

Evaluation of Wettability Alteration by Oil Doped with Organic Acid and Low-High Brine Solutions in Sandstone and Carbonate Rocks

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Petroleum reserves available worldwide are geologically based mainly on sedimentary and carbonate rocks, and the reservoir performance depends on the intrinsic properties of each rock and their response to changes in wettability. Recently, the change in wettability with low-salinity brine has been used to improve the oil recovery, which is an environmentally friendly and low investment, but there is no unanimity about the mechanisms of oil recovery process. Therefore, the aim of this study is to investigate the process involved in the wettability associated with interactions between the surface of powdered reservoir rock samples and the surrounding fluids. The reservoir rock surface (sandstone, calcite and dolomite) was evaluated under three different conditions. The total amount of adsorbed oil on aged samples was twice as high in carbonate rocks as in sandstone. The thermal gravimetric analysis (TGA) for the desorption steps of the organic fraction on dolomite and calcite indicates that the treatment under high brine concentration favored the oil desorption and the opposite result was observed for sandstone. This behavior suggests that carbonate rocks adsorb more strongly the organic phase compared to sandstone.

Keywords: wettability, brine solution, aging process, oil recovery, contact angle

Introduction

The available oil reserves worldwide are geologically mainly based on carbonate rocks; dolomite ($\text{CaMg}(\text{CO}_3)_2$) and calcite (CaCO_3), and sandstone rocks (SiO_2).^{1,2}

The structure of the reservoir's porous system and the mechanisms behind fluid flow play a critical role in the development and improvement of various applications such as enhanced oil recovery, water flooding, and geological sequestration of CO_2 . The reservoir performance is an intrinsic characteristic of each reservoir and is dependent on different variables, in particular, the wetting characteristic of the rock-fluid system. Wettability is a physical-chemical phenomenon defined as the tendency of a fluid to spread over or adhere to a solid surface in the presence of other fluids.² This characteristic is a result, therefore, of the cohesive and adhesive forces acting in the system.²

Until recently, hydrocarbon reservoir rocks were believed to be water-wettable, even after the migration of oil from the source rock to the reservoir rock. This understanding was based on the fact that almost all clean sedimentary rocks are strongly water-wettable.² Only after many studies,^{1,3-5} it was observed the change in the wetting character of oil reservoirs, from water-wettable to oil-wettable. It thus appears that this occurs due to the initial adsorption of polar organic, acidic or basic components, essentially found in the resin and asphaltene fractions. These species would act as anchors for crude oil macromolecules on the porous surface of rocks.^{1,5}

Despite the oil composition, the chemical nature of the rock, the chemistry of brine (potentially determining the ion concentration and composition), and the thermodynamic conditions of the reservoir, such as pressure and temperature,⁶ are factors that interfere in the wettability of the rock. The rock structure retains a high degree of heterogeneity of superficial charges along with the pores, which control the magnitude of the attractive forces acting on the oil in the presence of formation water.⁷ Besides, the

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surface charges of the rock can be affected by the pH of the formation water, and consequently, enable different levels of rock-fluid interaction.⁸

Several mechanisms have been proposed to understand the interface interactions of the rock-oil-brine solution system. In relation to electrostatic or columbic mechanisms,⁹ the most cited are those that propose ligand exchange (exchange of acidic hydroxyl groups with hydroxyl groups of the surface), cation bridges (act as a bridge between the mineral surface and polar groups), and anion or cation exchange (inorganic anions and cations are replaced by organic anions and cations). As additive mechanisms, van der Waals (vdW) interactions and hydrophobic effects (both non-polar) are mentioned. The vdW short-distance interactions are more significant in a high-salinity medium.⁹

Once the first organic molecules are absorbed onto the mineral surface, the hydrophobic effect acts by structuring the polar layer and minimizing the contact between the rock and the brine solution,¹⁰ which is often irreversible. In an attempt to elucidate the mechanisms that control the rock-fluid interaction, carboxylic acids¹¹⁻¹³ are generally used to promote a temporary artificial hydrophobic character in naturally hydrophilic rocks, while the non-polar environment is evaluated using aliphatic hydrocarbons, such as *n*-decane (C₁₀H₂₂) and *n*-dodecane (C₁₂H₂₆) as a mode oil.¹⁴

In the oil recovery process, usually, low salinity brine is used to remove strongly adhered oil on the rock surface. This method reduces the rock-oil attraction forces, expanding the water film, and consequently releasing the oil.⁷ The low salinity brine technique is called enhanced oil recovery (EOR), and consists of using high salinity brine followed by low salinity brine,^{15,16} applying forced or spontaneous flooding.

Pourakaberian *et al.*¹⁷ have demonstrated that the change in wettability due to low salinity is slow. The electrical behavior of the oil/brine and rock/brine interfaces and the geometry of the water film are expected to control both the transient hydrodynamic pressure and the time scale of ion transport in the film, and therefore the kinetics and degree of change in wettability.

Studies continue to be focused on gaining a better understanding of the positive effect of low salinity brine and its ionic composition on oil recovery. Karimi *et al.*¹⁸ employed the contact angle technique to investigate the effect of brine composition on changing the wettability of an oil-wet carbonate. They concluded that magnesium ions are able to remove the carboxylate group strongly adsorbed on the surface and change the wettability of the calcite surface to a more water-wet state. This process of wettability alteration is enhanced with the use of a surfactant.

Lashkarbolooki *et al.*¹⁹ investigated the effect of ions (monovalent and divalent) and the salt concentration of brine on the wettability alteration of a carbonate oil reservoir rock. Based on contact angle (CA) measurements, the authors concluded that monovalent cations bound with the chlorate anion showed a better performance in the alteration of the wettability of the oil-wet surface in comparison with divalent cations bound with the chlorate anion.

The presence of KCl changed the wettability of the surfaces from strongly oil-wet to strongly water-wet at all concentrations studied. However, in the case of NaCl, as the concentration decreased the change in the wettability increased. They evaluated the impact of salinity on the surface properties of a carbonate reservoir rock and concluded that altering the wettability of the rock surface with diluted seawater was more efficient than reducing the interfacial tension (IFT) in terms of improving the oil recovery.¹⁹

Taking into account the results obtained, the authors¹⁹ suggested that a combined mechanism based on three stages, including the salting-out effect, expansion of the double layer, and microscopic dissolution of the surface, could be used to describe the change in the wettability to more water-wet under low salinity conditions.

Khishvand *et al.*²⁰ carried out experiments to evaluate the effect of high and low brine flooding on the change in the wettability of sandstone reservoir rocks. Regarding the low salinity, the authors suggested that the mobilization of fine particles (due to an expansion of the electrical double layer, EDL) and multi-component ion exchange processes resulted in oil desorption from rock surfaces, leading to an improvement in the oil recovery, with a change in the wettability toward more water-wet.

Alhuraishawy *et al.*²¹ studied the effect of flooding with low salinity water in terms of improving the oil recovery from a sandstone oil reservoir rock with low permeability. The results showed that brine injection at a low concentration improved the oil recovery. A redistribution of the flow paths release sand particles and some fine minerals were also observed, thus creating a deviation of the fluid flow and, as a result, improving the displacement and removal efficiency.

Advanced water flooding is an environmentally friendly process and it does not demand high investment for additional surface facilities. Results have indicated that low-salinity water flooding can have positive outcome in the recovery of oil at relatively low costs. However, there are still several challenges and uncertainties and the processes involved are still not fully understood.^{22,23}

Therefore, this work aims to study the wettability of reservoir rock samples by surface treatment to

investigate the wettability process behind the oil recovery phenomenon. The experiments were performed on carbonate rocks; dolomite ($\text{CaMg}(\text{CO}_3)_2$) and calcite (CaCO_3) and sandstone (SiO_2) rocks with petrophysical characteristics and chemical composition similar to those from oil reservoirs. The reservoir rock surface was evaluated under three different conditions: (i) pristine powder (unmodified and considered as water-wet), (ii) after aging (exposed to a synthetic oil to achieve hydrophobic character), and (iii) after aqueous solution treatment at two different brine concentration and deionized water to simulate an oil recovery process.

The interactions between the surface of powdered rock and the surrounding fluids were evaluated by thermal gravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), zeta potential (ZP) and wettability analysis according to the Washburn capillary rise (WCR) method.

Experimental

Sample preparation

Brine solution

The synthetic brine solutions were prepared in deionized water from analytical grade salts (NaCl , KCl) from Synth (SP, Brazil) and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and Na_2SO_4 from Dinâmica (SP, Brazil) and used without further purification. Table 1 shows the synthetic brine composition and molar concentrations. The high salinity brine used was 80% v/v dilution and the low salinity brine used was 10% v/v dilution of the high salinity and was based on studies carried out by Karimi *et al.*²⁴ and Shabaninejad *et al.*²⁵

Table 1. Synthetic brine solution

Salt	Concentration / (mol L^{-1})
NaCl	1.0
KCl	0.05
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	0.007
Na_2SO_4	0.10
TDS = 77.71 g L^{-1}	

TDS: total dissolved salts.

Synthetic oil sample

The synthetic oil sample used as a model was *n*-dodecane 99% ($\text{C}_{12}\text{H}_{26}$) with the addition of 0.01 mol L^{-1} stearic acid 95% ($\text{C}_{17}\text{H}_{35}\text{COOH}$)²⁶ from Sigma-Aldrich (SP, Brazil) and used without further purification.

The density of the synthetic oil was 0.75 g L^{-1} at 25 °C and it gives a total acid number (TAN) of about

0.6 (mg of KOH g^{-1} oil) similar to a crude oil, TAN from 0.3 to 0.5.²⁴ The TAN is based on the mg of potassium hydroxide KOH , required to neutralize one gram of oil.²⁴

Rock samples

The rock samples used were sandstone (quartz, SiO_2) from Botucatu, SP, Brazil, silurian dolomite (calcium magnesium carbonate, $\text{CaMg}(\text{CO}_3)_2$), and calcite (calcium carbonate, CaCO_3) from Houston, TX, USA, supplied by Faber CNK Stone. The samples were ground in a Rocklabs Benchtop ring mill, (model 1A-BT, Scott Company, New Zealand) and sieved to obtain a particle size of < 150 μm . The samples were extracted from outcrop rocks with petrophysical properties and chemical compositions similar to those from oil reservoir rocks.

The specific surface area (SSA) of the rock samples was determined using an Autosorb-1 (Quantachrome Instrument, USA), applying the Brunauer-Emmett-Teller (BET), analysis by N_2 adsorption with 100 mg of the sample of particle size < 150 μm . The SSA results obtained from the BET analysis are shown in Table 2. A small SSA also has been reported by Saxena *et al.*²⁷ for sandstone (0.51 $\text{m}^2 \text{g}^{-1}$) and carbonate rocks (2.80 $\text{m}^2 \text{g}^{-1}$).

Table 2. Specific surface area (SSA) for pristine rock samples

Sample	SSA / ($\text{m}^2 \text{g}^{-1}$)
Sandstone (SiO_2)	8.62
Dolomite ($\text{CaMg}(\text{CO}_3)_2$)	10.13
Calcite (CaCO_3)	6.87

Wettability of the reservoir rocks

Changes in the wettability of the rock powder surface associated with surrounding fluids were evaluated through the rock surface under three different conditions:

(i) Processing: pristine rock powders sandstone, dolomite, and calcite without additive;

(ii) Sample aging process: to 1.0 g of each pristine rock samples (sandstone, dolomite and calcite), 10 mL of brine solution (Table 1), and 10 mL of the synthetic oil solution were added and left under an orbital shaker for 25 h at 65 °C,^{12,28,29} and then filtered and dried in an oven for 48 h at 40 °C;

(iii) Treatment: after condition (ii), the rock samples of sandstone, dolomite, and calcite were prepared by placing 1.0 g of each sample in 20 mL of deionized water, 1.0 g in 20 mL of 10% (v/v) brine solution, and 1.0 g in 20 mL of 80% (v/v) brine solution. All prepared samples were left in an orbital shaker for 25 h at 65 °C, filtered and dried in an oven for 48 h at 40 °C. The (iii) condition simulates the

recovery process through oil desorption.

Samples at condition (ii) and (iii) were filtered under vacuum over a qualitative filter paper using a Buchner funnel and a Kitassato and after dried the filtrate was removed with a stainless-steel spatula and weighed. Excess oil in condition (ii) was removed by washing the samples under vacuum with toluene and *n*-heptane prior to dry. Under condition (iii) the surfaces were washed out with deionized water prior to dry.²⁴ The conditions (ii) and (iii) are further evaluated in the results and the discussions of the rock samples chemical analyses. Table 3 shows the sample labels for each condition and in Table 4, an extra label was added due to the condition (iii).

Table 3. Sample labels used to summarize the conditions (i), (ii) and (iii)

Sample	Sample condition	Label
Sandstone	pristine (unmodified) (i)	SP
	after ageing (ii)	SA
	after aqueous treatment (iii)	ST
Dolomite	pristine (unmodified) (i)	DP
	after ageing (ii)	DA
	after aqueous treatment (iii)	DT
Calcite	pristine (unmodified) (i)	CP
	after ageing (ii)	CA
	after aqueous treatment (iii)	CT

SP: sandstone pristine; SA: sandstone aged; ST: sandstone treated; DP: dolomite pristine; DA: dolomite aged; DT: dolomite treated; CP: calcite pristine; CA: calcite aged; CT: calcite treated.

Table 4. Extra label added to condition (ii), after aqueous treatment, condition (iii) above

Aqueous treatment	Extra label	Label
Deionized water	DW	STDW, DTDW, CTDW
Low salinity	LS	STLS, DTLS, CTLS
High salinity	HS	STHS, DTHS, CTHS

STDW: sandstone treated with deionized water; DTDW: dolomite treated with deionized water; CTDW: calcite treated with deionized water. STLS: sandstone treated with low salinity solution; DTLS: dolomite treated with low salinity solution; CTLS: calcite treated with low salinity solution. STHS: sandstone treated with high salinity solution; DTHS: dolomite treated with high salinity solution; CTHS: calcite treated with high salinity solution.

Sample analysis

X-ray diffraction (XRD)

The rock samples were analyzed by X-ray diffraction (XRD) using a (RigakuMiniflex 600 device, TX, USA), with scan-interval of 5.0 to 85.0° at steps of 0.02° and speed of 1.4° min⁻¹. The profiles were analyzed using the WinPLOTR software.³⁰

Zeta potential (ZP)

The zeta potential (ZP) was determined using a Zetasizer Nano Series analyzer (Malvern, UK), applying the Smoluchowski equation.³¹ ZP profiles were obtained as a function of salt concentration at pH ca. 6.5. Deionized water and 0.1 mol L⁻¹ solutions of NaOH and HCl were used for the pH adjustment and this procedure was carried out immediately before the addition of rock powder and the ZP measurement.

Washburn capillary rise method (WCR)

The wettability of the rock samples was evaluated according to the Washburn capillary rise (WCR) method³² using a KSV Sigma 700 tensiometer (Vaasa, Finland) with a cylindrical tube. The WCR method is based on the physical phenomenon of capillarity exhibited by a sample when in contact with a testing liquid. The wettability of the sample is evaluated by monitoring the net mass gain over time.

The experiments were carried out in duplicate using deionized water as a completely wetting fluid, with a predefined exposure time of 240 s at 24 °C. To apply the WCR method, two sample cells were carefully filled and tapped to obtain the tightest possible packing and only the two reproducible results of the packing of the powder were used. Samples preparation followed the same procedure to ensure reproducibility and the wettability of the sample was evaluated by monitoring the net mass gain over time.

Samples subjected to tests based on the WCR method generally show three characteristic stages. Usually, the first is an inertial stage, with a discrete variation in mass ($m \times t$). In the second stage, there is an increase in mass, showing nonlinear variation over time ($m^2 \times t$) and in the third stage, there is zero mass variation, with a balance between capillary and gravitational forces.³²⁻³⁵

Fourier-transform infrared spectroscopy (FTIR)

The FTIR transmittance spectra were measured in the wavenumber range of 400-4000 cm⁻¹ using a Bruker Alpha spectrometer with Mentor software (Billerica, USA). The samples were prepared in KBr tablets and an average of 16 scans were taken with a spectral resolution of 4 cm⁻¹.¹²

Thermal gravimetric analysis (TGA)

The thermal gravimetric analyses (TGA) of the rock samples were performed by Shimadzu TGA-50 analyzer (Kyoto, Japan). The samples were continuously heated under N₂ with flow rate of 50 mL min⁻¹ up to 900 °C at a heating rate of 10 °C min⁻¹. The temperature range of TGA analyses used to estimate the amount of organic content was defined based on the degradation steps of the pristine and doped rock samples and previous studies on

the adsorption of alkanes and long-chain carboxylic acids on rock particles.¹⁸

Results

The XRD of sandstone analysis, Figure 1a, show mainly quartz (SiO₂) peak, with different positions and intensities, the highest being at 26.65°. In addition, calcium carbonate (CaCO₃) is observed as impurities, appears at 29.4°. The XRD results of dolomite, Figure 1b, show mainly CaMg(CO₃)₂ with a characteristic peak at 31.0°. The XRD results of calcite, Figure 1c, shows mainly CaCO₃ with a characteristic peak at 29.5°.

Zeta potential (ZP)

Figure 2 shows the zeta potential (mV) results for the pristine rock samples and aged: sandstone (Figure 2a); dolomite (Figure 2b) and calcite (Figure 2c) as a function salt concentration at pH ca. 6.5. The insert shows the pH profile in the range of 2.0 to 12.0 for the pristine rock samples.

The pristine sandstone sample (Figure 2a, inset) shows a negative zeta potential, as its chemical composition is almost pure SiO₂, as seen from the XRD results in Figure 1a, which has a negatively charged surface.⁴⁰⁻⁴³ As the pH increases, the negative surface charge also increases due to the negative charges from the pH species. In addition, the ZP profile against salt concentration of the pristine and aged sandstone, Figure 2a inset, showed a negative surface charge with a slightly decrease towards zero ZP as the salt concentration increases and this effect is more pronounced for the aged samples. This result indicates that increasing the salt concentration decreases the stability between particles towards coagulation and the effect is higher for aged samples.⁴⁰

The point of zero charge (PZC) was observed for pristine dolomite, Figure 2b inset, at low pH < 2.6 and for high sat concentration > 0.6 mol L⁻¹, Figure 2b. As reported by Zhang and Austad,⁴² the ZP of chalk (CaCO₃) are defined by the relative concentration of Ca²⁺ and CO₃²⁻ ions at the interface. In the case of the dolomite sample (Figure 2b, inset), the PZC appears at very low pH (< 2.6). As shown by the XRD results in Figure 1b, the main chemical component is CaMg(CO₃)₂, which gives a negative surface charge,^{44,45} although at very low pH some Ca²⁺ and Mg²⁺ can be solubilized and HCO₃⁻ species can be exposed. With the addition of salt, the balance is shifted towards a positive surface charge, as shown by equation 1:

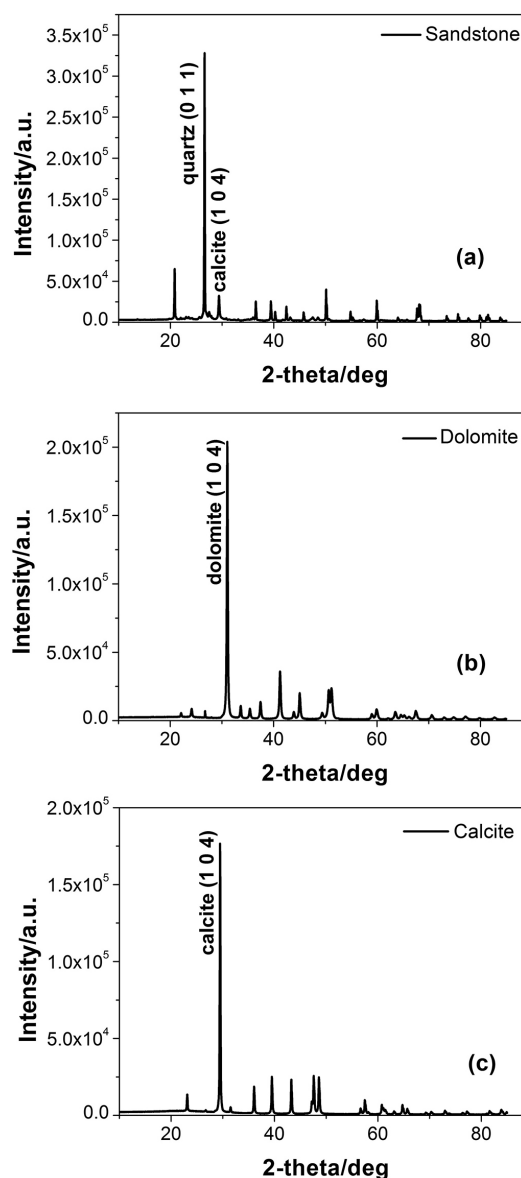
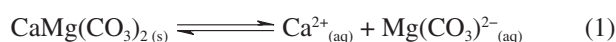


Figure 1. XRD analysis of (a) sandstone, (b) dolomite, and (c) calcite powder rocks.

The calcite sample (Figure 2c, inset) shows a negative potential in both profiles (pH and salt concentration), due to the desorption of Ca²⁺ and/or the effect of anions at the electric double layer,⁴⁶⁻⁴⁹ and the effect is higher on the pristine sample. Since the chemical composition is almost pure CaCO₃, as shown by the XRD (Figure 1c), high pH increases the negative charge of the surface (CO₃H⁻) and with the addition of salt, the electric double layer becomes slightly less negative due to the concentration effect of cations.

The ZP profile for carbonate rocks as a function of salt concentration is slightly lower for aged samples than for pristine samples, a similar behavior was also observed by Rezaeidoust *et al.*⁵⁰

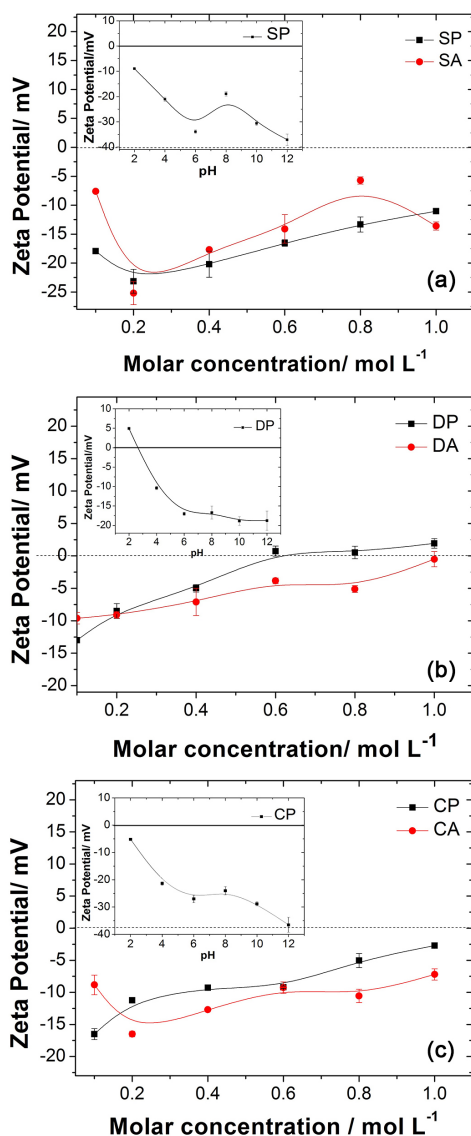


Figure 2. Zeta potential (mV) against salt concentration profile of (■) pristine and (●) aged rock samples: (a) sandstone; (b) dolomite and (c) calcite. The insert in Figures 2 show the zeta potential (mV) profile from pH 2.0 to 12.0 of pristine rock samples.

Washburn capillary rise method (WCR)

Figure 3 shows the WCR results for sandstone, dolomite, and calcite samples obtained under different conditions: (i) pristine (unmodified); (ii) after aging, and (iii) after aqueous solution treatment. The wettability of the pristine dolomite (Figure 3b) and calcite (Figure 3c) exceeded that of the pristine sandstone (Figure 3a). In addition to the adsorbed mass, calcite exhibited an initial step with a steep slope, showing distinct hydrophilic properties.

In the case of sandstone, the SP and STDW samples (Figure 3a) showed higher water adsorption in relation to the aged sample and those treated with brine solutions. The

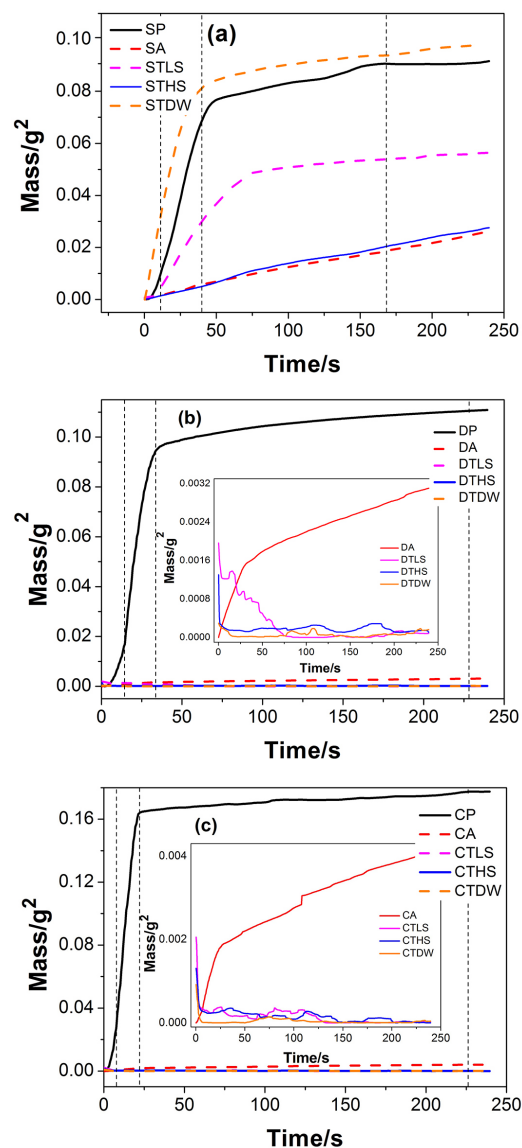


Figure 3. A capillary rise in function of time (s) for the samples under different conditions: (i) pristine (unmodified); (ii) after aging; and (iii) after aqueous solution treatment - (a) sandstone, (b) dolomite and (c) calcite. The dashed lines indicate approximately the three steps of an experiment based on the WCR method (unmodified sample).

STDW sample showed higher wettability than SP, which was not expected and may be related to an experimental discrepancy. In addition, the SA and STHS samples showed similar wettability behavior (oil-wet), indicating that, even with a high salt concentration, the oil remained adsorbed on the surface. Overall, treatment with deionized water and low brine concentration reduced the oil retention on sandstone surface.

There were substantial differences in the amounts of water adsorbed by the pristine dolomite and calcite samples (Figures 3b and 3c, respectively). However, after the aging procedure and after aqueous solution treatment, the change in wettability was negligible. This behavior

suggests that carbonate rocks adsorb more strongly the organic phase compared to sandstone, as also observed by Rezaeidoust *et al.*⁵⁰

Fourier-transform infrared spectroscopy (FTIR)

Figure 4 shows the FTIR transmittance *versus* wavenumber (cm^{-1}) spectra for the rock samples: (i) pristine (unmodified); (ii) after aging; and (iii) after aqueous solution treatment for sandstone (Figure 4a), dolomite (Figure 4b), and calcite (Figure 4c). The infrared bands seen in Figure 4 and Table 5 are in agreement with the XRD analysis regarding the composition of the rock samples.⁵¹

The FTIR spectrum for sandstone shows bands between 550 and 880 cm^{-1} associated with quartz (SiO_2), related to very well-defined Si–O and Si–O–Si vibrations.^{52,53} In particular, there is a wide band centered at 1075 cm^{-1} , attributed to the asymmetric enlargement/stretching vibration of oxygen at the Si–O–Si bridge.⁵⁴ In addition, a strong band observed at 1440 cm^{-1} was attributed to the stretching of the C–O bond of calcium carbonate.⁵⁵

The FTIR analysis of calcite reveals characteristic bands associated with the asymmetric angular deformations of the carbonate group at between 650 and 1000 cm^{-1} ,^{56,57} and two peaks (2513 and 1796 cm^{-1}) related to combined deformation of the same carbonate group.³⁸

The presence of organic contaminants in the sandstone was observed from two small bands at 2970 and 2860 cm^{-1} , which can be attributed to the asymmetric and symmetric stretching modes respectively of the C–H from the aliphatic methyl group (CH_3).⁵⁶ The presence of organic contaminants in the dolomite and calcite samples were observed from bands at around 2993 and 2897 cm^{-1} .⁵⁶

The vibration of H–O–H stretching of hydroxyl groups at around 3435 cm^{-1} is related to the clay structure.⁵¹ In the case of sandstone, this vibration is more evident. There was a band at 3618 cm^{-1} , attributed to the stretching of the O–H bond of the hydroxyl structural groups,^{51,55} and at around 1628 cm^{-1} , also associated with the angular deformation H–O–H from water trapped between the clay layers.⁵⁵

Table 6 shows FTIR changes after rock samples were exposed to synthetic oil during aging and after surface treatments. The *n*-dodecane oil is identified by FTIR analysis, showing three intense peaks between 3000–2850 cm^{-1} and a small peak at 1450 cm^{-1} .⁵⁸ Stearic acid also has characteristic peaks at around 2900 cm^{-1} and small peaks at 3560, 1780, 1450 and 1100 cm^{-1} .⁵⁸ In addition, the characteristic bands of rock samples showed two peaks at around 2900⁵⁹ and 1440 cm^{-1} .⁵⁴

The aged rock samples showed an intensification of the bands associated with the asymmetric and symmetric

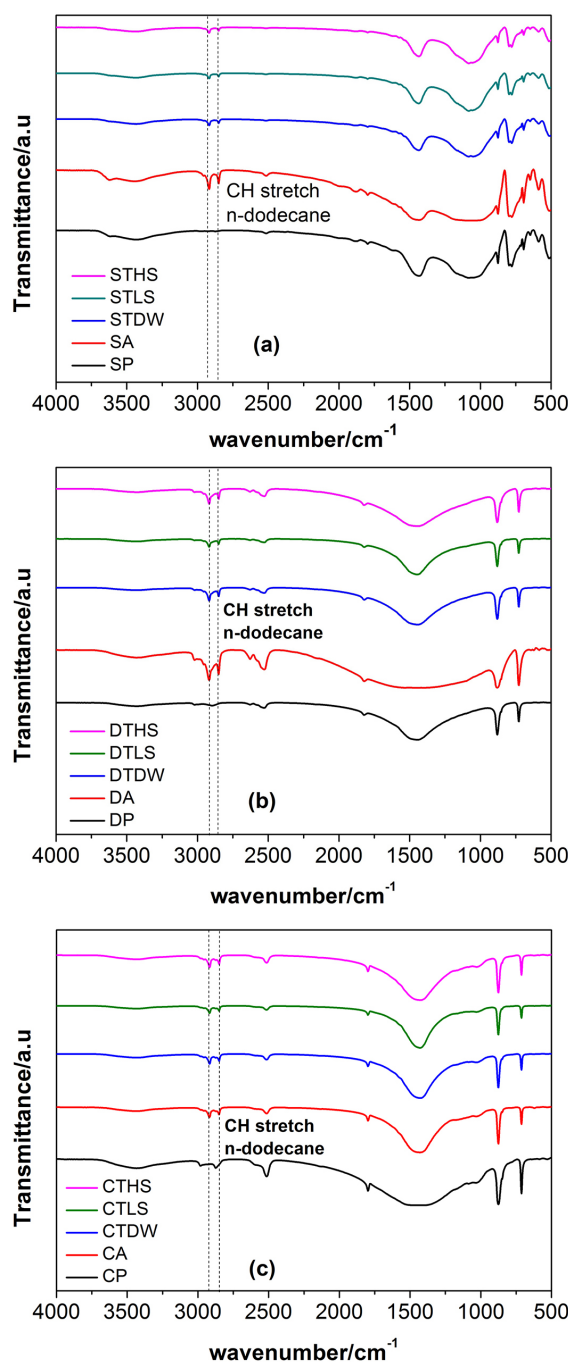


Figure 4. FTIR (KBr) transmittance *versus* wavenumber (cm^{-1}) spectra for the rock samples: (i) pristine (unmodified); (ii) after aging; and (iii) after aqueous solution treatment. (a) Sandstone, (b) dolomite, and (c) calcite.

stretching vibrations C–H of the aliphatic methylene group (CH_2) (around 2900 and 2850 cm^{-1}), suggesting adsorption of the synthetic oil onto the surface of the rock samples. Likewise, the band at around 1440 cm^{-1} was strongly affected by the treatment applied to the rock samples, suggesting the presence of stearic acid due to bending of the C–O–H plane of carboxylic acid.⁵¹ The FTIR spectra signals of the overlapping peaks related to the rock samples

Table 5. Assignment of the main bands on the FTIR spectra of rock samples

Composition	Wavenumber / cm^{-1}	Reference
Sandstone		
Quartz, SiO_2	1075, 880, 785, 696, 646	52-54, 56
Calcium carbonate, CaCO_3	1440	55
Dolomite		
Calcium magnesium carbonate, $\text{CaMg}(\text{CO}_3)_2$	3024, 2627, 2530, 1446, 880, 729	51
Calcite		
Calcium carbonate, CaCO_3	2982, 2874, 2513, 1796, 1424, 872, 708	56,57

Table 6. Assignment of the main bands on FTIR spectra of rock samples treated with synthetic oil

Assignment	Wavenumber / cm^{-1}		
	Sandstone	Dolomite	Calcite
Bending in the C–H plane-carboxylic acid ^a	1440	1450	1430
Asymmetric C–H stretching of the aliphatic methylene group (CH_2) ^b	2915	2920	2920
Symmetric C–H stretch of the aliphatic methylene group (CH_2) ^b	2850	2850	2850

^aCharacteristic band of the C–O–H bond stretching;⁵¹ ^bindicates the presence of *n*-dodecane and stearic acid.⁵⁶

composition become well defined after treatment with deionized water and brine solutions.

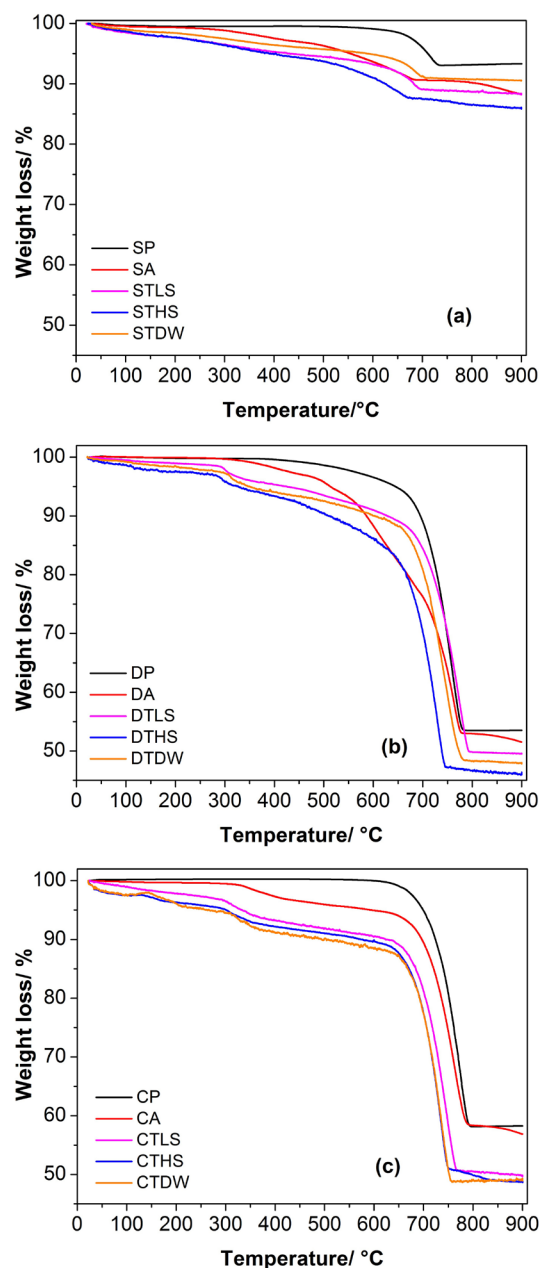
Thermal gravimetric analysis (TGA)

Figure 5 shows the TGA results for the rock samples: (i) pristine (unmodified); (ii) after aging; and (iii) after aqueous solution treatment of sandstone (Figure 5a), dolomite (Figure 5b), and calcite (Figure 5c). The TGA profiles for the modified rock samples were similar, with multiphase decomposition. Risoul *et al.*⁶⁰ showed that *n*-decane molecules adsorbed on carbonate degraded at 250–305 °C. Gomari *et al.*⁶ showed that stearic acid adsorbed on calcite degraded at 25–230 °C and stearic acid/*n*-decane degraded at 230–385 °C. In this study, the organic phase (*n*-dodecane/stearic acid) degradation range was estimated by both TGA and DTG, respectively, especially in low definition or overlapping thermal events. The temperature range used in the quantitative estimation of the organic phase was around 250–400 °C for the treated rock samples, using the best correlation obtained.

The pristine sandstone rock sample Figure 5a shows three stages of degradation and weight loss (wl) in the

ranges of 34.8–87.3 °C (0.3% wl), 87.5–167 °C (0.2% wl) and 463.6–736 °C (6.5% wl). The first two stages are related to the volatile fractions of water, which can be adsorbed on the sandstone surface as free water or bound/stored in the crystalline structure.⁶¹ The third stage refers to the degradation of carbonates, oxides, and carbon dioxide. Two important stages may occur in parallel in the third case, that is, the thermal decomposition of calcium carbonate (500–600 °C) and the changing of quartz crystallinity from α - to β - form at around 600 °C.³⁷

The aged sandstone rock samples showed an extra

**Figure 5.** TGA of rock samples: (a) sandstone, (b) dolomite, and (c) calcite; (i) pristine (unmodified); (ii) after aging; and (iii) after aqueous solution treatment.

degradation step, which is related to synthetic oil, between ca. 200-424 °C, representing around 2.16% wl. This step was also observed on samples treated in brine solutions, with an organic residue of 1.38% for STLS and 1.68% for STHS. However, the organic residue of the STDW sample was 1.13%, indicating the efficiency of water treatment in the oil recovery. The total ash contents of the SP samples were around 93%, with values of 88.3% for SA and STLS, 86.9% for STHS, and 91% for STDW. Despite the experimental errors, these data are consistent with the wettability tests, which indicate that the treatment under water and low brine concentration favored the oil desorption from the sandstone surface.

The pristine dolomite (Figure 5b) shows a small mass loss of ca. 0.2% wl in the range of 60-215 °C, related to the loss of water and also some organic contaminants. From 350 to 780 °C, a multiphase step occurs, corresponding to 46.6% wl, which can be attributed to the decomposition of MgCO_3 starting at ca. 400 °C and CaCO_3 at 600 °C.^{39,62} These species were also identified in the FTIR analysis.³⁹

The aged dolomite rock samples showed the release of water at 103 °C (0.13% wl) and undefined steps associated with the degradation of the organic phase and the decomposition of CaCO_3 . However, it is possible to identify steps at intermediate intervals of approximately 400-517 °C (2.5% wl) for MgCO_3 as well as 520-574 °C (3.2% wl) and 580-690 °C (14.4% wl) for CaCO_3 . The first two steps may be associated with the degradation of the organic phase and strongly adsorbed fragments.

The total ash content of the dolomite DP and DA samples was ca. 53% lower than the value for sandstone. The treated rock samples showed total ash contents of ca. 49.7% for DTLS, 47.7% for DTHS, and 48.2% for DTDW. The degradation steps for the organic fraction were observed in the range of 268-380 °C, with a residual amount of 3.06% (wl) for the DTLS sample, 2.88% (wl) for DTHS, and 3.0% (wl) for DTDW.

The pristine calcite rock sample (Figure 5c) showed degradation between 30-180 °C, with a mass loss of ca. 0.2%. This step may be associated with the loss of water or moisture and the degradation of organic contaminants. The amount of water in the modified rock samples CTLS, CTHS, and CTDW were ca. 2.44, ca. 3.9, and ca. 4.55%, respectively, higher than in the aged sample. In the case of the aged samples, the steps related to the release of water showed higher mass loss compared with the unmodified samples (ca. 0.42%). The degradation of the organic phase showed an elongated step between 270 to 380 °C, referring to ca. 3.44% (wl).

Regarding the total ash content, the pristine and aged calcite rock samples showed similar values (58.12 and

58.42%, respectively). When the rock samples were treated, these values were 50.47, 49.1, and 48.83% for CTLS, CTHS, and CTDW, respectively.

The decomposition of calcium carbonate (CaCO_3) occurred in the ranges of 600-850 °C for calcite and 691-780 °C for dolomite, in agreement with data reported elsewhere.³⁹ For dolomite, this temperature range represents the decomposition of its structure and the release of CO_2 from the carbonate group associated with Mg.³⁸ In addition, the total ash content was higher after the rock sample treatments and similar results have been reported elsewhere for calcium carbonate.⁶³ Regarding the degradation steps for the organic fraction, the results indicate that the treatment under high brine concentration favored the oil desorption from dolomite and calcite surfaces.

Discussion

The interactions between the surface of powdered rocks and the surrounding fluids associated with the changes in wettability were investigated considering the rock samples (sandstone, dolomite and calcite) under three different conditions: (i) pristine powder (unmodified); (ii) after aging; and (iii) after treatment with different aqueous solutions which simulates the recovery process. In the condition (i), the rock samples were unmodified and considered as water-wet.

The aging procedure under condition (ii) was carried out aiming to modify the initial wettability of the rock to oil-wet, and at condition (iii) the salt solution simulates the water flooding, modifying the wettability and simulate the oil recovery process. After treatment, all samples were rinsed with the synthetic brine solution in high and low concentrations, and with deionized water, to evaluate the degree of interaction promoted and the reversibility of the aging process.

Results from WCR and TGA showed that the adsorption of stearic acid was observed only after condition (ii), therefore the aging process was successfully carried out. This indicated that the mechanism of organic phase (*n*-dodecane/stearic acid) adsorption involves the acid groups but not exclusively. The presence of acid groups decreases the water-oil interfacial tension⁶⁴ and plays an important role in the oil/surface interaction. Furthermore, the desorption of the organic phase is further favored by the divalent cations of the brine solution,^{6,65} which constitutes the electric double layer (effect of potential determining ions).

The oil retention tendency from TGA analysis showed values of 1.38, 1.68 and 1.13% for STLS, STHS and STDW, respectively, for sandstone. The dolomite showed

oil retention values of 3.06, 2.88 and 3.0% for DTLS, DTHS and DTDW, respectively, and calcite showed slightly higher oil retention values of 3.8, 3.08 and 3.35% for CTLS, CTHS and CTDW, respectively. Thus, the total percentage of adsorbed oil on aged samples was twice as high in carbonate rocks as in sandstone. The TGA analysis for the degradation steps of the organic fraction on dolomite and calcite indicates that the treatment under high brine concentration favored the oil desorption and opposite result was observed for sandstone.

Electrostatic interactions are expected to play a major role in the adsorption process and thus it would be expected that the treatment condition (iii) would provide similar wettability for all rock samples. However, the wettability results for carbonates were similar, but different for sandstone, indicating a different mechanism involved in the oil adsorption for carbonates and sandstone.

The ZP of natural rock surfaces plays an important role in surface processes affecting the ionic interaction between rock surfaces and charged molecules in an aqueous medium.²⁷ The ZP profile shows that the sandstone and carbonate rock samples have a negative charged surface, except for pristine dolomite, at very low pH < 2.6, and high salt concentration > 0.6 mol L⁻¹, which changed from negative to slightly positive ZP. Most studies⁴⁰⁻⁴⁵ on oil recovery from carbonate rocks assume that the main function of the acid groups in the oil is to compensate for the surface potential of the mineral and, thus, change the rock wettability.

Overall, the rock samples (sandstone, dolomite and calcite) showed similar pH profile behavior of ZP, as the pH increases, the negative surface charge also increases toward repulsive particles interaction. However, regarding the salt concentration profile of ZP, as the salt concentration increases the negative charge decreases. In addition, the ZP profile for carbonate rocks as a function of salt concentration showed a slightly negative ZP for aged samples than for pristine and the opposite result was observed for sandstone. This result shows the effect of oil adsorption on the rock surface, which indicates a different adsorption mechanism from carbonates to sandstone.

Jackson *et al.*⁶⁶ results for carbonates showed that, if the ZP of the aged samples is more negative than that of the water-wet samples, then the oil-brine interface is negatively charged and the injection brine must be modified to produce a more negative ZP at the mineral-brine interface. According to their results, this can be achieved by dilution or by reducing the concentration of Ca²⁺ and/or Mg²⁺ or adding SO₄²⁻ which yield more negative zeta potential.

Gomari *et al.*⁶ showed that the presence of Na⁺ ions have no considerable effect on wettability of calcite in presence

of stearic acid. However, the presence of Mg²⁺ and SO₄²⁻ ions convert the calcite to more water-wet within pH 7.

According to Karimi *et al.*,²⁴ a high concentration of NaCl in the formation brine hinders the access of wettability influencing ions to the surface. Neither Na⁺ nor Cl⁻ are considered as wettability controlling ions. Although the Na⁺ and Cl⁻ are not part of the stern layer, they are active in the electrical double layer and may affect the access of the active ions, Mg²⁺ and SO₄²⁻, to the solid surface. In their earlier studies, Karimi *et al.*¹⁸ used the contact angle technique, to investigate the effect of brine composition on the change in wettability of an oil-wet carbonate. They concluded that magnesium ions were able to remove the carboxylate group strongly adsorbed on the surface and change the wettability of the calcite surface to a more water-wet state.

Awolayo *et al.*⁶⁷ studied the influence of the sulfate concentration on carbonate oil recovery, wettability and surface charge modification. They found that an increasing concentration of sulfate up to four times in a typical seawater (2.6 g L⁻¹ × 4 = 10.4 g L⁻¹), makes a crude oil/brine/rock system less oil-wet with an incremental recovery of about 10%. They stated that the higher the sulfate concentration, the greater the repulsive forces in the electrical double layer, thereby forming an aggregate and detaching the oil from the rock surface. Although, by increasing the sulfate concentration beyond four times seems ineffective as it gave a swift increase in pH and rock surface charges.

The brine solution used in our work was 0.1 mol L⁻¹ of Na₂SO₄ that contain 9.6 g L⁻¹ of SO₄²⁻ and the high brine concentration used was 80% by v/v of the initial concentration, which gives 7.7 g L⁻¹. Therefore, the results reported by Awolayo *et al.*⁶⁷ had higher SO₄²⁻ concentration than that used in our work, which can explain the oil desorption favored by the high brine concentration showed by the TGA analysis on carbonate rocks. TGA results of oil desorption are also in agreement with the ZP, which showed a slightly negative value for aged carbonate samples than for pristine and the opposite result was observed for sandstone.

Regarding the sulfate concentration, results obtained by Mahani *et al.*⁶⁸ showed that seawater enriched with SO₄²⁻ (13.5 g L⁻¹), result in a negative zeta potential of approximately -8 mV at pH = 6.5, for calcite. Thus, they conclude that by diluting seawater or adding sulfate, both made zeta potential more negative, which suggest that more water-wet-condition can be achieved in both conditions. The results from Mahani *et al.*⁶⁸ are quite similar to our results for calcite and dolomite at pH = 6.5 with sulfate concentration of 7.7 g L⁻¹. Although, the composition and the crystallinity of the rock samples must be taken into account regarding the zeta potential analysis.

According to Brugman *et al.*,⁶⁹ the mechanism of the carboxylic acid adsorption at the calcite surface completes the surrounding of Ca^{2+} and the topmost oxygen atom and in this way compensates for the unfavorable dangling bonds at the calcite surface. The adsorbed carboxylic acid molecule binds simultaneously to calcium and oxygen atoms. The oxygen atoms of organic acid are found in positions similar to those of water molecules at the calcite-water interface. In addition, they observed that under the same experimental conditions, stearic acid does not adsorb on muscovite mica functionalized with K^+ and Ca^{2+} because neutral molecules are not involved in the ionic bonds typical of the mica interface. They concluded that the differences in adsorption behavior between calcite and mica are similar to oil-solid interactions in carbonate and sandstone reservoirs.

The mechanism of the carboxylic acid adsorption at the calcite surface, according to Brugman *et al.*,⁶⁹ could explain our results in which the total amount of adsorbed oil on aged carbonate samples was twice as high as in sandstone. Moreover, the TGA analysis of the organic fraction indicates that the treatment under brine with high SO_4^{2-} concentration favored the oil desorption on carbonates and the opposite result was observed for sandstone. These results are also in agreement with the results reported by Awolayo *et al.*,⁶⁷ which can explain the oil desorption favored by the high brine concentration showed by the TGA analysis on carbonate rocks. The TGA results of oil desorption are also in accordance with the ZP, which showed a slightly negative value for aged carbonate samples than for pristine. According to Jackson *et al.*,⁶⁶ this can be achieved by dilution or by reducing the concentration of Ca^{2+} and/or Mg^{2+} or adding SO_4^{2-} which yield more negative zeta potential. From our results, it is clear that there are fundamental differences in the adsorption mechanisms of oil-protonated carboxylic acids on carbonate and sandstone.

Conclusions

In this work, we consider oil-brine-powder rock interactions to pursue wettability change under three different conditions: (i) unmodified powder; (ii) after aging in oil, and (iii) after aqueous solution treatment (high and low brine). The (ii) condition, aimed to modify the wetting character from water-wet to oil-wet, was performed efficiently for all rock samples, although to a lesser extent for sandstone compared with carbonate rocks. Infrared analysis showed the removal of acidic groups in aged rock particle clusters after treatment with solutions of high and low brine and water.

TGA analysis showed that the percentage of adsorbed oil on aged carbonate samples was twice as high as in

sandstone. In addition, the TGA analysis of the organic fraction on dolomite and calcite indicates that the treatment under brine with high SO_4^{2-} concentration favored the oil desorption and the opposite result was observed for sandstone. This behavior suggests that carbonate rocks adsorb more strongly the organic phase compared to sandstone, indicating a different mechanism involved in the oil adsorption for carbonates and sandstone. However, it is important to notice that the obtained results are mainly due to the composition of the brine, whose main component is SO_4^{2-} , which in higher concentrations normally works better in carbonate. Therefore, brines with lower SO_4^{2-} concentration or low salinity brines with added SO_4^{2-} could be more efficient in oil recovery.

Although natural oil reservoirs have a much more complex composition than the simple systems studied here, from our results, it is clear that there are fundamental differences in the adsorption mechanisms of oil-protonated carboxylic acids on carbonate and sandstone.

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Author Contributions

Veronica A. Santos was responsible for conceptualization, data curation, formal analysis, investigation, methodology, writing original draft visualization, writing review editing; Taís Felix for conceptualization, data curation, formal analysis, investigation, methodology, software, validation, visualization, writing original draft, writing review editing; Iara F. Mantovani for data curation, formal analysis, investigation, methodology, software, writing original draft; Rodrigo Balen for methodology, investigation, formal analysis, writing original draft; José A. B. da Cunha Neto for funding acquisition, project administration, resources, writing review editing; Celso P. Fernandes for funding acquisition, project administration, resources, supervision, writing review editing; Nito A. Debacher for funding acquisition, resources, supervision, writing original draft, writing review editing.

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