtained. The rocks were then prepared with initial water saturation Swi=10%, according to the procedure suggested by Springer et al. in 2003 [21]. Rockslides were cleaned with alcohol and water, and then they dried in a 60°C oven for a day. Afterward, the cleaned rocks were soaked in brine for at least 3 days at 60 °C. Such brine was similar to the formation water of the reservoir, with 200,000 ppm of dissolved solid content. The rock cylinders were placed in a desiccator until their weight reached 10% of water content. At this time, the rock plates were put in the crude oil at 60 °C for two weeks, a process of aging to restore the oil-wet state of the surfaces.

Results and Discussion
In the designing experiments, the first steel needle used, with 0.5 mm of internal diameter, produced a very large drop, which hindered the visualization of the drop edges through the sapphire window of the high-pressure cell, as can be seen in Figure 2.

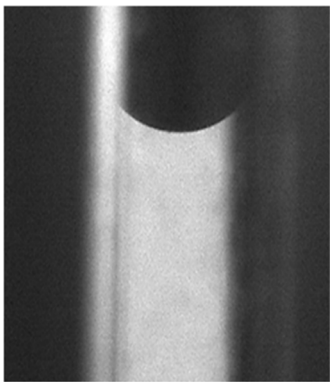

Fig. 2 Oil droplet attached to rock's surface, suppressing the view of drop edges.

A chromatography needle, with an external diameter (de) equal to 0.48 mm, was fitted inside the steel needle, with an internal diameter (di) equal to 0.5 mm, by gluing the extremity with epoxy adhesive, as shown in Figure 3.

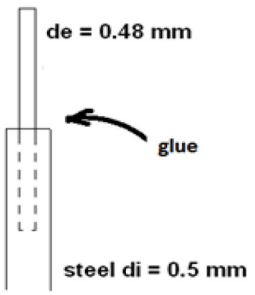

Fig. 3 Chromatography needle, inside the steel tubing.

After reaching the thermal equilibrium, at 63 °C, while the pump began injecting the oil, the brine was kept at 5,000 psi, utilizing back pressure, as seen in Figure 1. By using an injection rate equal to 1 ml/h, when the oil arrived at the tip of the needle, the hydrocarbon slipped through the outer surface of the needle, as shown by the sequence of images in Figure 4. The forces of attraction between the oil and the metal of the needle were very strong. The oil slip phenomenon was nullified, and this controlled the oil flow rate, adjusted to 0.1 ml/h.

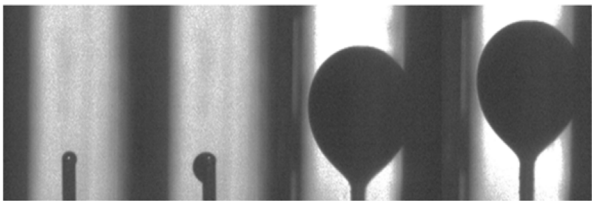

Fig. 4 Oil slipping at the outer surface of the needle.

In two instances, an unexpected effect was experienced. Instead of liquid oil, at 5,000 psi and 63 °C, something similar to a plume was released through the needle, as depicted in Figure 5. This problem was suppressed by shaking the oil recipient before the oil injection. Possibly, the crude oil presented instabilities, as another phase, during the storage in the high-pressure vessel.

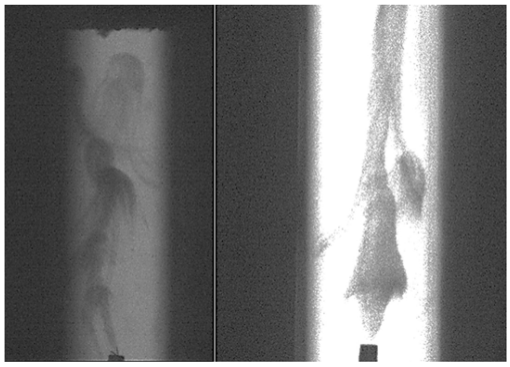

Fig. 5 The non-liquid phase of oil from the needle.

The software calculates interfacial tension using the pendant drop technique. So, the image captured by the camera was inverted, as seen in Figure 6.

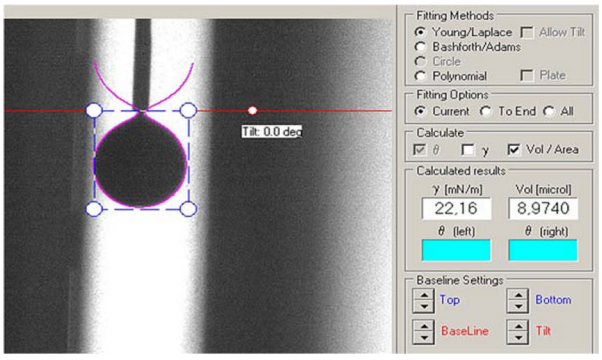

Fig. 6 Drop envelope to determine IFT, inverted image.

For the measurement of the contact angle, the image was also inverted as the drop was fixed on the lower surface of the rock. This inversion was necessary because the Attension software calculates the angle at that position. The measured angle is internal to the drop, as depicted in Figure 7.

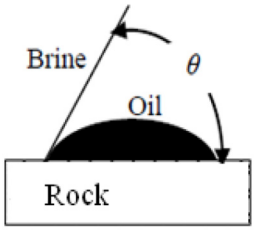

Fig. 7 The contact angle between the drop of oil and the rock.

Figure 8 shows the first oil droplet after it is released from the needle. In this figure,; an example shows the drop shape and the envelope produced by software with the contact angle measurement.

If this contact angle is less than 90°, the oil is wetting the rock. When it is above this angle, the brine will wet the solid. At times, the baseline (in red) needed to be tilted, for example, 1.5 degrees, due to the non-horizontality of the rock's surface. Among the factors that would provoke this inclination, one can consider the slope of the rock surface, position of the camera, one or more uneven tripod legs that sustain the camera, misalignment between the levels of the rock surface, and the lens.

Once the contact angle was measured, ten drops of oil were produced for ten measurements of interfacial tension. The system was cleaned, and the experiment was repeated twice. This methodology produced thirty IFT and three CA measurements.

IFT Measurements

By plotting all series together and varying the concentration of NaCl, Mg, and SO_4, the results for IFT, measured at 5,000 psi and 63°C, are shown in Figure 9. The concentration value equal to 28,520 mg/L was the same composition for the three series.

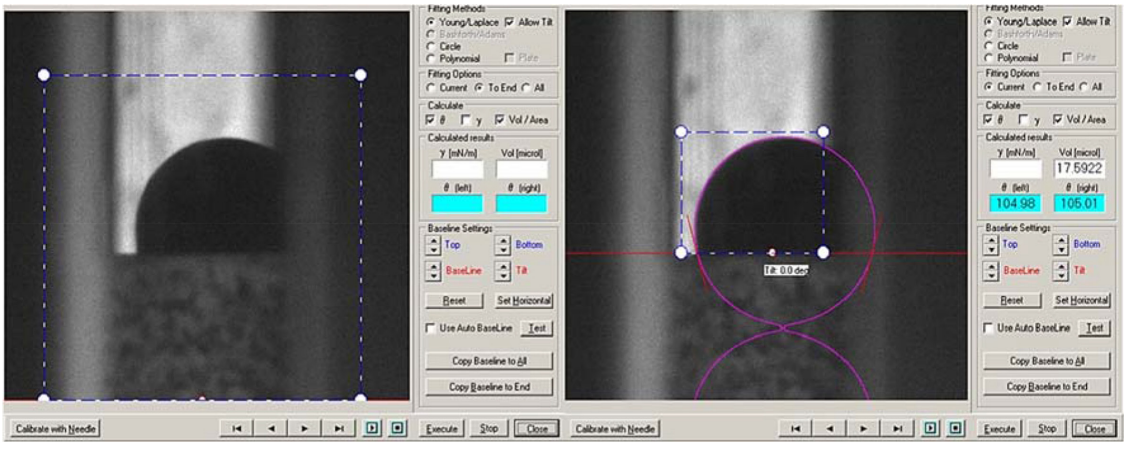

Fig. 8 Drop envelope and contact angle between oil drop and rock, inverted image.

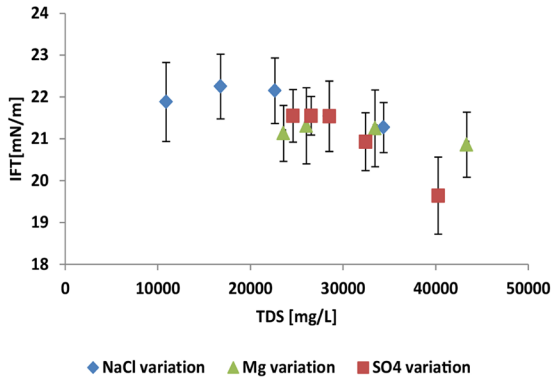

Fig. 9 IFT versus TDS, all series.

The IFT data results are the average and standard deviation values of thirty droplets. The IFT is the force balance at the interface of two immiscible fluids, depending on the size of this interface. When there are fewer dissolved solids, the tendency should be a decrease in the IFT. This behavior was not observed in the present tests. Electric charges imposed dominant forces at the interface. The presence of Na^+, Cl-, Mg^{2+}, and $SO4^{2-}$ ions, whose amounts were varied, apart from other cations such as Ca^{2+} and K^+ and anions such as HCO_3^-, introduced important agents into this balance. Each ion could have a proper tendency to go to the oil-water interface or return to the brine bulk, affecting the IFT. The results showed a maximum IFT and lesser values for increasing or decreasing TDS. This limit was a function of brine composition, whose modification resulted in changing the tendency of surfactant compounds of the oil moving to the interface, decreasing IFT, or moving to the bulk of the oil, thus increasing IFT. The presence of a carbonate rock probably enabled chemical reactions with brine ions, including dissolution of solid surface regarding high pressure and temperature, changing concentrations of calcium, magnesium, sulfate, and carbonate.

The effects of sodium chloride concentration on five brines are reported: SW, 0.75 NaCl, 0.50 NaCl, 0.25 NaCl, and 0 NaCl. The interfacial tension increased and then decreased, depending on the NaCl concentration. IFT was measured from 21.3 to 22.3 mN/m. Lesser values were observed using 0.75 NaCl and SW. Combined with the results for the contact angle, the concentration of 0.75 NaCl was chosen, because it should be easier to withdraw a lesser amount of this salt in the previous seawater.

When the magnesium concentration was altered in the brine composition of 0.75 NaCl, the interfacial tension increased and then decreased. The IFT was measured from 20.9 to 21.5 mN/m. Lesser values were observed using four times of magnesium concentration.

The interfacial tension, such as the function of sulfate concentration, was measured from 19.6 to 21.6 mN/m. Lesser values were observed using greater sulfate concentration. Sulfate concentration affected IFT more significantly than magnesium concentration, for the present crude oil tested. Considering the composition present in the tuned water (shown in Table 2), modifying the TDS resulted in such an arrangement of these ions that promoted alteration in the width of the oil-water interface due to interactions with the oil components (whose properties can be seen in Table 1). If this width was enlarged, the interface had less energy, and the IFT decreased. Figure 9 demonstrates that by increasing the salinity, IFT grows, possibly because a higher interface energy and a reduced width take place to a certain degree (around 16,000 mg/L for NaCl series, 28,000 mg/L for Mg and SO_4 series). Above such a concentration, the interface width was no longer affected, and the salinity increase resulted in more tendency for surfactant compounds of the oil to move towards the interface. The quantity of saturates, aromatics, resins, and asphaltenes in crude oil affects this result.

CA Measurements

In Figure 10, the contact angle data results are the average values of three droplets.

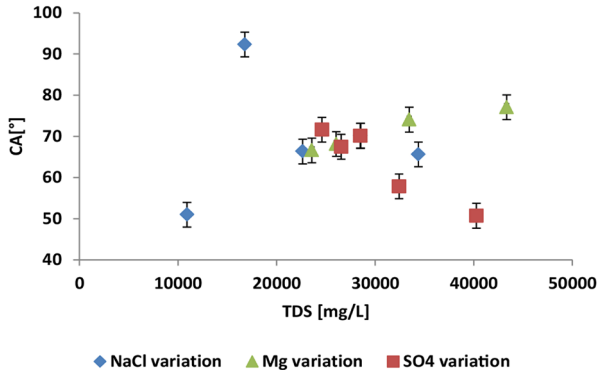

Fig. 10 CA versus TDS, all series.

In the NaCl series, the contact angle data indicated reservoir rock tendency to change from oil-wet to water-wet using 0.25 NaCl and 0.75 NaCl. The best-tuned water was chosen as 0.75 NaCl. The contact angle data indicated reservoir rock tendency to change from oil-wet to water-wet using a greater magnesium concentration. The contact angle data indicated reservoir rock tendency to change from oil-wet to water-wet using lesser sulfate concentration.

Contact angle measurements showed a consistent behavior only at magnesium series when the greater the amount of this compound, the stronger the tendency for itto be water-wet. The magnesium ion should be reacting with the rock surface, promoting the release of the carboxyl acid terminals in the oil. Changing the concentration of NaCl and SO_4 resulted in CA data that requires more tests because the three ions involved play an active role in rock wettability. Figure 11 includes the real images of oil droplets fixed at the carbonate rocks. It is noteworthy that the brine 1 Mg and the brine 1 SO_4 refer to 75% of NaCl in seawater.

The reservoir rock's surface presented fines attached to pore walls. These fines should be oil-wet or mixed-wet and they could have chemical reactions with some ions in the tuned water. The presence or removal of these fines promotes heterogeneous wetting conditions locally, affecting the contact angle.

Ion Concentration Analysis

The following analysis includes considerations regarding ion concentration in each series.

The IFT results can be plotted against the brine molality, as shown in Figure 12, for the NaCl series. The ion molality changed for Na^+ and Cl-, remaining constant for Mg^{2+} and $SO4^{2-}$. The error bars are omitted so as not to pollute the graph.

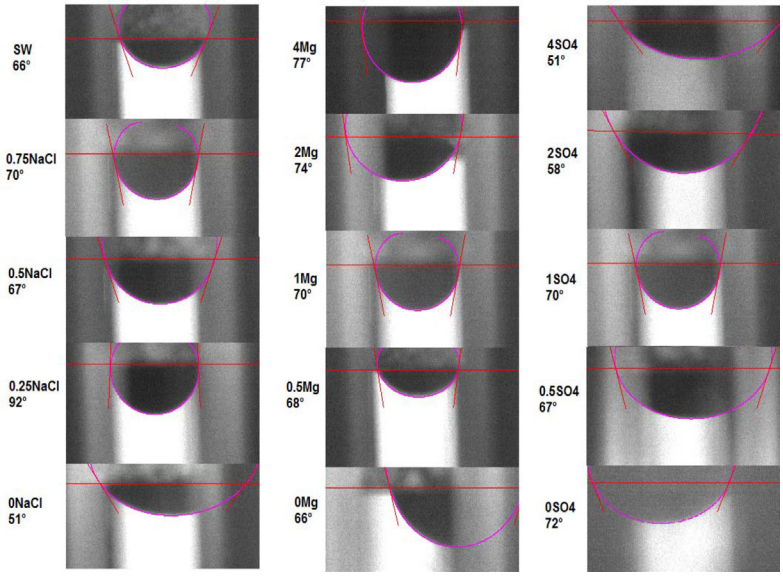

Fig. 11 Oil droplet at rock surface, all series.

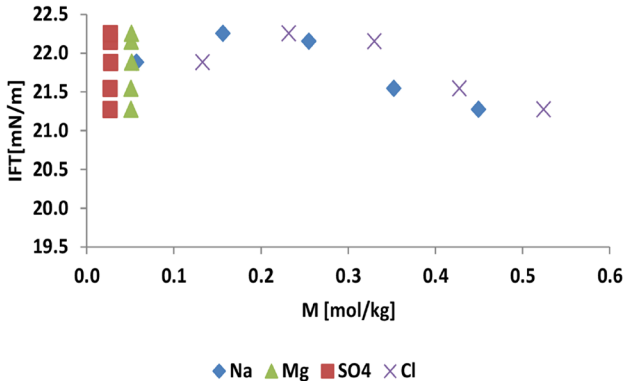

Fig. 12 IFT versus molarity, NaCl variation.

In Figure 13, corresponding to the magnesium series, the molality of sulfate was constant. The salt used for magnesium source was $MgCl_2.6H_2O$, so the molality changed for the Mg^+ and Cl^- ions. The sodium ion slightly varied due to the difference in density between each brine.

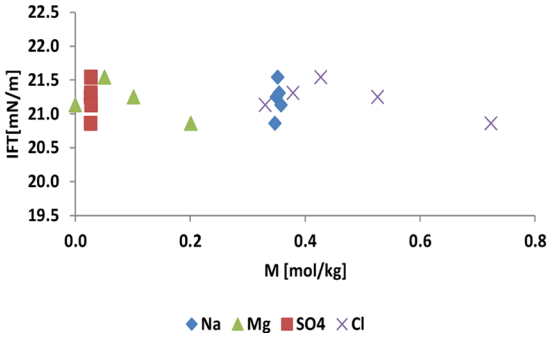

Fig. 13 IFT versus molarity, Mg variation.

At sulfate series, Figure 14, Na_2SO_4 was the salt amount modified in this step. Because of this, molality of the Cl^- and Mg^{2+} ions remained constant, varying the concentration of sodium and sulfate.

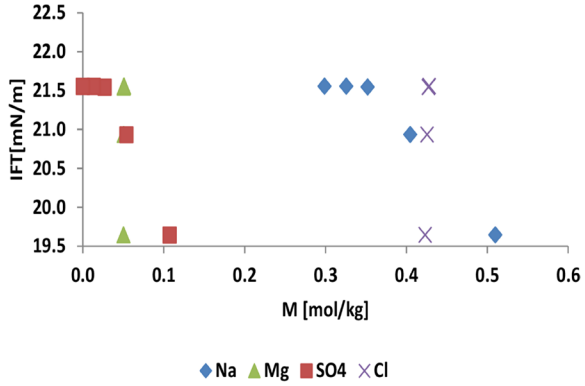

Fig. 14 IFT versus molarity, SO_4 variation.

Observing the last figures, it could be valuable to test other salts as sources of magnesium and sulfate, for instance: magnesium sulfate, calcium sulphate, or strontium sulphate. Taking into account the type of ions present in tuned water (Table 2), monovalent ions Na and Cl affected the IFT and CA as well as divalent ions Mg and SO_4.

However, the wettability alteration did not follow the trend in IFT. The oil recovery should be enhanced with IFT decrease and more water-wet surfaces.

Conclusions

In this study, the interfacial tension between oil and brine and the contact angle between the oil and a carbonate rock substrate in a brine environment was measured. The experiments were performed at 5,000 psi and 63 °C. There were tested variations in the concentration of three compounds of the seawater: sodium chloride, magnesium, and sulphate. Such results are new in the literature, as follows:

The level of interfacial tension ranged from 19.5 to 24.0 mN/m. By increasing salt concentration, the density of the brine increased; therefore, the density difference between the oleic and aqueous phase increases and leads to a higher IFT. This effect was not observed in all cases because other controlling mechanisms took place.

From the contact angle images, these carbonate reservoir

rock samples were oil-wet throughout the entire experiment, presenting a slight tendency to change toward water-wet.

The sodium chloride concentration was prepared with 0, 25, 50, 75, and 100 % of the quantity of the 0.75 NaCl in seawater. Interfacial tension increased according to the reduced amount of NaCl, except for brine with no NaCl, when the value diminished, even though it is higher than that of seawater. Decreasing the amount of NaCl did not reduce the interfacial tension, as observed by Honarvar et al. in 2019 [6]. One possible hypothesis is that in the present work, the migration of organic material in the oil toward the water-oil interface was hindered by the reduced NaCl concentration. The asphaltene particles were able to move to the interface region at certain conditions, and thereby the IFT is decreased due to changes in surface energy. The contact angle did not present a predictable behavior when the amount of NaCl was modified. A more water-wet condition was identified with 0.25 and 0.75 NaCl. The last one was chosen to be the standard brine in the following tests, based on the easier implementation by the crew in the production platform.

The magnesium concentrations were equal to 0.0, 0.5, 1.0, 2.0, and 4.0 times the quantity of the 0.75 NaCl in seawater. Interfacial tension decreased in the brines with less and more magnesium ion than in the standard brine. Starting with no magnesium, the contact angle showed a tendency to less oil-wet condition while increasing magnesium concentration, a different behavior was observed compared to the other two series.

The sulfate concentrations were equal to 0.0, 0.5, 1.0, 2.0, and 4.0 times the quantity of the 0.75 NaCl in seawater. Ultimately, interfacial tension was not sensitive to reductions in the amount of this ion but decreased in the brines with two and four times the sulfate concentration. Starting with no sulfate, the contact angle showed a tendency to a more oil-wet condition as the sulfate concentration increased.

Acknowledgments

The authors would like to thank Repsol Sinopec Brasil, who financially supported this study, ANP (Brazilian National Agency for Petroleum, Natural Gas and Biofuels), and the Mechanical Engineering Faculty and Center of Petroleum Studies (Cepetro) at Unicamp.

Nomenclatures

API: American Petroleum Institute gravity
CA: Contact Angle [°]
IFT: Interfacial Tension [mN/m]
PVT: Pressure, Volume, Temperature
SARA: Saturate, Aromatic, Resin and Asphaltene test
SW: Sea Water
Swi: Initial Water Saturation
T: Temperature [K]
TDS: Total Dissolved Solids [mg/L]
V1 to V8: valves

References

1. Yousef A, Al-Saleh S, Al-Kaabi A, Al-Jawfi M (2011) Laboratory investigation of the impact of injection-water salinity and ionic content on oil recovery from carbonate Reservoirs, SPE Reservoir Evaluation and Engineering, 578-593.
2. Al-Attar HH, Mahmoud MY, Zekri AY, Almehaideb R, Ghannam M (2013) Low-salinity flooding in a selected carbonate reservoir: experimental approach, Journal of Petroleum Exploration and Production Technology, 3: 139-149.
3. Klinger O., Peralta A, Ruidiaz E, Trevisan, O (2018) Oil recovery in carbonate reservoir rocks by reducing total salinity in injection water for core flooding tests, Rio Oil and Gas Expo and Conference, IBP1732-18.
4. Vijapurapu CS, Rao DN (2004) Compositional effects of fluids on spreading, adhesion and wettability in porous media, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 241: 335-342.
5. Lashkarbolooki M, Ayatollahi S (2016) Effect of asphaltene and resin on interfacial tension of acid crude oil/sulfate aqueous solution: experimental study, Fluid Phase Equilibria, 414: 149-155.
6. Honarvar B, Rahimi A, Safari M, Khajehahmadi S, Karimi M (2020) Smart water effects on a crude oil-brine-carbonate rock (CBR) system: further suggestions on mechanisms and conditions, Journal of Molecular Liquids, 299, Article 112173.
7. Rostami P, Mehraban MF, Sharifi M, Dejam M, Ayatollahi, S (2019) "Effect of water salinity on oil/brine interfacial behaviour during low salinity waterflooding: a mechanistic study, Journal of Petroleum, 5: 367-374.
8. Nasralla RA, Nasr-El-Din HA (2014) Impact of cation type and concentration in injected brine on oil recovery in sandstone reservoirs, Journal of Petroleum Science and Engineering, 122: 384-395.
9. Kakati A, Sangwai JS (2017) Effect of monovalent and divalent salts on the interfacial tension of pure hydrocarbon-brine systems relevant for low salinity water flooding, Journal of Petroleum Science and Engineering, 157: 1106-1114.
10. Sheng JJ (2014) Critical review of low-salinity waterflooding, Journal of Petroleum Science and Engineering, 120: 216-224.
11. Moeini F, Hemmati-Sarapardeh A, Ghazanfari MH, Masihi M, Ayatollahi S (2014) Towards mechanistic understanding of heavy crude oil/brine interfacial tension: the roles of salinity, Temperature and Pressure, Fluid Phase Equilibria, 375: 191–200.
12. Dehghan AA, Masihi M, Ayatollahi S (2015) Phase behavior and interfacial tension evaluation of a newly designed surfactant on heavy oil displacement efficiency; effects of salinity, wettability, and capillary pressure, Fluid Phase Equilibria, 396: 20-27.
13. Dehghan AA, Jadaly A, Ayatollahi S, Masihi M (2017) Acidic heavy oil recovery using a new formulated surfactant accompanying alkali–polymer in high salinity brines, Journal of Surfactants and Detergents, 20, 3: 725-733.
14. Shojaei MJ, Ghazanfari MH, Masihi M (2015) Relative permeability and capillary pressure curves for low salinity water flooding in sandstone rocks, Journal of Natural Gas Science & Engineering, 25: 30-38.
15. Maaref S, Ayatollahi S, Rezaei N, Masihi M (2017) The effect of dispersed phase salinity on water-in-

oil emulsion flow performance: a micromodel study, Journal: Industrial & Engineering Chemistry Research, 56, 15: 4549-4561.
16. Safavi MS, Masihi M, Safekordi AA, Ayatollahi S, Sadeghnejad S (2019) Effect of SO_4^{-2} ion exchanges and initial water saturation on low salinity water flooding (LSWF) in the dolomite reservoir rocks, Journal of Dispersion Science and Technology, 1-15.
17. International Association For The Properties Of Water And Steam, IAPWS R1-76 (2014), Revised Release on Surface Tension of Ordinary Water Substance.
18. Berry JD, Neeson MJ, Dagastine RR, Chan DYC, Tabor RF (2015) Measurement of surface and interfacial tension using pendant drop tensiometry, Journal of Colloid and Interface Science, 454: 226-237.
19. Yang J, Yu K, Zuo YY (2017) Accuracy of axisymmetric drop shape analysis in determining surface and interfacial tensions, Journal of Langmuir, 33: 8914-8923.
20. Silva CM (2018) Interfacial tension and contact angle in oil-rock-brine systems at high temperature and pressure, (in Portuguese), Master thesis, DECivil, Instituto Superior Tecnico, Portugal.
21. Springer N, Korsbech U, Aage HK (2003) Resistivity index measurement without the porous plate: a desaturation technique based on evaporation produces uniform water saturation profiles and more reliable results for tight north sea chalk, International Symposium of the Society of Core Analysts, SCA 459-470.