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Polytechnica 2 (1-2), 30-50 (2019)

DOI: <https://doi.org/10.1007/s41050-019-00014-1>

This version of the article has been accepted for publication, after peer review, but is not the Version of Record and does not reflect post-acceptance improvements, or any corrections. The Version of Record is available online at: <https://doi.org/10.1007/s41050-019-00014-1>.

From atoms to pre-salt reservoirs: multiscale simulations of the low-salinity enhanced oil recovery mechanisms

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Received: date / Accepted: date

Abstract The goal of this review paper is two-fold: bringing an updated survey on the literature of the proposed mechanisms behind the low-salinity enhanced oil recovery (EOR) and propose ways to model them based on simulations coupling atomic to reservoir scales. The low salinity water injection (LSWI) presents some advantages over other EOR techniques since it is a cost-effective method, has no inherent environmental damage and does not affect the subsequent stages of crude oil treatment and refinement. The LSWI is particularly interesting for exploration and production on pre-salt carbonate reservoirs. We couple the LSWI mechanisms with molecular modeling methodologies, addressing their use to describe the EOR via LSWI. From the molecular modeling, one can obtain parameters for the large-scale reservoir simulators, thus, improving their accuracy. Therefore, the molecular modeling approaches are complementary tools to optimize the EOR via LSWI. Among all the involved mechanisms on the LSWI, the wettability alteration is pointed out by several authors as the fundamental one, to explain the EOR. However, there are controversies related to its cause: salting-in effect, multi-component ionic exchange, pH alteration, electric double layer expansion, fines migration, limited release of particles and osmotic pressure are among the main proposals. In this sense, several molecular modeling techniques have been explored to foster theories that explain the possible mechanisms and optimize the oil pro-

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duction combining the molecular dynamics simulations and *Ab initio* calculations with reservoir simulators.

Keywords EOR-LSWI · Petroleum recovery · Molecular modeling · Reservoir simulators

1 Introduction

The global energy matrix is highly dependent on fossil fuels, as no viable substitute has been found without the need for massive new infrastructure, as already present for the hydrocarbons. Besides, the transition towards a carbon-neutral matrix has to be gradual, to avoid a global economic loss on the order of trillions of dollars [1]. Hence, research on this topic should not be neglected, as there are many open problems on the oil and gas industry. The environmental impacts of oil extraction could be minimized with the utilization of novel techniques, such as CO₂ injection on deep reservoirs [2].

The oil recovery procedure is divided into three stages: primary, secondary, and tertiary recovery [3]. The primary recovery is the one which occurs naturally due to the pressure difference in the reservoir, *i.e.*, with no external driving forces applied. The natural energy sources are the expansion of the rock and fluid, gas in solution, the influx of water and gravity. The secondary recovery occurs when the primary extraction process is saturated, which is usually called improved oil recovery (IOR), and it takes place from the external fluids injection, such as water or gas, aiming to maintain the pressure and the volumetric sweep efficiency. Finally, the tertiary recovery occurs as a final stage¹, and at this point, prepared fluids - such as chemical compounds in a brine solution, miscible gases, or thermal energy - are injected [3], what are called enhanced oil recovery (EOR) methods. Therefore, EOR is usually used as a tertiary recovery method to extend the producing time of a given reservoir.

EOR techniques play a critical role in the oil industry since a 1 % recovery increase can lead to a considerable amount, as reservoirs can have in the order of billions of oil barrels. A promising method for EOR is the low salinity water injection. This method has some advantages, as it is environment-friendly, since it uses natural resources, also, because the necessary supplies are available *in-situ*. The oil extraction is enhanced by low salinity water injection (LSWI), due to physical and chemical processes, which can occur among the oil, connate (formation) water², injected brine, rock surfaces and other components present in the reservoirs.

Carbonates such as calcite, magnesite, and dolomite are common in nature, as they account for more than half of the sedimentary rocks. The carbonates rocks are usually present in oil reservoirs [4–7] making its fundamental understanding necessary for the oil industry, in particular for the Brazilian pre-salt reservoirs. Around 90% of the carbonate surfaces are oil-wet or mixed-wet (oil- and water-wet). The carbonate surfaces, in particular, present higher adsorption energies of

¹ In some cases we can also have other extraction stages. Besides, an overlap of the different recovery processes can also be the case.

² Both connate and formation terms are found in the literature to classify the water in the reservoir before the extraction started.

the oil phase [8], which implies in a very strong interaction between the hydrocarbons and such surfaces [9, 10], leading to an inefficient primary recovery.

There is also interest from a basic science point of view, as some processes that happen on the oil extraction are still not well understood. Plenty of efforts have been applied to understand the low-salt EOR [3], that consists of higher oil extraction with the fluid injection with lower salinity than the seawater. The chemistry involved in the low-salt EOR happens for different kinds of minerals (silicates, carbonates, and clays), which might involve distinct processes [3].

Understanding the mechanisms involved in the low salinity EOR is fundamental for the oil industry, with the primary goal being the design of an optimal brine composition for a given particular reservoir condition, although different minerals and processes will require different compositions. There are numerous mechanisms proposals found in the literature [11–13], with no clear consensus about the dominant one(s). Therefore, the main question related to the EOR by LSWI remains unanswered: which mechanisms are the dominant ones? Moreover, is there indeed a dominant mechanism, or the combination between them leads to the EOR? In this sense, molecular simulations can offer a more assertive understanding of the mechanisms, since it allows us to isolate variables and to consider situations that would not be possible experimentally. Also, computational simulations tend to be cost-effective when compared to experimental studies. Hereupon, it is possible to maximize results and improve the exploration of variables.

In this work, we present an extensive review of the enhanced oil recovery mechanisms by low salinity water injection and its relationship with multiscale molecular modeling and reservoir simulators. The structure of this review article is the following: In Section 2 we introduce a review on the main mechanisms of EOR by LSWI and in Section 3.1 we detail how molecular modeling can be used to investigate those mechanisms, and what physical-chemical parameters can be obtained with this approach and how they can be applied in reservoir simulators. Finally, we conclude with the contributions of this approach to EOR.

2 Mechanisms

There are numerous mechanisms proposed in the literature [11, 12, 14] that try to explain the reasons why oil recovery can be optimized by low salinity water injection. The main mechanisms that we will tackle in this work are the salting-out effect, multicomponent ionic exchange, pH alteration, wettability change, limited release of particles, electric double layer expansion, particle mobilization (migration) and osmotic pressure. Altering the wettability decreases the rock’s oil affinity, making it more hydrophilic. In this way, the oil once adhered in the surface will be released into the medium, thus enabling its extraction by drag. Although there is no clear consensus about which mechanism is the dominant one, it is well known that rock’s wettability alteration is necessary for extracting oil in the secondary recovery. However, a better understanding of the causes which lead to this change is necessary in order to propose low salinity solutions with optimum composition, in order to maximize oil extraction. In the following subsections, a detailed discussion about the mentioned mechanisms will be shown.

2.1 Salting-in effect

The phenomenon known as salting-in/salting-out is widely reported in the literature as an analog of the protein precipitation tools, and it has an essential role in altering the critical micellar concentration (CMC). The salting-in effect is applied in organic solvents chemical extraction and surfactant optimization [15, 14]; also, it is was recently reported as one of the mechanisms responsible for oil recovery in silicate and carbonate reservoirs [14, 16].

The increase in the aqueous electrolyte concentration, known as the salting-out effect, is responsible for decreasing the oil solubility in water. The salting-in, an antagonistic effect, establishes that the salt concentration reduction is responsible for the increase of the oil solubility in water, due to the ionic strength reduction, also decreasing the interfacial tension. Moreover, ionic strength increases with the ion concentration and charge number, as shown in Equation 1 [14, 16, 17].

$$I = \frac{1}{2} \sum_{i=1}^n c_i z_i^2, \quad (1)$$

where I is the ionic strength that is given by the sum of the i terms, c is the concentration in mol/L , and z is the ionic valence. The so-called Setschenow equation can measure the efficiency of the salting-out/in phenomenon [18]:

$$\log \frac{S_0}{S} = k_s c, \quad (2)$$

where S_0 is the solute solubility in pure water, S is the solute solubility in brine, k_s is the Setschenow constant, and c is the salt concentration. For negative k_s , the salting-in effect is favored [15].

In the salting-out effect, anions with high charge density provide the electrical repulsion and as a consequence, the increase of the hydrophobic effect. This effect is responsible for the aggregation of the solvated molecules as a way to minimize the entropic penalty resulting from the hydration layer organization [15].

The salinity increase is responsible by the oil coalescence, due to hydrophobic interactions of nonpolar compounds, and also increases the adhesion of organic materials to the surface by the oil-wet alteration on rocks. Thus, when the salt concentration decreases, the solubility of the carboxylic compounds in the aqueous solution increases, leading to a decreasing in the possibility of bonding between the negatively charged carboxylic group and the positively charged carbonate surface, thereby weakening the oil/rock interactions [19].

For salting-in, there are two interpretations regarding this effect, both depending on the ion charge density. The first interpretation is that lipophilic ions, or with low charge density, can interact with oil and water through non-localized dispersion forces. Thus, these ions behave as surfactants, increasing the oil solubility in water (Figure 1a) [15]. The second interpretation proposes that the salting-in effect also improves the oil recovery by altering the wettability of the rocks, promoting the organic materials desorption with increasing water solubility (Figure 1b).

It is also a reason for a large number of studies highlighting the clay presence as a necessary condition for the low salinity effects [20]. Even in systems formed by carbonate rocks. The clay can play a prominent role in some mechanisms, among

them the multi-component ionic exchange (Figure 2), by the breakage of the ionic bridge (formed between the clay and the organic material) deposited in the rocks. The Hofmeister Series guide the ionic exchange [14,15]:

$$Li^+ < Na^+ < K^+ < Mg^{2+} < Ca^{2+} < H^+. \quad (3)$$

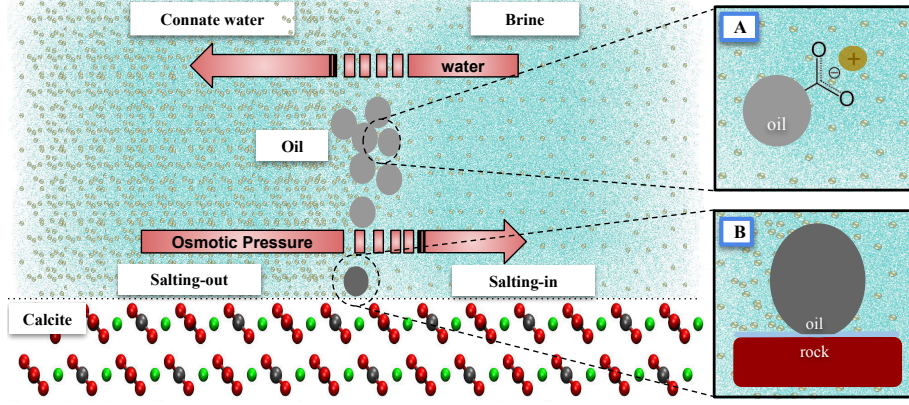


Fig. 1 Scheme to represent the system involving connate water and brine in a reservoir model containing calcite. The ions are represented by gold balls, illustrating the concentration gradient. The oil (gray ball) is surrounded by an aqueous medium and forms a semipermeable membrane that is responsible for concentration control. The LSWI decreases the salt concentration (salting-in effect) leading to migration of water molecules from brine to connate water (osmotic process). An opposite force to this movement is called osmotic pressure and helps to release and migrate oil particles from calcite. We also show two main processes arising from the salting-in. In (a) the charge interactions between the oil carboxyl group and brine cations, which stabilizes the oil-water interaction. In (b) the ionic exchanges due to the salt concentration changes, that lead to a water film formation on calcite, reducing the calcite oil-wetness.

2.2 Multi-component ionic exchange

The multi-component ionic exchanges [21] occur after the LSWI processes, due to the concentration difference between the injected low salinity water and the connate water. As sketched in the right part of Figure 2, this leads to ionic exchanges, among the mineral's ions, which are usually Ca^{2+} , Mg^{2+} , Ba^{2+} , SO_4^{2-} and CO_3^{2-} and the low salinity water ions. After being in contact, a new chemical equilibrium among the ionic components in the solution should be reached (left part of Figure 2). The injected water composition, as well as the ionic exchanges kinetics and chemical reactions which could occur, play a fundamental role in this mechanism. The pH alterations, as we will discuss later in this work, also influence the ionic exchanges.

Zhang *et al.* [22] proposed a mechanism for the ionic exchange between Ca^{2+} and Mg^{2+} ions, in which the negatively charged oil components interact directly with the calcite ($CaCO_3$) surface, as shown in Figure 2. In this mechanism, the ions in the solution (Ca^{2+} , Mg^{2+} , and SO_4^{2-}), when approaching the surface can be exchanged, releasing the oil into the medium and allowing its displacement.

The mechanism proposed by Zhang *et al.* [22] was later confirmed to be thermodynamically feasible by Sánchez and Miranda [23], based on *Ab initio* calculations, including the solvent effect. In this study, the authors varied the solvent dielectric constant to describe/model different solvation conditions.

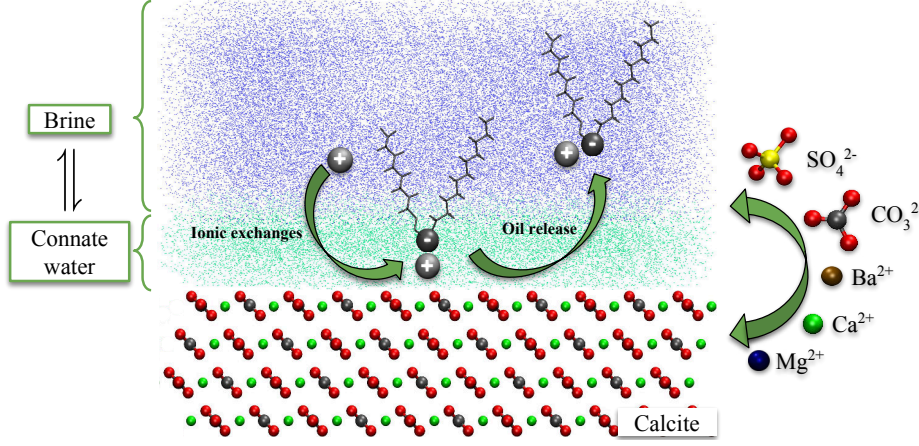


Fig. 2 Scheme for multi-component ionic exchange mechanism using calcite as an example for the carbonate mineral. The blue region represents the invading brine, and the cyan one represents the connate water (already present in the reservoir). Due to the presence of the invading brine, a new equilibrium has to be reached. The calcite surface interacts with the negatively charged oil components, mediated by one of its positive ions. The exchange of this positive ion, for example, Ca^{2+} by Mg^{2+} , will release the oil into the medium, allowing its extraction.

Mohammadkhani *et al.* [24] have recently proposed an ionic exchange mechanism to explain the decrease in the concentration of Ca^{2+} and the increase of Mg^{2+} observed in the effluent. The oil is initially adhered in the dolomite's surface magnesium ($CaMg(CO_3)_2$) by the negatively charged carboxylic group. Then, the surface magnesium is replaced by a calcium ion of the injected brine. The ionic exchange changes the surface wettability, leading to the oil release together with the magnesium ion. In the same work, the authors reported another mechanism which explained the observed decrease of Ca^{2+} in the effluent. In this case, the precipitation of $CaSO_4$ in the surface may also change the rock's wettability, which would also explain the observed improvement in oil recovery through the low salinity brine injection.

Nguyen *et al.* [25] reported a study on low salinity water injection combined with CO_2 , to analyze the geochemical reactions and ionic exchanges that occur during the LSWI processes. The brine injection, with the presence of calcite and CO_2 in the oil phase, showed the highest ionic exchange rate among all tests performed. Thus, the ionic exchanges are favored, and oil extraction can be improved. The authors also described the role played by the rock dissolution, which releases Ca^{2+} ions to the medium, favoring the ionic exchanges.[25]

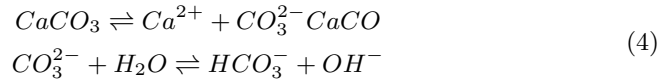
As we discussed in this section, the multi-component ionic exchanges are also a possible mechanism to explain the improvement in oil recovery with LSWI. In this case, the multi-component ionic exchanges occur due to the different ionic

concentrations of the injected solution and the connate water, as shown by the concentration gradient in Figure 1. The ionic exchanges will also be originated by the rock dissolution increasing the oil mobility, allowing its release into the medium and then increasing its extraction.

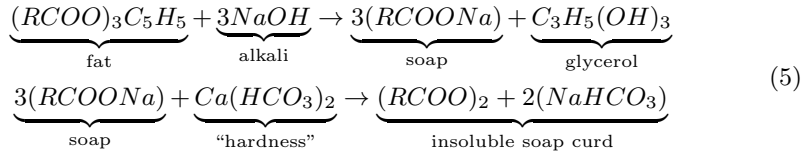
2.3 The pH alteration

The multi-component ionic exchanges, especially the cationic ones, also trigger other factors responsible for EOR by LSWI such as modifying the pH [21]. The increased pH , similar to alkaline injection, is also a possible EOR mechanism by LSWI, since it can be observed that the injected and effluent solutions' pH s are different [24, 26, 27]. In the reactions involving this mechanism, an adsorbed metallic cation on the clay's surface is replaced by a proton from a water molecule, releasing hydroxyl ions in this process [14]. Thus, pH variation may promote the rock's dissolution or a precipitation process.

One can say that in carbonate rocks the observed pH increase, after the low salinity water injection, occurs due to rock dissolution, which in turn, occurs due to the surface charge alterations, as part of the salting-in effect. As a consequence of this dissolution, an excess of the hydroxyl ions is released, causing the increase of the pH , as represented in the chemical reactions below:



The decrease of the carbonate ion concentration, which is consumed in the second stage of reaction 4, displaces the equilibrium of the first reaction towards the dissolution of the rock, according to the L  Chatelier principle [19]. This process leads to an excess of OH^- . In this case, a pH increase will be observed, which favors the saponification reactions of the organic acids (oil components) in the reservoirs, as shown in the chemical reactions below:



At higher pH s, *in-situ* soap formation is observed, as shown above, where the oil (fat) reacts with sodium hydroxide to form soap and glycerol. This soap, in turn, reacts with the "hardness" of the rock, forming a coagulated insoluble soap. This mechanism is similar to the one observed in the alkaline solution injection, because, at high pH s, the soap formation is favored, which leads to enhanced oil recovery [21]. The presence of soap in the reservoir will lead to a decrease in the oil/rock interfacial tension, thus, changing the surface's wettability. As discussed by Sheng [28], soap formation occurs at a pH of at least 9.5.

Mohammadkhani *et al.* recently analyzed the pH of the injected and effluent solutions for secondary (high salinity injection) and tertiary (low salinity water injection) recoveries [24]. The authors reported that it is possible to observe, for the secondary recovery (high salinity water), a higher pH for the injected solution

than for the effluent solution pH . This effect is reversed for the tertiary recovery with low salinity water injection, showing that the effluent pH is higher than the injected solution pH . For the experiment made with the lower salinity in the tertiary stage of recovery, the authors observed that the pH increase was due to an increase in Ca^{2+} concentration, also indicating that the rock was dissolved.

The EOR mechanism based on pH alteration occurs mainly due to the *in-situ* soap formation, which facilitates its drag by the injected solution. However, the pH and wettability change can be related by the varying contact angle. Mugele *et al.* [29] demonstrated an increase in the contact angle due to the pH increase in $CaCl_2$ and $NaCl$ solutions at different concentrations. As reported by the authors, the increased contact angle indicates increased wettability at the interface [30,29], as will be discussed in more details in the following subsection.

2.4 Wettability alteration

Wettability alteration can be seen as the primary cause of enhanced oil recovery, therefore a mechanism *per se* [31–34]. It can also be seen as a cause for other mechanisms such as the limited release of particles [35], and consequence of a more fundamental mechanism as the electric double layer expansion or ionic exchange, among others [11,36,12].

Although Sohrabi and co-workers [12] have pointed out wettability alteration as the primary cause of enhanced oil recovery, the mechanism behind was described as slightly different. The fluid-fluid interaction leads to the formation of microemulsions (micelles of water surrounded by indigenous surface-active compounds of the crude oil). The micelles formation impact was tested by experiments which identified and removed the natural surface-active components of the oil and also eliminated the role of clay.

The wettability describes the tendency of a fluid to spread on a solid surface when there is another immiscible fluid [37]. Depending on the rock surface's affinity to the fluids, it is classified as water-wet, oil-wet or mixed-wet. Reservoir rocks have a high area/volume ratio, an extensive network of pores and high surface energy. They can strongly adsorb polar molecules such as anionic surfactants and polymers, thus altering their wettability.

Another way of changing the wettability is the use of active agents present in the two phases (water and oil) that interact with the surface. In this sense, it is essential to understand the interactions between the reservoir and the rock surface which are responsible for the adhesion phenomena [38]. Karimi and co-workers [39] reported a study which combined the injection of low salinity brine and cationic surfactants during water flooding in carbonate reservoirs. The authors found that this combination could result in remarkable oil production during the spontaneous imbibition process. According to Derkani and co-workers [40], the wettability alteration was a result of ionic pair formation. The cationic surfactants and the negatively charged carboxylic layer that are adsorbed on the carbonate would form the ionic pairs. Thus, the resulting cationic-anionic complexes would release carboxylates from the rock surface. In carbonate rocks, the adsorption of negatively charged carboxylic materials ($-COO^-$), present in the heavy end fractions of crude oil (i.e., resin and asphaltene) onto positively charged surfaces,

results in large crude oil particles covering the surface and promoting mixed-wet or oil-wet characteristics [40].

The contact angle, which is the angle formed between the surface and the fluid-fluid interface, indicates the surface's wettability degree. The contact angles show the equilibrium between the interfacial tensions of the two fluid phases and their adhesive attraction to the solid surface. In a rock/oil/water system, the rock can be (i) water-wet if the water is the scattered fluid; (ii) mixed-wet if there is no preference between oil and water on the surface and (iii) oil-wet in water if the oil is the spreading fluid [40]. The wettability changes from mixed-wet to water-wet due to the brine injection is represented in Figure 3.

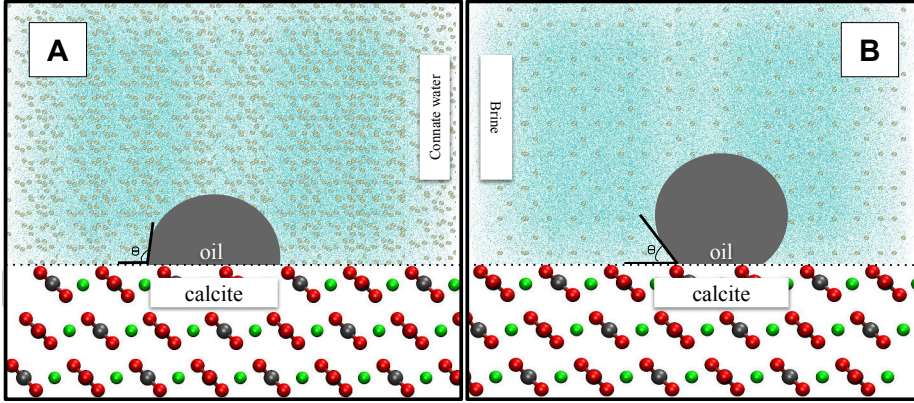
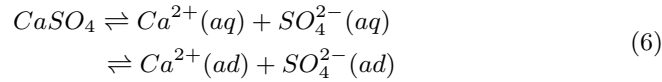


Fig. 3 Schematic representation of the contact angle variation due to wettability change. In (A) the rock is mixed-wet, and in (B) after the brine injection, the rock becomes water-wet, allowing the oil release to the medium.

The electric double layer formation and mineral dissolution can explain the wettability alteration. Austad *et al.* [41] discussed the chemical mechanism for the wettability change in carbonates, pointing out that the use of water with low $NaCl$ concentration is related to an increase in the non-active ion (Na^+ and Cl^-) at the ionic double layer on the carbonate surface, allowing access to the active ions (Ca^{2+} , Mg^{2+} , and SO_4^{2-}) on the surface. In carbonate reservoirs, the Ca^{2+} concentration is usually high, thus the sulfate is present as $CaSO_4(s)$ anhydride. Because of the decrease in solubility at high temperatures, the dissolved sulfate concentration in the connate water is low, precipitating and depositing into the rock. The following balance must be understood in order to explain the mentioned effects:



in which $Ca^{2+}(aq)$ and $SO_4^{2-}(aq)$ are dissolved ions in the pore's water, $Ca^{2+}(ad)$ and $SO_4^{2-}(ad)$ are adsorbed ions on the carbonate's surface. According to Austad *et al.* [41], the dissolution of the $CaSO_4(s)$ anhydride (the $SO_4^{2-}(aq)$ source)

depends on the brine composition and the temperature. The first one is (i) the solubility increases as the Ca^{2+} concentration in the formation water decreases. Then (ii) the solubility decreases as the $NaCl$ concentration decreases. Also, (iii) the $SO_4^{2-}(aq)$ concentration may also decrease as the temperature increases because of the increased adsorption at the carbonate surface, *i.e.*, $SO_4^{2-}(ad)$ increases.

The salinity also affects the efficiency of the wettability change, increasing the oil recovery with increasing temperature or with decreasing in $NaCl$ concentration in the injection brine [32]. The temperature and $NaCl$ concentration effects are conflicting: the $SO_4^{2-}(aq)$ concentration decreases as the temperature increases, but the surface reactivity leading to the wettability change increases as the temperature increases. Likewise, $SO_4^{2-}(aq)$ decreases as the quantity of $NaCl$ decreases, but, the surface reactivity increases. Therefore, for a carbonate system, it appears to be an optimum temperature window for observing the maximum low salinity effect, probably between 90 and 110 °C [32].

Ding *et al.* [11] considered the wettability alteration as the primary mechanism for enhanced oil recovery, for both sandstone and carbonate reservoirs. In the latter, the calcite dissolution would trigger the whole process, and the electrical double layer expansion would be the mechanism leading to this change. Dang *et al.* [26] also pointed out the wettability alteration as the dominant mechanism, but suggested that the ionic exchange and geochemical reactions are the cause of this change. Their results indicate that by increasing local pH , an increase in the concentration of divalent cations, mineralogical contributions, the influence of the connate water and the injected brine compositions, can be explained by the proposed LSW (low salinity water) model.

2.5 Electrical double layer

According to Lima *et al.* [42], the wettability alteration is related to the presence of thin water films, formed at the oil-rock interface. The film's thickness plays a crucial role in the stability of the system. More stable films are associated with the repulsive forces that tend to separate oil and rock, changing the contact angle and making the rock more water-wet. On the other hand, unstable films can lead to rupture, leaving one or a few molecular water layers with the oil in close contact with the rock surface.

One can explain this film formation by the charge balance on the electrical double layer (EDL). The EDL refers to two parallel layers of opposing charges around the given system, which may be a molecule, ion, or even on a solid surface, as the case discussed here. The charge separation causes it at interfaces of an ionic system in a fluid phase. The EDL is divided into two regions, the first one (nearer to the object), is called Stern or Helmholtz layer, composed by adsorbed ions. The second one is called the diffuse layer, composed of attracted ions (Figure 4) [19, 43, 3].

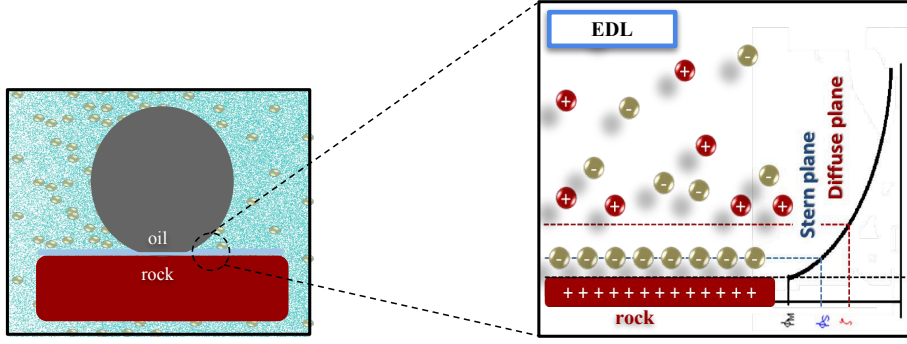


Fig. 4 Schematic representation of a water film formed upon calcite, the cations positive charges on carbonate rocks interact with the brine negative charges and break the oil-rock interactions. This charge structuring is called electrical double layer.

The low salinity water injection can to lower the carbonate rock surface's positive charge, which leads to a release of the oil acidic components from the rock surface. The EDL expands, driving a reduction in the carboxylic components adhesion on the carbonate surface, and it induces wettability alteration [19].

The EDL is one of the parameters which contributes to the 'disjoining pressure,' defined as the force tending to separate two phases (oil and water), which in turn results from molecular and ionic interactions among the rock, oil and brine phases [11]. It is divided into three components: electric (double layer), molecular (van der Waals) and structural interactions, represented by the equation 7:

$$\Pi(h) = \Pi_{VDW}(h) + \Pi_{EDL}(h) + \Pi_{str} , \quad (7)$$

where $\Pi(h)$ is the disjoining pressure, as a function of the film thickness h . Π_{VDW} is the van der Waals interaction, Π_{EDL} is the electrostatic interaction (due to the electric double layer formed by the oppositely charged ions on the surface), and Π_{str} is the structural force.

The DLVO theory (Derjaguin, Landau, Verwey, and Overbeek) [44–46] explains the balance between attractive and repulsive forces (van der Waals and electrostatic repulsion), clarifying the EDL stabilization and expansion for colloids [14, 19, 11, 3]. Among these forces, the electrostatic ones are the main forces which contribute to the disjoining pressure, described by the DLVO theory, and it is used to explain stability in thin films [19]:

$$\Pi_{EDL}(h) \approx 64cN_Ak_B \tan(h) \left(\frac{ze\psi_1}{4k_BT} \right) \tan(h) \left(\frac{ze\psi_2}{4k_BT} \right) \exp(-hk) , \quad (8)$$

Where $\Pi_{EDL}(h)$ is the electrostatic interaction in the electrical double layer, N_A is the Avogadro number, k_B is the Boltzmann's constant, c is the molar concentration, z is the ion valence, e is the electron charge, h is the film thickness, T is the temperature, k is the inverse of the Debye length, and ψ_1 and ψ_2 are surface and particle potentials, respectively.

Thus, the disjoining pressure increases the water film thickness. The film thickness of the wettable phase (in this case, water) is the result of the competition

between attractive and repulsive forces. The repulsion between the charges/ions at the brine/oil and brine/rock interfaces prevents the oil from reaching the rock surface. Thus, the wettability of the rock is altered. In oil-wet reservoirs, it is desirable to change the wettability to water-wet, also increase the water film thickness as much as possible, thereby increasing the oil mobility, and consequently its recovery. One can note that the potentials ψ_1 and ψ_2 (9) are often estimated by the zeta potentials ζ_1 and ζ_2 , respectively, which are easier to measure experimentally (Equation 9) [19].

$$\psi_i = \frac{e\zeta_i}{k_B T}. \quad (9)$$

in which ψ_i is the potential of i , e is the electron charge, ζ_i is the zeta potential of i , k_B is the Boltzmann constant and T is temperature.

The electrical double layer charge separation generates the zeta electric potential. Measurements of zeta potential corroborate the occurrence of the electric double layer expansion during the low salinity water injection. The zeta potential became more negative as the injected solution salinity decreases [19]. Also, increasing the pH increases the zeta potential of the brine/rock and brine/oil interfaces towards the more negative values due to carbonate rock dissolution.

Based on equation 8, the value of Π is positive when ψ_1 and ψ_2 are negative. Thus, the disjoining pressure has a larger magnitude when the potentials become more negative. Therefore, the salinity reduction makes possible a more negative zeta potential at both interfaces of the brine films, which leads to the electric double layer expansion, resulting in an increased water-wet character for the rock and an improvement on the oil recovery process [19,11]. With the EDL expansion, the desorption of organic molecules is also favored, due to the decrease in ionic strength [47]. The contact angle (θ) variation, in carbonate substrates (showed in Fig. 3), can be related to the electric double layer expansion.

Experimental studies carried out by Sari *et al.* showed that θ decreased linearly with the increase of the parameter Z , which is given by the sum of the zeta potential for the oil/brine and brine/rock interfaces [30,48]. When the zeta potential at the oil/brine and brine/rock interfaces have the same polarity, repulsive forces act on the EDL, whereas, the opposite polarity implies in an electric attraction, which stabilizes the EDL [48]. The interaction between the surface charges and the brine ions can be either attractive or repulsive depending on the thickness of the EDL diffuse part, known as the Debye length, k^{-1} :

$$k^{-1} = \left(\frac{\epsilon_r \epsilon_0 k_B T}{2 N_A e^2 I} \right)^{1/2}, \quad (10)$$

where ϵ_r is the brine relative permittivity (dielectric constant), ϵ_0 is the vacuum permittivity, k_B is the Boltzmann constant, T is the temperature, N_A is Avogadro's number, e is the electron's charge, and I is the ionic strength [19]. The Debye length increases as the ionic strength decreases, which is caused by the salting-in effect. Thus, the EDL expands to become more diffuse, and the interaction becomes weaker. As a result, the reduction of the contact angle is observed, since the two interfaces experience a greater electrostatic repulsion. In this way, the interactions between the brine-oil-rock interfaces influence the film's stability. The negative disjoining pressure, which is produced by attractive interactions between the two interfaces, causes the water film between rock and oil to collapse

(decreasing h). On the other hand, the repulsive interactions lead to positive contributions on the disjoining pressure, stabilizing the film, and increasing h [19]. Thus, the presence of repulsion in the electric double layer stabilizes the water layer and improves the water wettability of the rock [14].

In order to remove the oil from the carbonate surface, the low salinity water injected must overcome the capillary pressure to enter the pores. In the oil/brine/rock system, the increased Young-Laplace equation gives the capillary pressure:

$$P_c = \Pi(h) + \frac{2\sigma_{OW}\cos\theta}{r}, \quad (11)$$

in which P_c is the capillary pressure between the aqueous and oily phases, $\Pi(h)$ is the disjoining pressure, σ_{OW} is the interfacial tension, θ is the contact angle and r is the mean radius of the pores.

It is possible to establish a quantitative relationship between wettability (expressed as contact angle), disjoining pressure, and the ionic strength, as follows:

$$\cos\theta = 1 + \frac{1}{\sigma_{OW}}I, \quad (12)$$

where,

$$I = \int_0^{P_c} h d\Pi. \quad (13)$$

in which P_c is the capillary pressure between the aqueous and oily phases, $\Pi(h)$ is the disjoining pressure, h is the thickness film, σ_{OW} is the interfacial tension, θ is the contact angle, and I is the ionic strength.

In summary, the charge balance on the EDL is promoted by the salting-in effect, the pH alteration, and ionic changes. It is described by the DLVO theory and represented by the disjoining pressure, which is a parameter used to evaluate the water film stabilization. This structure reduces the oil-rock interactions forces, and the wettability alteration can be measured by the relation between the contact angle and the disjoining pressure. The oil drops could be released from the surface due to wettability alteration and afterward coalesce, forming an oil aggregate.

2.6 Fines Migration

Among the enhanced oil recovery mechanisms listed by Sheng [3], the terms “fines migration” and “limited release of fine particles” are classified as different phenomena. However, several works from the literature, including the Tang and Morrow’s work [35] use such terms as interchangeable. Here we distinguish between the two mechanisms based on their effect. Thus, this section will focus on fines migration, and the limited release of fine particles will be discussed in the next section.

The migration or mobilization of fine particles refers to the transport of small clay particles, quartz, and other materials throughout the oil reservoir due to dragging during the production. The fine particles migration may result from an unconsolidated or unstable formation or the use of an incompatible treatment scheme that releases fine particles. About fifty years ago, some researchers attempted to inject low salinity water into sandstone samples, in order to evaluate the impact

of clay content and a reduction in the permeability due to clay swelling. The fines migration mechanism was first explained using the colloids theory in the 1940s [45, 46]. Subsequently, Bernard *et al.* [49] performed experiments in which they inject *NaCl* brine and distilled water into three types of samples: sandstone, Berea, and Wyoming cores. Their results indicated that the injection of distilled water increased oil recovery. The authors also observed a significant increase in pressure drop from the secondary and tertiary modes during constant flow experiments. They stated that the increase in oil was due to the blocked pore connecting channels, deflecting the water flow to the uncured pores, improving the efficiency of the microscopic sweep. Although there may be some fine particles movement with diluted brine flow, several authors have reported no catastrophic reduction in permeability when injecting distilled water [50, 51]. Jones *et al.* [50] observed that small proportions of calcium or magnesium in the reservoir and the injected brine can significantly restrict clay blockade and that a gradual decrease in the salinity gradient may also prevent losses in permeability.

Tang and Morrow [35] observed the release of fine particles (mainly kaolinite clay fragments) from the rock surface with a decrease in salinity for different sandstone cores. The authors used three types of sandstone samples: Berea, Bentheim and Clashach, and crude and refined oil. Total Dissolved Solids (TDS) in seven different brines changed from 35960 to 15150 *ppm*. From the results, they suggested that the fines mobilization has occurred due to the exposure of the underlying surfaces, which would increase the water wettability of the system. These observations corroborate the efficiency induced by clay swelling and clogging of channels that connect the pores by the fine particle migration.

In another study, Zhang and co-workers [52] observed an enhanced oil recovery when injecting low salinity water in two different sandstone samples and three types of crude oil, both in the secondary and tertiary modes. The oil recovery depends on the brine salinity, whereas, the permeability showed no sensitivity to the salinity. This result was attributed to the presence of chloride. In most cases, the samples reacted to the low salinity brine in the secondary mode, but not in the tertiary mode. The low salinity effects became more pronounced as the initial water saturation increased. The authors observed that the effluent *pH* also increased (*pH* variation in EOR was discussed in detail in an earlier section).

In contrast with Tang and Morrow observations [35], Rivet [53] and other British Petroleum (BP) researchers [27, 54–58] performed numerous tests resulting in enhanced oil recovery without observation of any fines migration during their experiments. Based on these results, many works have questioned the relationship between fines migration and enhanced oil recovery. Following the same line, Song and Kovscek [59] observed notorious reductions in reservoir permeability; therefore, in the oil recovery. The real-time visualization showed that the fine particles blocked the preferred flow paths, thus, diverting injection fluid to unexplored regions, thereby increasing oil production.

Bedrikovetsky *et al.* have extensively researched the relationship between permeability and brine injection. Initially, they proposed an analytical model of water flooding, considering the pressure decrease in the production wells [60]. The results showed a permeability decrease in the water-swept zone, caused by the injected water composition and the fines migration. They have found that the particles have significantly lower velocities than the carrier fluid velocity, resulting in long periods of permeability stabilization [61–63]. Recently, they have studied the permeability

variation effect during the injection of LSW as a function of the kaolinite content in the rock [64–66]. A new phenomenon was observed, the permeability increased throughout the injection of high salinity water into rocks with low kaolinite content. The later is explained by the re-adsorption of the fine particles mobilized at high salinity and could be explored within the EOR process. Although the mechanism of fines migration in LSWI was initially proposed for sandstone reservoirs, later, this mechanism also has been suggested for carbonates [67–69].

The fines migration occurs when the ionic force of the injected brine is smaller than a critical flocculation concentration. This concentration is highly dependent on the divalent cations density. The variety of results cited above can be explained by considering the differences in the injected brines composition, the lithology, and minerals within the samples. From the reviewed works, it becomes clear that LSWI obtains an additional oil recovery in both cases: with and without fine particles migration.

2.7 Limited release of particles

The limited release of particles mechanism, described by Tang and Morrow [35], needs mixed-wet fine particles adhered to the pore walls to occur. This mixed-wet characteristic is because they are in contact with connate water and oil, having polar components of the oil absorbed to its surface. According to this mechanism, from the injection of low salinity water, the electrical double layer expansion occurs in the aqueous phase, causing the release of these particles from the walls and aggregate, at the same time as the oil adhered to them coalesces. This process is represented in Figure 5.

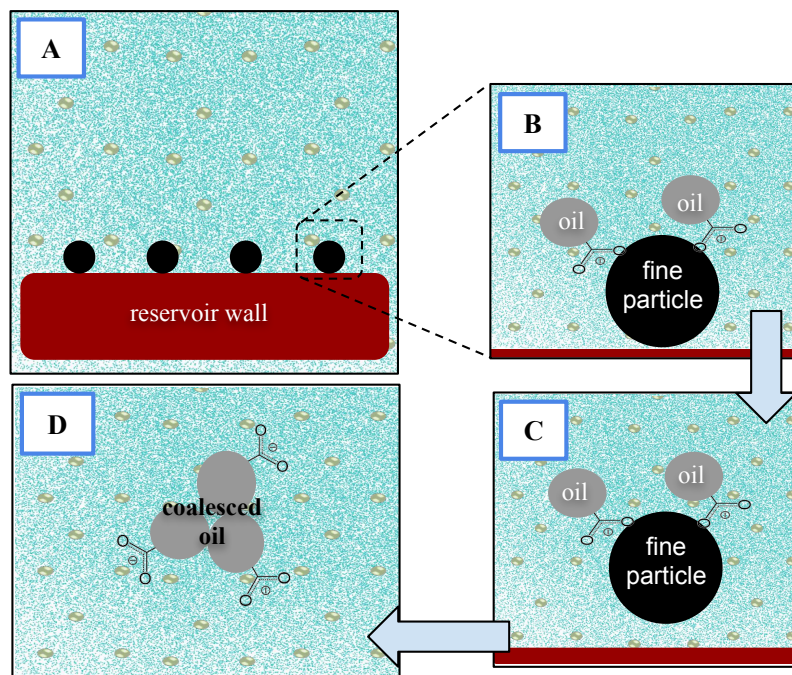


Fig. 5 Model for the limited release of particles. In the first chart, (A) the fine particles adhered to the reservoir wall are represented, and (B) represents a zoomed view with oil components at the particle's surface. A particle (C) which is dragged by the fluid is then released and (D) shows the oil components coalescence.

Fogden and Buckley [70] performed a microscopic study, analyzing the changes in the particles and organic matter positions, deposited as a consequence of the low salinity water injection. The authors did an image analysis of the particles mobilization, observing a clear link to the local wettability alteration. It was also observed an increase of asphaltene films on the rocks, besides the contribution of the migration of the mixed-wet particles, when the released particles increased the newly exposed rock surface.

Removal of the mixed-wet particles from the pore walls depends on the balance between mechanical and colloidal forces. Mechanical forces include capillarity resulting from the adhesion of the oil to the particles and viscous forces that tend to promote particles removal. The colloidal forces between the fine particles will depend on the balance between the van der Waals attractive forces and the electrostatic repulsion. The description of this mechanism as the main responsible for the enhanced oil recovery using low salinity water is controversial. Boussour *et al.* [71] observed in their experiments that there was no additional recovery, despite the significant production of fine particles, the suggesting that the change in wettability from the adsorption of organic matter on the rock surface is more significant than the fines migration.

2.8 Osmotic Pressure

The osmotic pressure is resulting from the formation of a salinity gradient between the connate water and the low salinity brine. Due to the salinity gradient, osmotic pressure will be present to induce molecular diffusion between the two phases. Molecular diffusion by osmosis occurs in systems in which a semipermeable membrane separates phases with different concentrations, allowing to pass only pure solvents, like water, and not solutes, for instance, salts [72]. As a result, the osmotic pressure gradient causes water molecules to move from low salinity to a high salinity area concentration. The water transport through the membrane will drop when the ionic concentration reaches the equilibrium.

For a given oil, water, and rock system, it is plausible that osmotic diffusion occurs with the oil intermediate layer acting as a semipermeable membrane, which transports water molecules from the low salinity to the high salinity side. [73] As a result, the water will expand and move the oil layer towards the low salinity phase, thus, improving oil recovery. The amount of water flow determines the osmotic diffusion degree through the semipermeable membrane. The water flow can be calculated using Fick's law given as,

$$J_A = -D_{AB} \left(\frac{\partial C_A}{\partial x} \right), \quad (14)$$

where J_A is the low salinity water flow $\frac{\partial C_A}{\partial x}$ is the concentration gradient between aqueous phases and D_{AB} is the diffusion constant, from low salinity, A , to high salinity, B [74].

The concentration gradient depends on the relative difference of the salt concentration between the two aqueous phases. The water flow through the membrane generally begins to cease as the concentration gradient decreases, by the dilution of the high salinity water. Fick's law also states that the amount of water flow is proportional to the diffusion constant, D_{AB} . This constant depends on temperature, which means that diffusion will increase by increasing temperature. The Stokes-Einstein equation gives the relation among the diffusion constant, temperature, and viscosity:

$$D_{AB} \propto \frac{T}{\mu}, \quad (15)$$

where T is the temperature and μ is the dynamic viscosity of the fluid. The diffusion constant can be measured for various oil compositions. The higher the viscosity, the lower will be the diffusion constant.

The osmotic pressure effect, caused by salinity differences, has also been used to improve oil production. In the oil reservoirs, the water molecules diffuse from the low to high salinity region in the porous medium. As explained above, water transport occurs because of the difference in chemical potential between the aqueous phases (Fig. 6 (a)). The water molecules diffuse to restore thermodynamic stability, thus achieving the equilibrium of chemical potential [40, 75, 76].

On the other hand, when an oil membrane separates the high and low salinity brines, osmosis can happen [77, 78]. The oil phase acts as a semipermeable filter, allowing only the water molecules passage from the low salinity side (Fig. 6(b)). The diffusion will take place until achieving the chemical potential equilibrium of the system.

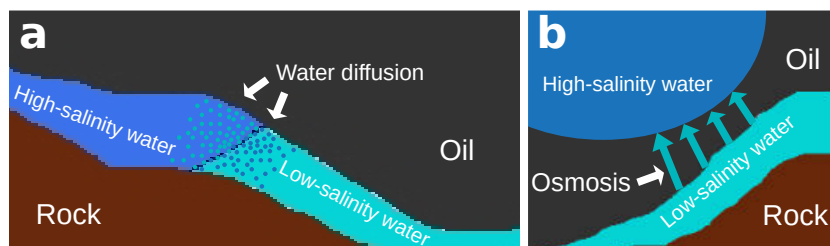


Fig. 6 Schematic representation of osmosis effects between two aqueous phases. (a) Due to the osmotic gradient, the water diffuses in both directions, low-salinity and high-salinity connate brine, until reaching the chemical potential gradient equilibrium. (b) due to the oil thin film acting as a separating membrane between the two aqueous phases, allowing only the passage of less saline water in the direction of the connate brine.

Experiments conducted by Ellila [73] showed that the water flow through the oil phase improved with increasing osmotic gradient. In thermodynamic terms, the diffusion process through the oil membrane is a result of the chemical potential difference between the two aqueous phases. For low salinity water, the chemical potential will be high, while for high salinity water, there will be a low chemical potential. When the chemical potentials difference is zero, the system is at equilibrium. In a porous medium, this is equivalent to the point at which the low salinity water completely dilutes the high salinity brine. The results showed an improvement in oil displacement with the low salinity water injection.

2.9 Summary of mechanisms

As discussed in the previous sections, there are many proposed mechanisms to explain the observed enhanced oil recovery (EOR) by low salinity water injection (LSWI). However, the connection among those mechanisms as well as which one can be interpreted as a cause or effect is not clear. Thus, Figure 7 summarizes the main mechanisms which are responsible for the enhanced oil recovery with low salinity water injection, showing the connections among them and which one could be seen as cause or consequence of each other. Mostly, it suggests that wettability alteration plays a crucial role in the EOR process, as have been pointed out by many authors in both experimental and computational studies.

This review shows that the mechanisms which can explain this enhancing are connected, being at the same time cause and consequence of the interfacial phenomena. Also, wettability alteration seems to be the main consequence of most mechanisms, such as changes in the electrical double layer, ionic exchange, and pH alteration. The pH change mechanism is based on the *in situ* surfactants formation, which could lead to an increase in the interfacial tensions of the oil/rock interfaces, facilitating its drag through the injected solution. On the other hand, the pH increase is mainly due to the ionic exchanges and the dissolution of the rock, releasing Ca^{2+} to the medium and generating an excess of hydroxides (OH^-) in the solution.

The difference in the ionic concentration and composition between the injected solution and the formation water lead to the multi-component ionic exchanges and the salting-in effect. The reduction of the salt concentration (salting-in effect), is

responsible for the electric double layer expansion, with that a thin water film can be formed between the carbonate rock and the adsorbed oil, reducing the oil/rock interaction, favoring the release of particles from the surface. In addition to increasing the available rock surface, increasing its wettability by water, this mechanism allows the mobilization (or migration) of particles, usually clay or quartz, among others, inside the oil reservoir due to drag forces during the production. This phenomenon causes suspended particles in the fluid to pass through the reservoir's pores and eventually, to accumulate in the thinner regions of the channels, promoting the clogging of pores that causes the fluid to travel through uncharted channels, enhancing the oil recovery.

Salinity concentration gradients induce osmotic pressure. In the considered systems, there are two aqueous phases with different salt concentrations (connate water and the injected low salinity water), in which both phases are separated by oil, which constitutes the semipermeable membrane. The gradient of the formed osmotic pressure will induce the molecular transport of water from the low salinity regions to the ones with higher solutes concentration. As a result, the oil will be displaced to regions with lower salt concentration. However, there is no clear consensus about what are the dominant mechanisms, although there is an idea that wettability change is necessary to release the oil from rock surfaces.

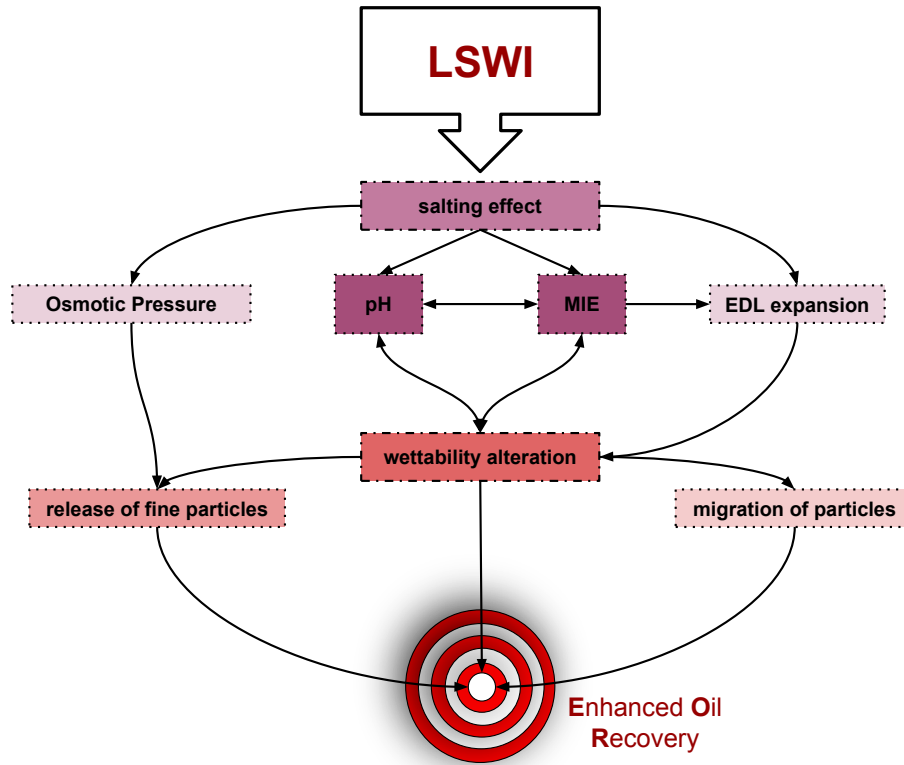


Fig. 7 We show the relation between the different mechanisms, as explained in this work. Our review suggests that the low salinity water injection has the decreasing of salts concentration as a direct consequence. This concentration reduction is called salting in effect, and it can affect the pH , start the ionic exchanges, and expand the EDL. All these effects are responsible by wettability alteration, which can lead to the release and migration of particles. Osmotic pressure is affected by the salting-in effect, and it also leads to the release of fine particles. The combining of all effects enhances oil recovery.

3 Computational Simulations

There is a vast bibliography of experimental and computational approaches in the area of petrophysics which aim to understand the EOR mechanisms via LSWI and their relevance in improving and increasing the oil recovery. Computational simulations or the so-called *in silico* studies, usually have good accuracy with feasible cost and time, allowing the control of parameters. In this way, it may be possible to disentangle variables, which experimentally, it could be challenging. Hereupon, it is possible to maximize results and improve the exploration of mechanisms.

Figure 8 shows the computational simulations methodologies which can be used over small size and time scales, according to the system's behavior. In this way, initially, we have the electronic structure level based on quantum mechanics, applied to fundamental system blocks such as molecules and surfaces.

Ab initio calculations follow the idea that any physical property of a system could be obtained by solving the Schrödinger equation for all the atoms/electrons

which constitute the system. Mainly, the *ab initio* technique we focus on this review is the density functional theory (DFT), which solves the Schrödinger equation as a function of the electronic density [79–81]. Unfortunately, it is computationally costly for thousands of atoms, so a set of approximations which could make these calculations viable were proposed. Each set of approximations defines a ‘level of theory,’ which can be appropriate or not for a given system depending on the kind of accuracy one wants to obtain.

In this approach, the solvent effects such as brine, oil, or water, can be described with continuum models [82]. These continuum models allow higher time and size scales on the simulations since they are not as computationally expensive as treating explicitly at electronic scale, all the solvent’s atoms.

The interactions at atomic scale among oil, brine, and the minerals can be simulated using classical molecular dynamics calculations [83], being possible to deal with larger systems (size scale) and phenomena which require longer simulation time (time scale). Finally, when one wants to simulate at the pore level (mesoscopic scale), the lattice Boltzmann method [84] can be used. In this manner, those simulations can be used to provide input data for further macroscopic reservoir scale simulators, such as the chemical equilibrium and kinetic constants, activation energies, chemical activities, ionic strength and reaction order, among others [26].

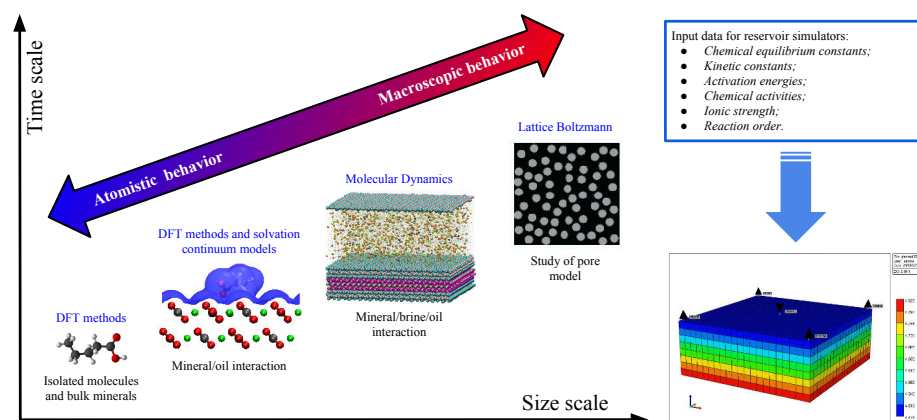


Fig. 8 Multi-scale computational methodologies that can be used to simulate the EOR processes via LSWI and, in the end, provide the required input data for reservoir simulators (represented with a snapshot taken from a GEM simulation). The size (time) scale is increasing from left (bottom) to the right (up). The methods for each scale are presented according to the system’s behavior, from atomistic to macroscopic.

Although computational simulations can model the system at various levels and scales, as shown in 8, we focus our review on methodologies for submicron scale systems. To explain electronic interactions, one needs to employ quantum mechanics based methodologies. For events occurring between the nanoscale and the microscale, when the electronic interactions can be approximated, molecular dynamics calculations based on classical mechanics are used. Both quantum and classical methodologies are classified as molecular modeling. In the next section,

we have selected some relevant references that use molecular modeling as an alternative way of exploring the mechanisms that have been listed here.

3.1 Molecular Modeling

Some chemical reactions and physical processes are inherent to the enhanced oil recovery processes, which in turn are dependent on the interaction mechanisms among the system components. Chemical constants such as reaction constants, equilibrium constant, partition coefficient, activity coefficient, and physical quantities such as contact angle, interfacial tensions, among others, are dependent on the thermodynamic conditions. It is possible to access such thermodynamic properties through molecular modeling, determining the fundamental properties and enabling the application in practical problems. Thus, allowing a bridge between fundamental science and problems relevant to the oil industry [9,85–89].

Molecular dynamics simulations are useful tools for investigating systems with up to hundreds of thousands of atoms, and simulation times up to microseconds. However, the limitation of classical models lies in the inability to predict purely electronic phenomena, such as the formation and breaking of chemical bonds, which require *ab initio* calculations. However, the quantum approach has a higher computational cost; therefore, it is applied to smaller systems and time scales [90].

Therefore, combinations of computational methodologies have been used to study the surface and interface properties between rock/oil/brine (water) system components [23,87,91–93]. Thus, we have collected some references that use molecular modeling to elucidate some of the mechanisms and effects listed in the previous section, focusing on carbonate-based systems. We divided the studies into two parts: *i*) electronic, based on *ab initio* calculations, and *ii*) atomistic, based on classical molecular dynamics.

3.1.1 *Ab initio* methodologies

From an electronic point of view, changes in wettability could be quantified by the oil components adsorption and desorption onto surface models. *Ab initio* calculations based on density functional theory (DFT) have been used to study the adsorption and desorption of hydrocarbons; also, the role of solvation and brine's composition can be taken into account [85]. Rigo *et al.* [92] studied the hexane and benzene adsorption on calcite and dolomite surfaces. Their results suggested that *Ca* sites were the most energetically favorable for hydrocarbon adsorption on both minerals. Sánchez and Miranda studied solvation effects in similar systems [23], considering both implicit and explicit solvation models. For implicit solvation, they have observed substantial changes in the adsorption energy, due to the increase of the hydrocarbon-surface hydrogen bond, whereas for explicit solvation (represented as a water monolayer) a minor energy variation was observed.

Bevilaqua *et al.* [94] performed an *ab initio* study on the adsorption of hydrocarbon molecules such as benzene and hexane on calcite surface, using DFT with Solid State Nuclear Magnetic Resonance (SS-NMR) calculations. The NMR technique results introduced an additional spectral dimension which provided further information regarding the nature of the molecules adsorbed on the calcite surface [94]. Also, the high sensitivity of the technique made it useful for probing

the interactions of the organic molecules and the mineral surface, allowing for the distinction of the molecule adsorbed over a given surface site, with implications for enhanced oil recovery from reservoirs.

Ataman *et al.* [95] carried out an extensive study of the adsorption of organic molecules on calcite's surface, considering different sizes and functional groups: nonpolar molecules as benzene, ethane and carbon dioxide, oxygen-containing polar molecules as water, alcohols, aldehydes, among others. It was also investigated the difference in behavior which resulted from the attachment of a hydrogen atom, ($-H$) or methyl ($-CH_3$), ethyl ($-C_2H_5$), or phenyl ($-C_6H_5$) side groups. The main results pointed out that the nonpolar molecules, benzene, and ethane, adsorbed completely, as a result of dispersion. The carbon dioxide adsorbed as a result of a combination of dispersion and electrostatic contributions. The authors suggest that side groups affected the adsorption energies in two ways: (*i*) by either changing the electronic structure of the functional group, which changes the strength of electrostatic interactions and hydrogen bonding, or (*ii*) by modifying the strength of the dispersion interaction between the adsorbed molecule and the surface. It was observed that the adsorption energy increased with the side group size as a result of a higher dispersion interaction: carboxylic acids adsorbed more strongly than alcohols and water, which adsorbed more strongly than aldehydes. Water was found to be the only exception: the H atom attached to the hydroxyl functional group, hydrogen bonding to a surface oxygen atom, which resulted in relatively high adsorption.

Escamilla-Roa *et al.* [91] used DFT calculations to perform adsorption studies of water and organic molecules on dolomite surfaces. The authors found that water adsorbed more strongly (16.27 kcal/mol) than the investigated organic molecules ($3.14 - 5.00 \text{ kcal/mol}$), due to the lack of H bonding and electrostatic interactions that are present in the adsorption of water.

Alvim *et al.* [96] explored the adsorption of asphaltenes on calcite (10.4) surface by first-principles calculations. The authors considered water and toluene as implicit solvents; their calculations indicated that there is a steric hindering for the effective interaction of the asphaltene aromatic region on the calcite surface. Moreover, the lowest unoccupied molecular orbital (LUMO) localized in the aromatic region of the asphaltene favors the adsorption on the calcite surface by $\pi - \pi$ stacking [96].

Aiming to understand the wettability alteration on carbonates, Stipp *et al.* evaluated the influence of divalent cations exchanges on the calcite surface by estimating the contact angle, using a DFT approach. They reported that Sr, Ba, and Pb made the surface more hydrophobic, and when Mg and transition metals (Mn, Fe, Co, Ni, Cu, and Zn) were incorporated into the system, the calcite has become more hydrophilic [97].

In another work, Stipp *et al.* also showed the relation between ions exchange and wettability alteration. They described that when Mg^{2+} replaced 10% of surface Ca^{2+} , the contact angle between calcite and water changed dramatically, from 40° to 70° converting a hydrophobic into a hydrophilic surface. The energy involved in those replacements also was investigated by DFT calculations [98].

Regarding osmotic pressure simulations using DFT calculations, Yang *et al.* [99] used a mixed-method which combined DFT and molecular dynamics, applying it to represent some fluid systems [100,101]. In particular, in the cited work, the authors studied a semi-permeable membrane. They chose the parameters in

order to meet the equality in the chemical potential of pure hard-core Yukawa (HCY) fluid model between DFT and molecular simulations. It was observed that the osmotic pressure decreased as the permeable particle size increased, while it increased with the bulk density.

Gillespie and co-workers [102] used DFT calculations of fluids, to examine the effect of finite ion size in nanofluidic devices [103]. The authors showed that osmosis could be qualitatively different for the same nanofluidic device, influenced by the size of the ions in the fluid. Interestingly, Yang et al. [104] also calculated the osmotic pressure using DFT, by modeling of the reference fluid density/weighted correlation approximation (RFD/WCA). The DFT calculations of the forces and the ion exchange were in agreements with Monte Carlo simulations and consistent with experimental observations.

3.1.2 Classical molecular dynamics

The calcite/oil/brine interfaces were studied by Sedghi and co-workers [105] through molecular dynamics calculations using two different calcite models (*i.e.*, two force fields) and different water models. The first calcite force field was developed by Raiteri *et al.* [87], and was fitted to reproduce the thermodynamical properties of the calcite surface, rather than the mechanical properties. The authors used the Buckingham functional form for the van der Waals interactions among all the atoms, having a repulsion term which is softer than that of Lennard-Jones potential, being better suited to simulate the ionic structure of calcite. Sedghi considered (*i*) the “flexible model” based on the Raiteri model and (*ii*) the “rigid model” as a combination of the Lennard-Jones parameters from the CHARMM36 and the partial charges from Raiteri, with constrained atomic positions for the calcium and carbon atoms, by applying a harmonic force with elastic constant equal to $1.0 \times 10^6 \text{ kJ/mol nm}^2$.

Freeman *et al.* pointed out the need for a force field capable of accurately simulating structures as diverse as surfaces (mineral), organic molecules (oil) and solvent (water), especially the terms representing the interactions among these three groups, the so-called cross-term potentials. In order to obtain these cross-terms, the Lorentz-Berthelot combination rules [106], however, point to overestimated energy values at the interfaces [107]. Freeman’s approach to the parameters are listed below: (*i*) using the method of Schröder *et al.* [108], which readjusting the existing potentials for mineral structures so that they are consistent with the Coulomb interactions between atoms of the mineral and the other atoms; (*ii*) when (*i*) is not possible, the potentials are generated to fit the mineral structures; (*iii*) potentials that do not include strong Coulomb interactions are chosen based on their presence within the organic or mineral force field following the modified combination rules; (*iv*) if no combination rule can be used because of the lack of the required mineral-mineral potential, the mineral-organic potential used is a duplicate of the appropriate organic potential. The validity of the Freeman methodology was tested by comparisons between results obtained by DFT and classical calculations, using other potentials. Results suggested compatible values of adsorption energies for organic molecules/water and the calcite surfaces obtained using DFT and the proposed potential. The procedure was accurate to generate cross-term potentials without the need for a systematic adjustment and can be transferred to a range of different minerals.

Mikami *et al.* [109] investigated the interfacial behavior of asphaltene molecules at the oil-water interface using classical molecular dynamics simulations. Results have shown a preferable distribution of asphaltene in the oil phase or the interface, depending on the organic molecules (heptane or toluene) present in the oil phase. Also, it was observed that the interfacial tension (IFT) of the system containing small amounts of asphaltene is close to a pure heptane-water system. Although the IFT of the system containing large amounts of asphaltene molecules was reduced.

Kunieda *et al.* [110] investigated a water/oil model interface by classical molecular dynamics (MD) simulations (revised version of the CHARMM27 force field to model the hydrocarbons [111], SPC-E [112,113] for water), using a so-called light-oil model. This work suggested that the aromatics accumulation in the interface is driven by the interfacial tension difference between aromatics-water and the other potential hydrocarbon-water interface combinations. According to them, when aromatic molecules accumulated at the interface, the configuration entropy decreased, and the Gibbs free energy increased within the interface system. Also, it was observed that the accumulation of aromatics caused a decrease in interfacial tension, therefore decreasing the potential energy of the total system.

Hakin *et al.* investigated the structure and behavior of the organic compounds isopropanol, methanol, pentanol, and octanoic acid at the calcite-organic interface, employing classical molecular dynamics simulations. The authors investigated the surface ordering under ambient conditions and the thickness of the adsorbed layer based on molecule length and density. Their results showed that the compounds have bounded to the surface, with the hydrophilic functional groups, through strong interactions, standing perpendicular to the surface with the aliphatic tail pointing away. The smaller molecules (methanol and isopropanol) formed layers with a similar total thickness (20 to 21 Å). The pentanol and octanoic acid formed ordered adsorbed layers with a 6.7 Å thickness for pentanol and 10.5 Å for the octanoic acid. The force field used in this study was a hybrid of the AMBER [114,115] and Pavese [116] potential functions, with the cross-terms proposed by Freeman *et al.* [107].

Sedghi and co-workers [105], performed a systematic molecular dynamics study, on the confinement effects of oil, water, and brine in calcite nanopores. In order to create a realistic model of crude oil, they used mixtures of various polar and nonpolar oil molecules. The authors obtained the interfacial tension (IFT) and contact angle (CA) for different oil compositions, brine salinities, temperatures, and pressures. MD simulations were also used to obtain the “threshold capillary pressure (TCP)” (pressure difference needed for a fluid to displace another fluid in a pore with a given geometry and wettability). The usual method to obtain the TCP of macropores is a model developed by Mayer-Stowe-Princen (MSP model). The MSP model is based on the minimization of the Helmholtz free energy, and the results from MD calculations obtained in Sedghi’s work were compared with values obtained using the MSP model. Their results indicated that the addition of polar components in the crude oil decreased the IFT while increasing the CA, although calcite remained strongly water-wet. On the other hand, increasing the salinity did not affect the contact angle, but increased the interfacial tension. It was observed that MD simulations produced higher threshold capillary pressures compared to the MSP results. This discrepancy was attributed to the adsorption of water layers on the pore walls and the strong ordering of water molecules in the adsorbed layers.

Molecular dynamics is also utilized to obtain the osmotic pressure in solutions as reported by the work of Murad and in other authors [117–119]. Murad *et al.* created a method to understand these phenomena at the molecular level. Roux *et al.* improved the methodology to compute the osmotic pressure directly from molecular dynamics. Simple models using Na^+ , K^+ , and Cl^- were tested to reproduce the experimental osmotic pressure at high salt concentration. The CHARMM parameters for these ions were able to reproduce the experimental osmotic pressure up to 1 M precision. Carrillo *et al.*, applied a hybrid Monte Carlo/molecular dynamics simulation method to model salt ion exchange between the salt reservoir and polyelectrolyte solution of chains with the degree of polymerization $N = 300$. This simulation technique showed that there is a dependence of the solution osmotic pressure on the polymer and salt concentrations. This approach has a great potential to underlying the mechanisms of LSWI-EOR, and it can be successfully implemented to study the osmotic pressure effect since it has already been exploited in other systems with salt solutions.

The dissolution free energy of the surface ions in an aqueous medium can be calculated by performing a series of MD calculations [120,121]. In this context, the dissolution/precipitation in carbonate rocks, adsorption energy calculations and the electric double layer structuring, can use this approach, as the ions are displaced out of the surface and their forces calculated as a function of the distance to the surface [122,123,93,124,121,43]. One obtains the free energy by integrating the potential of mean force (PMF) over the relaxed ionic distances from the surface. The reverse-path (adsorption) can also be evaluated. [122,123].

According to the second law of thermodynamics, one can choose any path (physically possible or not) between the initial and the final state, and the only condition is that this process should be reversible. The accuracy of thermodynamic integration depends on sampling and can be determined by histograms. Thus, the Gibbs free energy along the reaction coordinate can be calculated by the weighted histogram analysis method (WHAM) from quadratic restricted dynamics or umbrella sampling [125,126]. The WHAM acts on the principle that, from a discrete number of states, a histogram can be created with discrete constraints that provide a relative probability of observing the states of interest, considering the constraints on any selection of the reaction path. From these probabilities, free energies and other observables can be calculated.

The PMF mentioned here has been explored as a method for the free energy calculation of an asphaltene molecule aggregation on calcite surface by Boek *et al.* [127]. In this preliminary study, the adsorption free energy was obtained as -110 kJ.mol^{-1} . A similar methodology was performed by Kobayashi *et al.* [123] to obtain the Stern layer profile of EDL and to describe the wettability alteration. They studied the stability of model acidic oil molecules adsorbed on muscovite surfaces in aqueous solution. Their findings suggested that the presence of Ca^{2+} on the muscovite surface enhanced the adsorption of acidic compounds analyzed and that the ion effect was intensified when the acid was protonated. In another work, the authors explored the hydration structure in the Stern layer on the muscovite surface [122]. The results obtained from eight different cations (Na^+ , K^+ , Rb^+ , Cs^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+}) indicated the presence of three different possible adsorption sites (inner-sphere 1 and 2, and outer-sphere) in line with previous experimental results [122,123]. The relative density of water molecules, as a function of distance, was utilized to explore the hydration struc-

ture of other systems by Liu *et al.*. In their work, molecular dynamics simulations were performed to understand the electric double-layer capacitance of graphene electrodes in mono-valent aqueous electrolytes [128].

3.2 The connection between molecular modeling and reservoir simulations

As previously discussed, it is essential to understand the physical-chemical fundamentals of the LSWI. In this task, to develop a model that captures the LSWI mechanisms, the geochemical reactions which take place also becomes fundamental. A desirable feature is the proposed model to be efficient in the modeling of hybrid LSWI processes, allowing the coupling with the multi-phase flow equations in a robust compositional simulator. Reservoir simulators allow us to investigate the geochemical processes that occur during the low salinity water injection process for enhanced oil extraction [26]. These tools are necessary for a better understanding of the processes that co-occur and are very complex.

If on the one hand, the reservoir simulators include relevant information about the processes which are occurring during the LSWI process; on the other hand, the input data for those simulations should be provided. One possible way of providing this input data is by molecular simulations, as we discussed in the previous section. The input data that need to be provided to perform simulations using reservoir simulators are, in general, the kinetic constants of the chemical reactions which are taking place, the values of their activation barriers, the temperature, among others. In order to obtain such data, it is necessary first to understand the mechanisms that may be involved in the EOR process, as discussed in previous sections. Obtaining such input data by molecular simulations can significantly reduce uncertainties by increasing the predictive power of reservoir simulators and facilitating the optimization and understanding of the processes involved in the injection of low salinity fluids.

As we have also discussed in previous sections, the Gibbs free energy of the chemical processes involved in EOR by LSWI can be determined by both molecular and *Ab Initio* methodologies. From the Gibbs free energy, we can obtain, among other properties, the kinetic constants of the respective chemical reactions. Thus, we will briefly discuss in the next subsections how the molecular modeling for the study of the mechanisms involved in enhanced oil recovery through the injection of low salinity water, previously presented in this review, can be coupled to reservoir simulators.

3.2.1 Physical-chemical parameters

The intra-aqueous reactions and the dissolution/precipitation reactions of the reservoir minerals are taken into account in reservoir simulators. Considering a chemical reaction identified by β with kinetic constant k_0 at a reference temperature T_0 , its kinetic constant k at any temperature T for a given simulation is obtained by:

$$k_\beta = k_{0,\beta} \exp \left[-\frac{E_a}{RT} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] , \quad (16)$$

where E_a is the activation energy, and R is the universal gas constant. The reference values, as discussed in previous sections, can be obtained using the molecular modeling simulations that can be carried out considering the chemical reactions involved in the dissolution of the minerals as well as the ionic exchanges. The activation energy can be obtained by DFT calculations, for instance. In this case, the total energy of the molecules involved in a given chemical reaction will be extracted from these calculations.

The reactive processes between the aqueous phase and the reservoir minerals will lead to the dissolution or precipitation of the minerals, whenever the system is out of equilibrium. In this case, the dissolution/precipitation rate per unit bulk volume of the porous medium, r_β , is calculated by:

$$r_\beta = \hat{A}k_\beta \left[1 - \frac{Q_\beta}{K_{eq,\beta}} \right], \quad (17)$$

where β identifies the mineral, $\hat{A}$ is the area of the reactive surface per unit of bulk volume, k_β is the kinetic constant, $K_{eq,\beta}$ is the chemical equilibrium constant, and Q_β is the activity product of the reaction involving precipitation or dissolution of the mineral, defined by:

$$Q_\beta = \prod_{k=1}^n (a_k)^{\nu_{k\beta}}, \quad (18)$$

in which the product is done for all chemical species with n being the total number of species, a_k is the activity of those chemical species and $\nu_{k\beta}$ is the stoichiometric coefficient of each k species involved in the chemical reaction identified by β . If a chemical reaction is under equilibrium, *i.e.*, $Q_\beta = K_{eq,\beta}$, the dissolution/precipitation rate shown in Equation 17 will be null.

An important aspect that must be taken into account in reservoir simulators is the fact that the area of the mineral's reactive surface, $\hat{A}_\beta$, is changing since the rock/mineral is dissolving or receiving precipitated material. Nghiem *et al.* [129] have proposed a way to deal with this and adjust the area of the surface, as shown in the following equation:

$$\hat{A} = \hat{A}_0 \left(\frac{N_\beta}{N_{\beta 0}} \right), \quad (19)$$

where $\hat{A}_0$ is the initial reactive surface area (before the dissolution/precipitation process is started) and N is the initial number of mols of the mineral per block volume (the used grid), $N_{\beta 0}$, and after the dissolution/precipitation have occurred, N_β .

3.2.2 Ionic exchanges in reservoir simulators

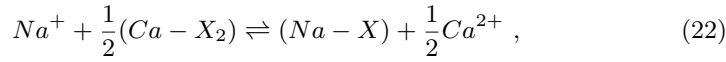
The multi-component ionic exchange mechanism, as discussed before, is one of the mechanisms which can explain the enhanced oil recovery observed by LSWI. The ionic exchanges between calcium, magnesium, and sodium can be studied utilizing the selectivity coefficients and are operational variables of the simulator. Those coefficients are obtained according to Gaines-Thomas work [130] and are represented by:

$$K'_{Na/Ca} = \frac{\zeta(Na - X) \{m(Ca^{2+})\}^{0.5}}{\{\zeta(Ca - X_2)\}^{0.5} m(Na^+)} \times \frac{\{\gamma(Ca^{2+})\}^{0.5}}{\gamma(Na^+)} , \quad (20)$$

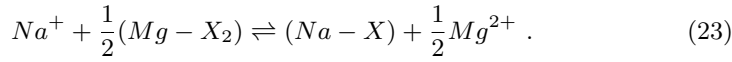
and

$$K'_{Na/Mg} = \frac{\zeta(Na - X) \{m(Mg^{2+})\}^{0.5}}{\{\zeta(Mg - X_2)\}^{0.5} m(Na^+)} \times \frac{\{\gamma(Mg^{2+})\}^{0.5}}{\gamma(Na^+)} , \quad (21)$$

where X represents the clay mineral of the rock under study (in these cases the considered reservoirs are the ones containing clay) and the equivalent fractions of each ion is given by $\zeta(Na - X)$, $\zeta(Ca - X_2)$ and $\zeta(Mg - X_2)$. In these expressions, m is the molarity, and γ is the activity coefficient of the respective ions. Thus, using these coefficients, we can simulate in the reservoir simulators the most common ionic exchange reactions which are occurring in the reservoir, given by:



and



3.3 Summary of the connection between molecular modeling and reservoir simulations

As discussed in this section, the reservoir simulators are essential to evaluate the chemical reactions and processes occurring during the LSWI. In the meantime, it is necessary to provide the input data for those simulators. Regarding the molecular modeling applied to EOR via LSWI, the equilibrium constant of chemical reactions as well as its kinetic constants can be directly obtained via molecular simulations and thus provide the required input data for reservoir simulators. In summary, the molecular simulations can play a crucial role in the petrophysics area, providing the required parameters for reservoir simulators, at the same time elucidating the EOR mechanisms behind the LSWI.

4 Conclusions

This review has shown that the proposed mechanisms underlying the EOR by low salinity water injection, as well as other mechanisms adjacent to them, are connected and can occur concomitantly. In this respect, molecular simulations can be a handy tool and a critical factor in helping to unravel and understand the mentioned mechanisms.

Through molecular simulations, we can explore each of these mechanisms separately and also explore their correlations. Thus, LSWI itself, identified as the salting-in/out effect, can be modeled by molecular dynamics simulations, by varying the concentration and composition of the injected brine.

The effects of the interactions in each interface, *i.e.*, brine-oil, brine-calcite, and calcite-oil, as well as the triple interface, can also be investigated. Mechanisms

which lead to wettability alteration can be explored with these simulations, using interfacial tension measurements.

Also, desorption and adsorption processes of organic molecules into mineral surfaces could be studied employing *ab initio* calculations. It could also be used to understand the ionic exchanges and mineral dissolution and growth. The DFT based free energy calculations could also be used to explore thermodynamical parameters of the ionic exchanges, to calculate the adsorption energy on calcite, and to predict wettability alterations. The implicit and explicit solvation on molecular modeling associated with ionic exchanges can elucidate the *pH* effect.

Besides the thermodynamic parameters, the kinetic values and the EDL profile can be explored by PMF on MD. The input data for further reservoir simulations using appropriated software, such as kinetic and equilibrium constants of the chemical reactions involved in the LSWI processes, can be provided by molecular and *ab initio* simulations.

Computational simulations are a promising alternative to guide, explore, and optimize future EOR processes. Those simulations can be effectively used to calculate the physical-chemical parameters of the oil reservoirs. From these parameters, we could understand the relation among the mentioned mechanisms, the reservoir conditions, and the environment composition. Finally, the optimum brine composition for the EOR process could be proposed. However, more precise and efficient molecular simulations are needed to improve our understanding of these factors and to address these challenges effectively.

5 Abbreviations

The following abbreviations are used in this manuscript:

BP: British petroleum

CA: Contact angle

CMC: Critical micellar concentration

DLVO: Derjaguin, Landau, Verwey, and Overbeek

EDL: Electrical double layer

EOR: Enhanced oil recovery

DFT: Density functional theory

IFT: Interfacial tension

IOR: Improved oil recovery

LSW: Low salinity water

LSWI: Low salinity water injection

MD: Molecular dynamics

MSP: Mayer-Stowe-Prince

pH: Potential of hydrogen

PMF: Potential of mean force

TDS: Total dissolved solids

VDW: Van der Waals

WHAM: Weighted histogram analysis method

Acknowledgements The authors acknowledge the financial support provided by PETROBRAS.

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