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Review of low salinity waterflooding mechanisms: Wettability alteration and its impact on oil recovery

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ABSTRACT

Low salinity waterflooding (LSW) has attracted attention of numerous researchers as a promising technique for enhanced oil recovery, yet its application is still limited because of incomplete mechanisms and unreliable predictions. This paper summarizes relevant mechanisms for predicting responses of LSW. Since the wettability alteration is generally regarded as the most important one among possible LSW mechanisms, two aspects of predicting LSW responses are reviewed: prediction of wettability alteration and effects of wettability alteration on oil recovery. For the first aspect, the importance of more quantitative prediction of wettability alteration is addressed because experimental results have suggested that the optimal wettability may not be water-wet as imagined. From the relation between wettability and interaction forces in the oil-brine-rock systems, mechanisms of wettability alteration are reviewed along with quantitative calculation. The extended Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, which has been often used to calculate the contact angles, is not available to obtain an accurate contact angle anymore. For the second aspect, an overview of the optimal wettability for oil recovery is given with relevant pore-scale fluid mechanisms. Though experiments found the maximum oil recovery from weakly water-wet or neutral wet rocks, the results were not elaborate enough to reveal the relation between the contact angle and the oil recovery. The pore-scale simulation is a powerful tool to investigate such relations but so far it still needs further developments on scaling and validations with experimental data.

1. Introduction

The significance of crude oil to the modern industry cannot be exaggerated enough. Traditional oil recovery techniques leave around 50% of oil trapped in reservoirs, thus are not sufficient to meet the increasing demands [1]. Low salinity waterflooding (LSW), also known as the modified salinity waterflooding or smart waterflooding, is a technique to improve oil recovery by modifying the ionic compositions or concentrations of injected brines during waterflooding. Compared with other enhanced oil recovery techniques like thermal injection [2] and chemical injection [3], LSW has the advantage of being low-cost and eco-friendly. Though the earliest studies on LSW date back to the 1960s [4,5], it was not until a couple of LSW experiments were done in the 1990s that the potential of this technique was widely noticed [6–12], and it has attracted the attention of numerous researchers since. The ultimate goal of LSW studies is to obtain the relation between input and output of LSW, especially the relation between the injected brine compositions and the oil recovery, so that the responses of LSW can be predicted and the optimal brine compositions can be found. Thus understanding the mechanisms of LSW is the key to this challenge.

However, despite increasing interests in this field over the past decades, the industrial application of LSW is limited because the mechanisms of LSW are still under debate and the responses of LSW cannot be predicted reliably. Amongst various proposed mechanisms of LSW, wettability alteration is now generally accepted as the major one, and mechanisms of wettability alteration in sub-pore scale have been extensively studied [13–18]. However, there are two difficulties if one wants to utilize the current works on LSW mechanisms to predict oil recovery. First, more quantitative instead of qualitative predictions of wettability alteration are needed, especially when it has been suggested by many studies that the optimal wettability for best oil recovery is not corresponding to the strongest water-wet rocks [10,12,19–22]. Second, how the wettability alteration impacts the oil recovery is still not clear, especially during the coupled process of wettability alteration and multiphase displacement. These two aspects have not been addressed enough in some previous LSW studies and review papers, which just supposed that altering the rock to more water-wet conditions was better for oil recovery.

This work aims to provide a review of mechanisms of LSW to shed light on the prediction of oil recovery from injected brine compositions,

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with special attention paid to the prediction of wettability alteration and the impact of wettability alteration on multiphase displacement. The following parts are organized as follows: First, an overview of possible LSW mechanisms is given in Section 2, where it is discussed why wettability alteration is the most important mechanism. The mechanisms of wettability alteration are reviewed in detail in Section 3, along with an introduction and evaluation of the extended DLVO (Derjaguin-Landau-Verwey-Overbeek) theory used to predict wettability alteration in LSW. After that, the impact of wettability alteration on oil recovery and relevant pore-scale mechanisms are reviewed in Section 4. Conclusion and perspectives are presented in Section 5.

2. Overview of LSW mechanisms

This section introduces different mechanisms of LSW in literature, along with their experimental or numerical evidence. Note that in some papers, the mechanisms causing wettability alteration, including electrical double layer expansion, multicomponent ion exchange, change of interfacial tension and pH and so on, were classified as mechanisms of LSW. However in this work, we consider those as mechanisms of wettability alteration, which are introduced in Section 3, rather than direct mechanisms of LSW.

2.1. Wettability alteration

Wettability alteration of the oil-brine-rock (OBR) system is the most commonly accepted mechanism of LSW. Multiple mechanisms can contribute to wettability alteration during LSW, which will be discussed in detail in Section 3. A simple but rather common belief is that altering rocks to be more water-wet helps to release more oil from rock surface and to enhance the water imbibition, so that the oil recovery is improved. However, some core flooding experiments showed that the optimal wettability for best oil recovery was weakly water-wet [10,12,19–22], indicating that the relation between wettability and oil recovery could be more complicated than expected [23]. Effects of wettability alteration on multiphase flow and oil recovery will be explored in Section 4.

There are abundant experimental evidence supporting this mechanism, which includes two aspects: the evidence showing that wettability is altered by LSW and the evidence showing that LSW-induced wettability alteration can improve oil recovery. For the first aspect, researchers measured the contact angle of oil droplet in various OBR systems to examine the effect of different salinity, and generally found that low salinity brine altered the system to more water-wet, on both sandstone and carbonate surfaces [13,24–34]. To obtain evidence for the second aspect, one common approach was to conduct laboratory coreflooding tests and measure the wettability before and after LSW [24,28,35]. Results showed that there was a strong correlation between wettability alteration and oil recovery, but by this approach it seems unclear whether wettability alteration actually leads to better recovery or they were both outcomes of LSW. Another approach was to prepare core samples of different wetting conditions by aging with oil, and do LSW with the same brine, so that the effect of wettability on oil recovery could be directly shown [6,12,20,22]. In addition, simulations can also easily use wettability as an input parameter to examine its impact [36]. Both experiment and simulation results suggested that oil recovery was highly influenced by wettability. Therefore, it is concluded that wettability alteration is one dominant mechanism of LSW.

2.2. Osmosis

Osmosis was first proposed and explained as one of LSW mechanisms by Sandengen and Arntzen in 2013 [37]. The functioning of this mechanism requires the existence of high salinity connate water, and the system needs to be oil-wet so that connate water is separated by oil films. During LSW, oil acts as a semipermeable membrane between high

salinity and low salinity water, allowing only water to be transported through the membrane. The high salinity water phase then expands, relocating oil and possibly improving oil recovery by mobilizing otherwise stagnant oil. Some works also proposed that the rock matrix could act as the membrane [38,39], but it should depend on the rock type.

The water transport and oil mobilization that agreed with the osmosis hypothesis in oil-wet systems were observed by flow visualization in 2D micromodels and core samples [37,40,41]. However, whether the osmotic phenomena could lead to better recovery lacks solid evidence. Pollen and Berg attempted to evaluate the contribution of osmosis to oil recovery, but failed to find a strong correlation [42]. Besides the limitation of requiring high salinity water and oil-wet systems, the osmosis mechanism also cannot explain the sensitivity to ion types in some LSW experiments. Therefore, it might not be a major LSW mechanism.

2.3. Viscoelastic liquid interface

Another mechanism related to the liquid-liquid interaction is the viscoelasticity of the oil-water interface [43]. Low ionic strength makes the oil-water interface more viscoelastic regardless of ion types, and increased interfacial viscoelasticity helps oil recovery in two ways. First, snap-off in water-wet cores is suppressed and therefore the amount of trapped oil during LSW is decreased. In addition, trapped oil droplet tends to be larger when snap-off occurs, possibly blocking pore throat and opening new flow pathways.

While it was confirmed that the viscoelasticity of the oil-water interface was generally bigger when the brine salinity was low [44], the trend of viscoelasticity against salinity may not be monotonic [45]. More importantly, the contribution of interfacial viscoelasticity to oil recovery lacks validation, as it is difficult to exclude the effects of wettability alteration during LSW. Alvarado et al. did coreflooding experiments and argued that the improved oil recovery was due to the viscoelastic interface because the effects of wettability alteration was diminished by the mild temperature of 40 °C [46]. This conclusion is questionable because wettability alteration did occur even at ambient temperature and had an impact on oil recovery [13,35]. Besides, snap-off is mostly characteristic in water-wet OBR systems, therefore in other wetting conditions this mechanism is in principle not important.

2.4. Fines migration

One of the earliest proposed mechanisms of LSW is the migration of fines [8]. Clay fines are generally negatively charged in brine due to surface interactions or adsorption of ions. Similar to the mechanism of electric double layer expansion introduced in Section 3.3.1, as the salinity decreases, the electrostatic repulsion between fines increases, leading to their detachment and migration. Those migrated fines could block pore throat and divert flow to otherwise inaccessible paths, increasing microscopic sweep efficiency and oil recovery [8].

However, this mechanism has been challenged by many experimental studies. First of all, very few or no clay fines were produced in experiments, and evident permeability reduction was generally not observed [18,23,47–49]. There was neither an evident correlation found between fines migration and improved oil recovery: better recovery could be achieved without fines migration and fines migration did not necessarily lead to better recovery [50–53]. Therefore, it is now generally agreed that fines migration is not a major LSW mechanism.

Note that instead of changing the core structure, fines migration may contribute to oil recovery as a wettability alteration mechanism by releasing oil-wet fines from the rock surface and making the system more water-wet. Although this mechanism is also quite controversial as fines are not commonly observed in the effluent, it is discussed as a mechanism of wettability alteration in the following sections nevertheless.

2.5. Discussion

Among the four LSW mechanisms introduced, wettability alteration is regarded as the dominant and most important one for two reasons. Firstly, wettability alteration has been confirmed to occur and improve oil recovery by a plethora of studies in various OBR systems and different scales [54]. The other three mechanisms in theory have some limitations: osmosis requires the existence of high salinity water and oil-wet systems, interfacial viscoelasticity suppresses snap-off mostly in water-wet systems, and fines migration certainly cannot happen if clay fines are not present. Experimental works on those three mechanisms are relatively much fewer, have not been able to give substantial evidence on their contributions to oil recovery, and some even got contradictory results. Secondly, the other mechanisms do not deny the significant contribution of wettability alteration. In fact, one major difficulty to validate the other mechanisms is to exclude the effects of wettability alteration. It is likely that more than one mechanism cooperates during LSW, but wettability alteration is definitely present and has considerable impact. Therefore, the rest of this paper focuses on wettability alteration as an LSW mechanism.

3. Wettability alteration: mechanisms and prediction

This section aims to not only review possible wettability alteration mechanisms during LSW, but also show a clear physical picture of how each mechanism works and how it can be quantitatively predicted. First, some fundamentals of wettability are introduced, including the derivation of Young-Dupre equation from an energy perspective and the relation between interfacial energy and interfacial forces in OBR systems. Then an overview of interfacial interactions in an OBR system is given, with emphasis on the electrical double layer interaction, and the extended DLVO theory used to predict the wettability alteration based on interfacial forces is introduced. After that, possible mechanisms of wettability alterations are reviewed. Finally, the reliability of wettability prediction by the extended DLVO theory is evaluated.

3.1. Fundamentals of wettability

Wettability is the ability of a liquid to maintain contact with a solid surface in a three-phase system. The most common description of wettability is the contact angle, defined as the angle between the tangent to the liquid-fluid interface and the tangent to the solid surface, as Fig. 1 shows. When the solid wall is not smooth, the value of the apparent contact angle depends on the measuring scale. The wetting property of a three-phase system is determined by the interfacial tension or interfacial energy which equals the free energy needed to create a unit area of the interface, and by the relation between contact angle and interfacial tension which can be derived strictly from an energy perspective as in Marmum's work [55].

As illustrated in Fig. 1, the system consists of a solid surface, a liquid droplet and surrounding fluid, which will be referred to as solid, liquid and fluid phase after. Given the profile of the liquid droplet and the solid wall and the interfacial tension between phases, the total free

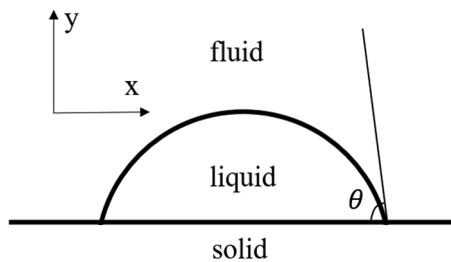


Fig. 1. Diagram of a typical three-phase system, with the contact angle of liquid indicated.

energy of the interfaces can be expressed as:

$$\int_0^X [\sigma_{lf} \sqrt{1 + (y')^2} + (\sigma_{sl} - \sigma_{sf}) r(x)] x^k dx, \quad (1)$$

where x is the distance from the center of the droplet, $x = X$ the position of the contact line, σ_{lf} , σ_{sl} and σ_{sf} respectively the liquid-fluid, the solid-liquid and the solid-fluid interfacial tension, y the profile of the droplet, $r(x)$ the local ratio between the real solid surface area and its horizontal projection, and k indicates whether the drop is two-dimensional ($k = 0$) or axisymmetric ($k = 1$) [56]. The system subjects to the constant liquid volume constraint:

$$2\pi^k \int_0^X x^k (y - y_s) dx = V, \quad (2)$$

where y_s is the profile of the solid wall, and V is the volume of the droplet. The equilibrium of the system requires minimization of Eq. (1) under the constraint of Eq. (2). For details please refer to Marmum [55]. Solving the problem gives the general expression for the apparent contact angle:

$$\cos \theta = \frac{r(X)(\sigma_{sf} - \sigma_{sl})}{\sigma_{lf} (1 - y'_s \tan \theta)}. \quad (3)$$

For a smooth, homogeneous, rigid and insoluble solid and constant interfacial tension, Eq. (3) is reduced to the famous Young-Dupre equation:

$$\cos \theta = \frac{\sigma_{sf} - \sigma_{sl}}{\sigma_{lf}}. \quad (4)$$

This expression has also ignored the molecular interaction at the contact line, often captured by the concept of the line tension. When the line tension is considered, the equation changes:

$$\cos \theta = \frac{\sigma_{sf} - \sigma_{sl} - \tau/R}{\sigma_{lf}}, \quad (5)$$

where τ is the line tension and R is the contact line curvature.

It can be seen from the derivation that the Young-Dupre equation gives the thermodynamic equilibrium contact angle, with the assumptions that the solid is smooth, homogeneous, rigid and insoluble, the interfacial tensions are constant and the line tension is ignored. The equation also shows that the larger the interfacial tension is, the smaller the corresponding interface area tends to be, which agrees with the minimum free energy constraint.

The relation between interfacial tension and interfacial interaction in such system is quite straightforward, as the increase of free energy equals the work done by external forces in a reversible process of bringing two surfaces from infinity to contact:

$$\sigma = \frac{1}{2} \int_{y_0}^{\infty} P(y) dy, \quad (6)$$

where $P(y)$ is the force per unit area between the two surfaces at a separation of y and y_0 is the distance at contact because of finite molecule sizes. The integration is divided by two because bringing two surfaces of unit area into contact decreases the interfacial area by two unit areas. Based on Eqs. (4) and (6), it can be inferred that an attractive force between the liquid and solid will decrease the interfacial tension and decrease the contact angle, and a repulsive force has an opposite effect. In a common OBR system, it means that an attractive force between oil and rock will make the system more oil-wet, and a repulsive force will make it more water-wet. However, in OBR systems there is often a water film between the oil droplet and the solid wall due to the equilibrium of van der Waals, electrostatic and structural force, therefore traditional Young-Dupre equation no longer applies. Hirasaki viewed the water film as a single interface and obtained the modified expression of contact angle of water by thermodynamic analysis [57]:

$$\cos \theta - 1 = \frac{1}{\sigma_{ob}} \left[\int_{D_0}^{\infty} \Pi(D) dD + D_0 \Pi(D_0) \right], \quad (7)$$

where $\Pi(D)$ is the total pressure between the oil-brine interface and brine-rock interface at a separation of D , also called the disjoining pressure, and D_0 is the water film thickness at equilibrium. Note that, similar to the original Young-Dupre equation, it is also assumed that the solid is ideal, the interfacial tensions are constant and the line tension is negligible. Another important difference is that in Eq. (7), the contact angle is of the surrounding fluid instead of the liquid drop, which adds up to 180°.

Eq. (7) is the most important equation in this section. It shows that the wetting property of an OBR system is determined by the oil-brine interfacial tension, the disjoining pressure across the water film, and the equilibrium water film thickness. Therefore, a wettability alteration mechanism must change one or more of these three parameters.

3.2. Interfacial interactions in OBR systems and the extended DLVO theory

Eq. (7) shows that the wettability of a typical OBR system is controlled by the oil-brine interfacial tension, the pressure across the water film and the equilibrium water thickness. All of the three factors are determined by relevant interfacial interactions. Therefore, this subsection gives an overview of existing interfacial interactions in OBR systems, and introduces theoretical calculations for each interaction. After that, the extended DLVO theory often used to predict wettability alteration is introduced.

3.2.1. Electrical double layer interaction

Multiple wettability mechanisms are related to the electrical double layer (EDL) at the oil-brine and the brine-rock interface, and EDL interaction energy is one major contribution to the interfacial tension. Often the surface of solid and oil will be charged when in contact with water, due to the ionization and dissociation of surface groups on solid or oil surface or due to adsorption of ions from the solution. The net charge on the surface will attract ions of the opposite polarity in the solution, forming another layer close to the surface equally but oppositely charged to balance the charged surface layer. Those two layers are called the electrical double layer [58]. The characteristic thickness of EDL is generally very small, down to micrometer, leaving the bulk region in the solution electrical neutral. However, when two EDLs are so close to each other that they overlap, as in the OBR system where a thin water film separates oil and rock, the charge distribution will be altered and the total free energy will be changed, leading to a pressure between the oil-brine and the brine-rock interface. The rock and the oil surfaces both are usually negatively charged in brine thus a repulsive force presents due to EDLs overlapping. For a detailed introduction on the calculation of EDL structure and interaction in OBR systems, please refer to Tian and Wang [16]. Here we only demonstrate the final governing equations.

The electric potential distribution in the overlapped EDLs can be solved by the Poisson-Boltzmann equation, a combination of Poisson's equation and the Boltzmann distribution of ions in the solution:

$$\nabla^2 \phi = -\frac{eN_A}{\epsilon_0 \epsilon_r} \sum_i z_i c_i^\infty \exp\left(\frac{-z_i e \phi}{k_b T}\right), \quad (8)$$

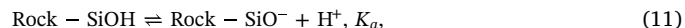
where ϕ is the electric potential, e the elementary charge, N_A the Avogadro constant, ϵ_0 the vacuum permittivity, ϵ_r the relative permittivity of solution, z_i the valence of the i -th ion in the solution, c_i^∞ the bulk concentration of the i -th ion, k_b the Boltzmann constant and T the temperature. Because the electric potential varies most along the direction perpendicular to the interface, it is often preferred to use the dimensionless one-dimension Poisson-Boltzmann equation:

$$\frac{d^2 \psi}{dY^2} = -\frac{1}{2} \sum_i z_i C_i^\infty \exp(-z_i \psi), \quad (9)$$

where $C_i^\infty = c_i^\infty / I$, $\psi = e\phi / k_b T$ and $Y = y / \kappa$. The characteristic quantities are the ionic strength $I = \sum_i z_i^2 c_i / 2$ and Debye parameter $\kappa = \sqrt{2e^2 N_A I / \epsilon_0 \epsilon_r k_b T}$. Solving Eq. (9) requires specifying the potential or charge at the two boundaries, namely the oil-brine and the brine-rock interface in an OBR system. If the boundary potential and charge are both not given, the electrostatic equilibrium condition and the surface charging model can each provide two additional equations on the relation between boundary surface and charge. The electrostatic equilibrium condition is basically Gauss's law:

$$\sigma_1 = -\epsilon_0 \epsilon_r \left. \frac{d\phi}{dy} \right|_{y=y_1}, \quad \sigma_2 = \epsilon_0 \epsilon_r \left. \frac{d\phi}{dy} \right|_{y=y_2}. \quad (10)$$

The index 1 and 2 indicates value at two boundaries. The surface charging model depends on the specific charging mechanism at the interface, and can vary a lot in different OBR systems. For example, the rock surface can be charged by the dissolution of silanol groups [59]:



where K_a is the equilibrium constant for this reaction. Given the density of silanol groups on the rock surface, the chemical equilibrium of Eq. (11) and the conservation of mass together provide another relation between boundary charge and potential. Therefore, Eq. (9), (10) and the surface charging model combined can give the electrical potential distribution and the charge distribution in the EDL. It is worth noting that in an actual OBR system there can be much more reactions or complexation happening than Eq. (11) on the rock surface, and the charging mechanism for oil is no less complicated. Many surface complexation models in OBR systems have been developed and modified for the oil-brine and the brine-rock interface [60–65] and it is still a debated topic, especially the surface charging mechanism for the interface between water and nonpolar oil [66–72].

Solving the potential or charge distribution of EDL is only the first step to obtain the EDL interaction across the water film. For details, readers are recommended to refer to Tian and Wang [16]. The idea is to first calculate the work done during an imaginary reversible process of forming two interacting EDLs, which equals the free energy of the EDLs, then the EDL interaction force can be obtained by the variation of total free energy against the separation. For example, imagine two interacting EDLs are formed by repeating the following process called surface charging: an infinitesimal amount of ions is absorbed to the interfaces, then the equilibrium charge distribution is quickly restored by the rearrangement of ions in brine. Suppose that at a certain time of the charging process, the charges on the two interfaces are respectively σ_1' and σ_2' , the potential differences obtained by the electrostatic equilibrium condition Eq. (10) and Poisson-Boltzmann equation between the bulk and two interfaces are ϕ_1^e and ϕ_2^e respectively, and the potential differences obtained by the surface charging model between the bulk and two interfaces are respectively ϕ_1^c and ϕ_2^c , then the total free energy needed to form the EDLs can be written as [16]:

$$F(h) = \int_{(0,0)}^{(\sigma_1(h), \sigma_2(h))} (\phi_1^e(\sigma_1', \sigma_2', h) - \phi_1^c(\sigma_1')) d\sigma_1' + (\phi_2^e(\sigma_1', \sigma_2', h) - \phi_2^c(\sigma_2')) d\sigma_2', \quad (12)$$

where h is the separation of the EDLs and σ_1, σ_2 are the actual charge at the interfaces, namely the charge at the end of the imaginary charging process. Therefore, the increase of energy due to two EDLs interacting can be calculated by $F(h) - F(\infty)$, and the interaction force equals the variation of the interaction energy.

However, the complexity of the surface charging model makes solving for ϕ_1^c and ϕ_2^c very hard. In practice, the surface charging model is often replaced by the constant charge or constant potential boundaries to solve for the interaction energy of EDLs. For a 1:1 electrolyte solution at low surface potential, the EDL interaction under the constant

potential boundary has a simple analytic solution [73]:

$$\Pi_{EDL}(D) = nk_b T \left(\frac{2\phi_1\phi_2 \cosh(\kappa D) - \phi_1^2 - \phi_2^2}{(\sinh(\kappa D))^2} \right), \quad (13)$$

where $\Pi_{EDL}(D)$ is the pressure across the water film due to EDL interaction and n is the bulk ion concentration. This is one of the most used forms of EDL interaction, though its limitation has long been pointed out [16,74]. The Debye parameter κ can be easily calculated once the salinity is given, but the boundary electric potential has to be solved by the electrostatic equilibrium condition and the surface charging model.

3.2.2. Van der Waals force

Van der Waals force is a universal force existing between all molecules. It consists of three parts: the dispersion force, which has a quantum mechanical origin, the induction force and the orientation force, which are both electrostatic force. In spite of different physical origins, the total van der Waals interaction energy between two molecules can be expressed by one unified equation [58]:

$$w = -\frac{C}{r^6}, \quad (14)$$

where r is the separation between molecules and C is a coefficient depending on molecule types. In a typical OBR system, we are most interested in the interfacial force across the water film. Assuming the oil-brine and the brine-rock interfaces are flat, the van der Waals force per unit area between oil and rock in the medium of water can be calculated by integration of Eq. (14) [58]:

$$P = -\frac{A}{6\pi D^3}, \quad (15)$$

where D is the separation between the two interfaces, and A is a coefficient called the Hamaker constant. However, the Van der Waal force is in principle non-additive, which makes the integration problematic. Lifshitz solved the problem by considering van der Waals force from a continuous point of view [75,76]. The Lifshitz theory showed that Eq. (15) could still hold with the expression of the Hamaker constant modified, assuming the absorption frequencies of oil, water and rock are identical and ignoring extra terms in the full Lifshitz theory:

$$A = \frac{3}{4}k_b T \left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \right) \left(\frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3} \right) + \frac{3h\nu_e}{8\sqrt{2}} \frac{(n_1^2 - n_3^2)(n_2^2 - n_3^2)}{(n_1^2 + n_3^2)^{1/2}(n_2^2 + n_3^2)^{1/2} \{ (n_1^2 + n_3^2)^{1/2} + (n_2^2 + n_3^2)^{1/2} \}}, \quad (16)$$

where ε_i and n_i ($i = 1, 2, 3$) are the relative permittivity and refractive index of oil, rock and water, h the Planck constant, and ν_e the main electronic absorption frequency. The first term on the right side of Eq. (16) is the electrostatic part, or the zero frequency contribution, and the second term is the dispersion part, or the non-zero frequency contribution.

The dispersion contribution of van der Waals force between macroscopic bodies has the retardation effect due to the finite speed of light. At small or relatively large separations, there is no retardation effect, but at medium separations, also called the transition region, retardation will make the interactive force weaker than given by Eq. (15). Although it is captured by the full Lifshitz theory, with the simplified Eq. (16), Eq. (15) needs to be modified to include this effect. The most used empirical form considering the retardation effect was proposed by Gregory [77]:

$$\Pi_{VDW}(D) = -\frac{A(15.96(D/\lambda) + 2)}{12\pi D^3(1 + 5.32(D/\lambda))^2}, \quad (17)$$

where $\Pi_{VDW}(D)$ is the van der Waals pressure across the water film, A the non-retarded Hamaker constant and λ a characteristic length which is often chosen to be 100 nm. Eq. (17) has been proven to agree well with experiments in the transition region for non-polar molecules. It is worth noting that only the dispersion part has retardation effect.

Therefore, the Hamaker constant in Eq. (17) should really be only the second term of Eq. (16), and the induction and orientation part should still be calculated by Eq. (15) and the first term of Eq. (16).

Another modification needed on the van der Waals force in OBR systems is related to the screening effect of brine. Free ions in the brine will be polarized by electrostatic fields, effectively screening the electrostatic part of van der Waals force. Without retardation, the electrolyte screening effect can be expressed as [78]:

$$A = A_{v=0} e^{-2\kappa D} (1 + 2\kappa D + 2\kappa^2 D^2) + A_{v>0}, \quad (18)$$

where κ is the Debye parameter, $A_{v=0}$ and $A_{v>0}$ respectively the first and second term on the right side of Eq. (16). Eqs. (15)–(18) combined give the total van der Waals force across the water film in an OBR system, with the retardation effect and electrolyte screening effect considered.

3.2.3. Structural force

The structural force is an interaction between two surfaces or particles in a medium when the separation is very small. It is often called the solvation force when the medium is a solvent and the hydration force if the solvent is water. Depending on the property of the force, it is also called hydrophobic or hydrophilic force. The full nature of the structural force is still under debate [58,79–81]. There are two main explanations for its origin. The first explanation states that the structure of the solvent molecules is changed when compressed, leading to a force between the approaching surfaces [82–84]. Another explanation considers the structural force to be a purely steric repulsion due to the finite size of molecules [58].

The manifestation of structural force varies in different systems. It can be oscillatory with distance, or roughly exponential monotonic repulsive, or even attractive [85–87]. In OBR systems, experiments of structural force mostly showed a monotonic repulsive trend, and Hirasaki proposed an empirical form [88]:

$$\Pi_{STR}(D) = A_s \exp\left(-\frac{D}{D_s}\right), \quad (19)$$

where $\Pi_{STR}(D)$ is the steric repulsive pressure across the water film, A_s and D_s are both empirical parameters, chosen to be 1.5×10^{10} Pa and 0.05 nm by Hirasaki [88].

3.2.4. Hydrogen bond

Hydrogen bond is an interaction between hydrogen atoms covalently bonded to electronegative atoms and nearby electronegative atoms. It is essentially an electrostatic force between electric dipoles, but much stronger due to the small radius of hydrogen [89]. In OBR systems, the hydrogen bond between surface groups of oil and rock may add to the attraction and lower the interfacial tension. There is no one simple and accurate expression of hydrogen bond interaction energy, but it can be approximated as a charge-dipole interaction [58]:

$$w(r) = -Q_H u \cos \theta / 4\pi \varepsilon_0 \varepsilon_r r^2, \quad (20)$$

where $w(r)$ is the interaction energy of one hydrogen bond of length r , Q_H the magnitude of the charge, u the dipole moment, θ the angle between the direction of the dipole and the line joining the charge and the center of the dipole. However, the charge Q_H is not the full charge of one hydrogen ion. It is affected by the atoms forming the hydrogen bond and is generally not known in advance. Therefore, it is difficult to apply in a real OBR system.

3.2.5. Chemical interaction

The surface groups of oil and rock can form chemical bonds either directly or with high valence cation as a bridge, as Fig. 2 shows. Note that if no ligand forms in the cation bridge case, the interaction is purely electrostatic and included in the EDL interaction. Such chemical complex would lower the interaction energy and make the system more

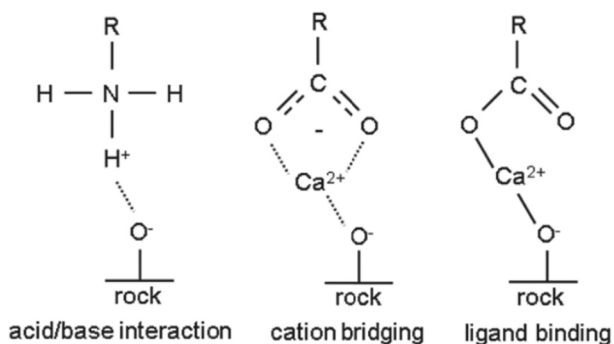


Fig. 2. Schematics for some chemical interactions. Reproduced with permission from Tian and Wang, *Surface Science Reports*; published by Elsevier, 2017.

oil-wet. The magnitude of chemical interaction generally has to be obtained by experiments and does not have simple expression.

3.2.6. Extended DLVO theory on wettability alteration

Eq. (7) shows that wettability alteration in OBR systems happens when the aforementioned interfacial interactions are changed. Therefore, tracking the interfacial forces is necessary for studying wettability alteration. The most commonly adopted theory is the extended DLVO theory, which adds structural force into the original DLVO theory that includes EDL interaction and van der Waals force [90,91]. The most commonly adopted expressions of EDL interaction, van der Waals force and structural force are Eqs. (13) (17) (19). The total disjoining pressure across the water film is then:

$$\begin{aligned} \Pi(D) &= \Pi_{EDL}(D) + \Pi_{VDW}(D) + \Pi_{STR}(D) \\ &= nk_b T \left(\frac{2\phi_1 \phi_2 \cosh(\kappa D) - \phi_1^2 - \phi_2^2}{(\sinh(\kappa D))^2} \right) - \frac{A(15.96(D/\lambda) + 2)}{12\pi D^3(1 + 5.32(D/\lambda))^2} + A_s \exp\left(-\frac{D}{D_s}\right). \end{aligned} \tag{21}$$

Fig. 3 illustrates the general trend of the three contributions of disjoining pressure against film thickness. For the total disjoining pressure, there are three types of possible trends, as Fig. 4 shows. The equilibrium film thickness is given by:

$$\Pi(D_0) = P_c, \tag{22}$$

where P_c is the capillary pressure between oil and water. For the first type of trend of disjoining pressure, water film can be stable over a wide range of thicknesses according to the capillary pressure. For the second type and for capillary pressure lower than Π_0 , there is a stable film thickness at small separation and a meta-stable film thickness at larger

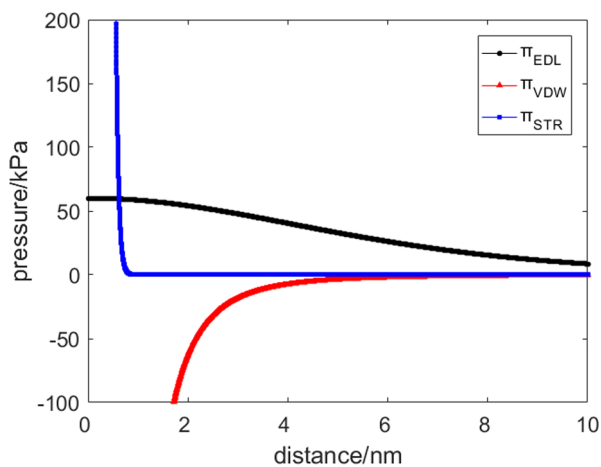


Fig. 3. The general trend of the three contributions of disjoining pressure: the electric double layer interaction, the van der Waals force and the structural force.

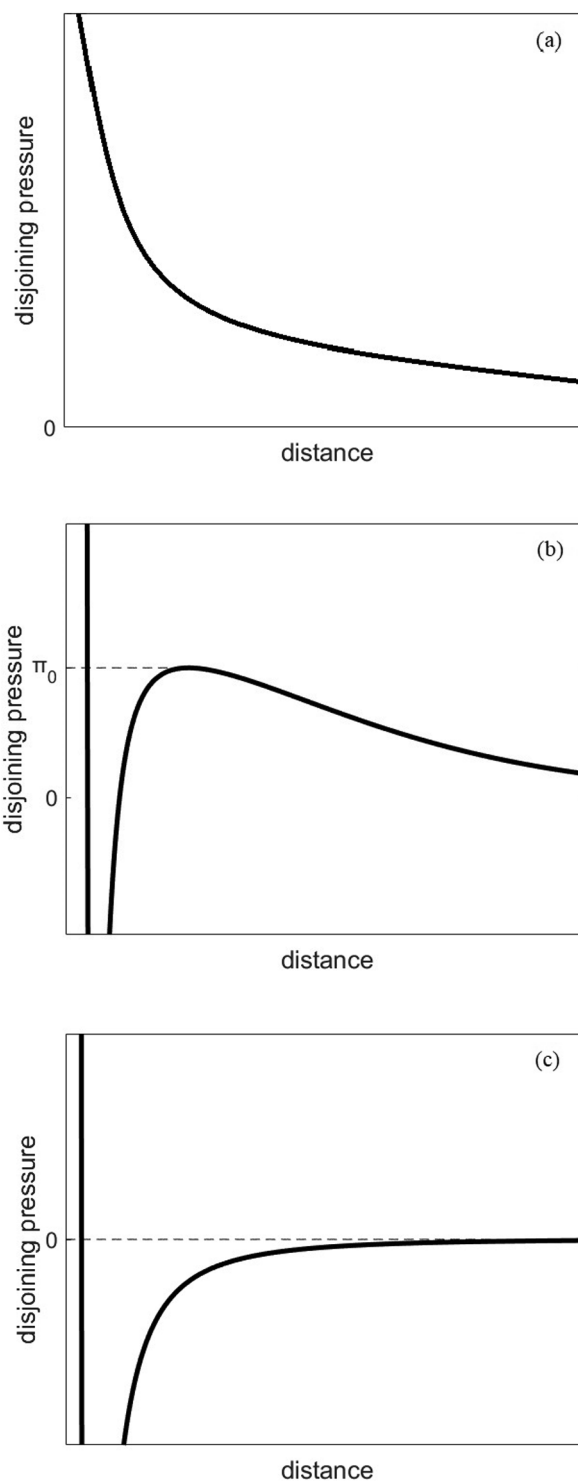


Fig. 4. A diagram of three typical trends of disjoining pressure against distance. (a) disjoining pressure increases as distance decreases over all range; (b) with distance decreasing, disjoining pressure first increases to a finite positive value, then decreases due to van der Waals attraction, and finally increases due to steric repulsion; (c) the trend is the same as in (b), but the disjoining pressure is always negative until steric repulsion dominates at small separation, therefore only one equilibrium film thickness is possible.

separation. For capillary pressure higher than Π_0 , only one small stable film thickness is possible, which is also the case for the third type for any capillary pressure. In a typical OBR system, given the oil-brine interfacial tension and the disjoining pressure curve, the contact angle can be calculated by Eq. (7).

3.3. Proposed mechanisms

From the previous sections, it is clear that the wettability of an OBR system is determined by the interfacial interactions, especially interactions across the thin water film between oil and rock. A wettability alteration mechanism is therefore essentially a mechanism affecting those interactions. In this sub-section, the currently proposed mechanisms of wettability alteration are reviewed, along with their experimental evidence and how each mechanism can be considered quantitatively, if possible.

3.3.1. EDL expansion

EDL expansion was proposed as a main mechanism of wettability alteration by Ligthelm et al. [92]. As introduced in Section 3.2.1, the rock and oil surfaces both are usually negatively charged in brine thus a repulsive force presents across the thin water film due to EDLs overlapping. The characteristic length of EDL is proportional to the inverse of the Debye parameter κ . From the definition of κ , it can be seen that during LSW, the EDL thickness is increased due to low ionic concentration. Therefore, the EDLs overlap more and the repulsive force across the water film in Eq. (13) is generally enhanced, making the system more water-wet.

The contribution of EDL interaction to wettability alteration can be verified by measuring the zeta potential and the change of contact angle in brines of different salinity, and multiple experiments have found correlation between the change of zeta potential and contact angle [93–95]. Nasralla and Nasr-El-Din did an experiment to prove that EDL expansion was the primary mechanism of wettability alteration [96]. Their idea was to adjust the pH of the low salinity brine so that the change of EDL interaction due to EDL expansion was suppressed. Results showed that suppressing the EDL expansion made the system more oil-wet, therefore it was concluded that EDL expansion was a dominant mechanism. This conclusion could be challengeable because adjusting the pH might also affect other mechanisms and the wettability change could be due to other affected mechanisms.

Under constant potential assumption, the effect of EDL expansion can be easily calculated by Eq. (13). It should be noted that EDL expansion is just one of the mechanisms that affects EDL interaction. The EDL interaction is determined by the Poisson-Boltzmann equation, the electrostatic equilibrium condition and the surface complexation model. Therefore, in addition to changing the bulk concentration of salt ions which affects the Poisson-Boltzmann equation, any change related to the chemical equilibrium in the surface complexation model will have an impact on EDL interaction as well, for example changes of pH. Besides, lowering the salinity does not necessarily enhance the EDL repulsion. As Eq. (13) shows, when the salinity is decreased, n , κ and strictly speaking both ϕ_1 and ϕ_2 will change and affect the interaction. Not to mention that there is also the possibility that oil and rock surfaces are oppositely charged, in which case the interaction will be attractive. Therefore, the mechanism of EDL expansion is just a special case of the change of EDL interaction energy brought about by the change of salt ion concentration.

3.3.2. Multicomponent ion exchange

The mechanism of multicomponent ion exchange (MIE) states that high valence ions contribute to the formation of ion bindings and ligand bindings between oil and rock by functioning as a bridge, and lowering the concentration of those ions during LSW breaks such bindings, making the attraction between oil and rock weaker and the system more water-wet [47]. It can be speculated that MIE will have no effect when there are no high valence ions in the original brine. This mechanism also explains the big impact of certain ions like sulfate in carbonate, often referred to as potential determining ions. Sulfate tends to precipitate with calcium in carbonates, suppressing the formation of calcium bonds between oil and rock and altering wettability.

Lager et al did an experiment to verify this mechanism [47]. They

first did LSW for a core sample and proved that oil recovery could be improved by LSW for this sample. Then the core was washed by NaCl solution until there were no high valence ions. They aged the core, did LSW again with NaCl solution, and no additional oil recovery was found, which implied that EDL expansion without MIE did not contribute to better oil recovery. This conclusion seems to be in contradiction with some other studies that considered EDL expansion a more dominant mechanism than MIE [92,97]. Besides, whether oil recovery is improved or not is not a good evidence to verify a wettability alteration mechanism, because altering the OBR system to more water-wet condition is not necessarily better for oil recovery, as will be discussed in Section 4.

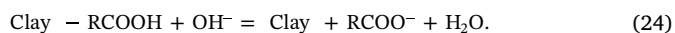
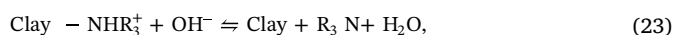
Calculation of the wettability alteration caused by MIE is currently lacking. MIE alters wettability mainly by breaking the chemical bonds between oil and rock, and quantitatively calculation requires knowing not only the magnitude of the interaction energy of each bond, but also how many of those bonds or bridges are broken. For a given OBR system, it is possible to obtain such information by experiments, but whether it applies to other OBR systems is another issue.

3.3.3. Change of bulk oil-brine interfacial tension

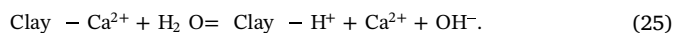
Mechanisms affecting the overlapped EDLs across the thin water film also affect the EDL at bulk oil-brine interface away from the thin water film, therefore the free energy of it changes, and the interfacial tension changes. It can be directly seen from Eq. (7) that a smaller oil-brine interfacial tension leads to more water-wet condition. It agrees with intuitive notion as well: the bulk oil-brine interface tends to expand if its tension decreases, therefore the contact angle of oil is increased. While the decrease of bulk oil-brine interfacial tension was confirmed by experiments, the variation of it was often not large enough to cause notable wettability change [74,94,98,99]. Therefore, the decrease of the bulk oil-brine interfacial tension is often viewed as only a supplementary mechanism.

3.3.4. Change of pH

pH has a big impact on the equilibrium of surface interactions, like the adsorption of organic components to rock surface [100]:



Increasing pH will desorb both acidic and basic components, altering wettability to more water-wet by breaking bonds between oil and rock and modifying the surface charging property [101]. The effects of pH change on the charging properties can be calculated via the corresponding surface complexation model. During LSW, the increase of pH is generally due to the replacement of hydrogen ion with adsorbed high valence ion on the rock surface [100]:



This is quite similar to MIE and some suggested that this type of pH increase was only a phenomenon of MIE [16].

It was also proposed that in addition to wettability alteration, an increase of pH can enhance saponification and emulsification like in alkaline flooding [102]. However, multiple works showed that the typical pH during LSW was not high enough to have such effect [3,47]. In addition, it was suggested that this mechanism lost impact in field scale [103]. Therefore, the change of pH is not a well-recognized LSW mechanism.

3.3.5. Fines migration

Fines migration has been mentioned as an LSW mechanism in Section 2.4 by blocking pore throat and diverting flow. However, it was also proposed that fines migration could make the system more water-wet by releasing the oil-wet fines on the surface, changing the surface properties and thus changing relevant interaction.

This mechanism is highly debatable similar to the reason fines migration as an LSW mechanism is debatable. Fines are not commonly observed in the effluent and no strong correlation is found between wettability alteration and fines releasing [47–49]. Quantitative calculation is difficult as it requires the knowledge of the properties of original and exposed fines.

3.3.6. Salting-in and mineral dissolution

Salting-in effect means organic components on the rock surface become more soluble when the ion concentration is lowered during LSW, consequently altering the surface to more water-wet by changing the surface charging properties and thus EDL interaction [18]. However, the salting-in mechanism is debatable and the evidence substantiating this mechanism is rather lacking [101,104]. A related mechanism is the mineral dissolution during LSW, which stresses the role of ions released by dissolution [53,105]. This mechanism is challenged a lot as well [13,106,107]. In addition, both mechanisms are not expected to take effect at field scale because the brine will become equilibrated as it proceeds [108,109].

3.3.7. Formation of micro dispersion

The formation of micro brine dispersion in the oil phase near the oil-brine interface during LSW was observed by direct flow visualization and it was proposed that those micro dispersions could contribute to wettability alteration [110]. The polar components in crude oil that are originally in the oil-brine interface will be attracted to those dispersions in bulk oil, thus the charging property of the oil-brine interface is changed and the bonds formed by those polar components are broken, therefore the system becomes more water-wet due to enhanced EDL repulsion and weakened bonding between oil and rock.

There were also experimental results supporting this mechanism [110–113]. Sohrabi et al. did coreflooding experiments where the oil was depleted of micro dispersions and thus polar components, and compared the resulting recovery with coreflooding tests of original crude oil [112]. They found that when micro dispersions were removed, oil recovery by spontaneous imbibition and force imbibition were both decreased, therefore it proved that the formation of micro dispersion altered wettability to more water-wet condition and was good for oil recovery. However, they did not directly measure the change of contact angle. Calculation of wettability alteration by this mechanism is also lacking and it requires some understanding of formation process of micro dispersions.

Besides wettability alteration, it was also suggested that the formation of micro dispersion could directly impact the multiphase flow in a way similar to osmosis [112]. This is considered a special case of osmosis here and not as another LSW mechanism.

3.4. Evaluation of wettability prediction by the extended DLVO theory

Predicting the magnitude of wettability alteration is key to the prediction of LSW responses, and it also helps identify and verify different mechanisms. In Section 3.2.6, the extended DLVO theory to quantitatively calculate wettability alteration has been introduced. However, there has not been good agreement between the experimental measured contact angle and the theoretical predicted value [74,114–116]. This indicates that the current theory does not capture the full physical picture of an OBR system. First, some interfacial forces are not considered by the extended DLVO theory, especially chemical interactions, which are the key to the MIE mechanism. Second, the model for forces in the extended DLVO theory may be oversimplified. For example, Eq. (17) for the retarded van der Waals force is often adopted in the integration of Eq. (7) over all range, but it only works best at transition region, and the electrolyte screening effect Eq. (18) is usually ignored, which might lead to considerable error as some studies suggested [74]. Third, there are several empirical parameters in the extended DLVO theory that were commonly used by most studies, but

the same parameter may not apply to all OBR systems, especially parameters for the structural force, which were rarely verified against experiment results.

Therefore, this section aims to evaluate the reliability of wettability prediction by the extended DLVO theory, by examining the impact of some aforementioned limitations of the current model. The contact angle of water is calculated with or without considerations of certain factors, to see their influence on the wettability prediction results. If not otherwise specified, Eqs. (7) and (21) are adopted to calculate the contact angle, and parameters are chosen as follows: $\sigma_{ob} = 0.025 \text{ N/m}$, $n = 0.01 \text{ M}$, $T = 298 \text{ K}$, $\phi_1 = \phi_2 = -0.04 \text{ V}$, $A = 1 \times 10^{-20} \text{ J}$, $\lambda = 100 \text{ nm}$, $A_s = 1.5 \times 10^{10} \text{ Pa}$, $D_s = 0.05 \text{ nm}$, $P_c = 20 \text{ kPa}$.

3.4.1. EDL interaction: Stern layer and the plane of origin

It has been introduced that EDL consists of a charged surface layer and another layer of counter-ions in the solution attracted by the charged layer. It was suggested that ions in the solution could be further divided into a Stern layer and a diffuse layer. The Stern layer is so close to the charged surface that ions in this layer are strongly bonded and immobile, while ions in the diffuse layer can move freely. Because ions in the Stern layer does not follow the Boltzmann distribution, the governing equations in Section 3.2.1 are actually for the diffuse layer and the boundary conditions should be applied at the shear plane where ions start to move freely instead of the surface. This makes the separation for EDL interaction different from that for van der Waals force, which was neglected in lots of works.

Since the structural force in OBR systems is mostly viewed as steric repulsion, we assume the separations for the EDL interaction and the structural force are identical, and then the total disjoining pressure considering the Stern layer can be expressed as:

$$\begin{aligned} \Pi(D) &= \Pi_{VDW}(D) + \Pi_{EDL}(D) + \Pi_{STR}(D) \\ &= nk_b T \left(\frac{2\phi_1\phi_2 \cosh(\kappa D) - \phi_1^2 - \phi_2^2}{(\sinh(\kappa D))^2} \right) - \frac{A(15.96(D/\lambda + 2\delta/\lambda) + 2)}{12\pi D^3(1 + 5.32(D/\lambda + 2\delta/\lambda))^2} \\ &\quad + A_s \exp\left(-\frac{D}{D_s}\right), \end{aligned} \quad (26)$$

where the separation for van der Waals force is increased by 2δ . The shift in separation usually is around a few angstroms [58] and we choose $\delta = 0, 1, 2 \text{ \AA}$ to see its impact. The contact angle is calculated for two charging cases: $\phi_1 = \phi_2 = -0.04 \text{ V}$ and $\phi_1 = -\phi_2 = -0.04 \text{ V}$. Results are plotted on a contact angle against film thickness curve with the stable equilibrium film thickness D_1 and meta-stable one D_{eq} indicated by markers in Fig. 5.

It can be seen that shifting the origin of plane for different interactions for just a few angstroms can have a non-negligible influence on the contact angle predicted, causing deviation as much as 10° especially in water-wet condition. Considering that in most studies utilizing DLVO theory to calculate wettability alteration, the largest variation in contact angle was generally less than 20° , the deviation brought about by the Stern layer could totally invalidate the prediction.

3.4.2. EDL interaction: boundary conditions

The exact EDL interaction should be solved by Eq. (9) (10) (12) with the full surface charging model considered, the corresponding boundary condition called the charge regulation boundary. For simplicity, most works assumed the boundary potential remained constant as two interfaces approached, and used Eq. (13) for EDL interaction. There are other kinds of simplified boundary conditions like constant charge boundary, and some studies suggested that the combination of constant charge and constant potential boundaries worked the best [74].

However, Tian and Wang [16] compared the charge regulation boundary and the simplified boundary, and concluded that at small separations all simplified boundary would lead to unphysical results. They calculated the EDL interaction energy for two typical OBR systems with charge regulation boundary and constant potential boundary, and

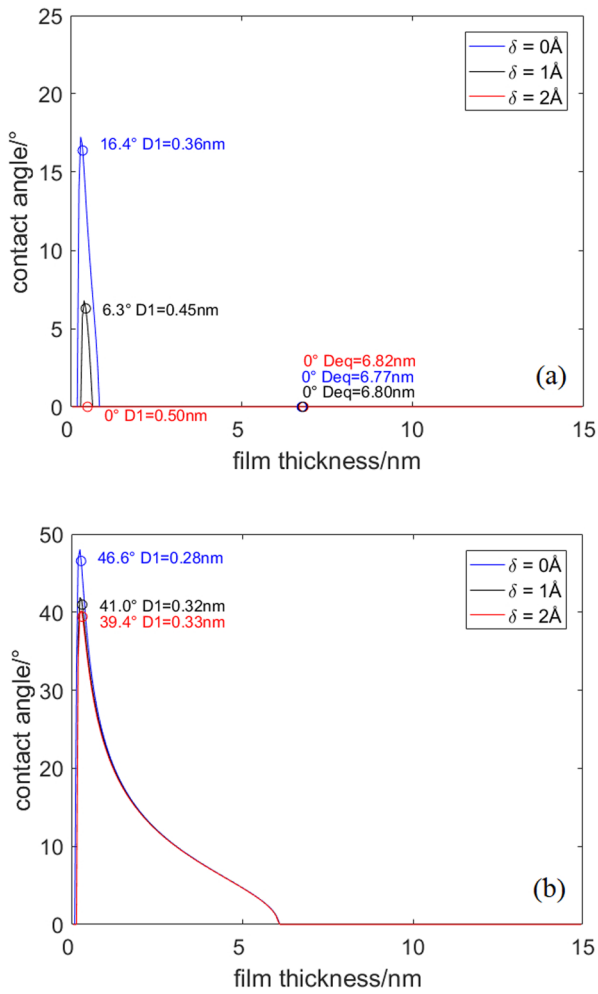


Fig. 5. The contact angle calculated by Eq. (7) given the film thickness, with the equilibrium value indicated by markers. (a) electric potential of both boundaries equals -0.04 V ; (b) potential at one boundary is changed to 0.04 V compared with (a).

found that constant potential boundary led to huge deviation once the water film thickness became less than $1/\kappa$. On the other hand, as long as the film thickness was not too thin, for instance larger than 4 times the inverse of Debye parameter, the constant potential boundary agreed well with the full charge regulation boundary. Their study indicated that the constant potential boundary can only be adopted when the equilibrium water film thickness is sufficiently large.

3.4.3. Van der waal force: retardation effect

Eq. (17) is the most used form of van der Waals force with retardation effects. However, this equation works best only at transitional region, and at small or large separations there should not be any retardation effect. A piecewise function for the retarded van der Waals force per unit area across the water film is better over the whole range [77]:

$$\begin{aligned} \Pi_{VDW}(D) &= \frac{A}{\pi} \left[\frac{0.1684}{D^3} - \frac{0.093}{D^2} \left(\frac{\pi}{\lambda} \right) + 0.019 \left(\frac{\pi}{\lambda} \right)^3 - 0.0052 \left(\frac{\pi}{\lambda} \right)^4 D \right], D \\ &\leq 3\lambda/2\pi, \Pi_{VDW}(D) \\ &= \frac{A}{\pi} \left[\frac{0.1224}{D^4} \left(\frac{\pi}{\lambda} \right) - \frac{0.0344}{D^5} \left(\frac{\pi}{\lambda} \right)^2 \right], D > 3\lambda/2\pi. \end{aligned} \quad (27)$$

Fig. 6 illustrates the van der Waals force with simple retardation, with piecewise retardation and without retardation at small, medium and large separations. It clearly shows that the piecewise function

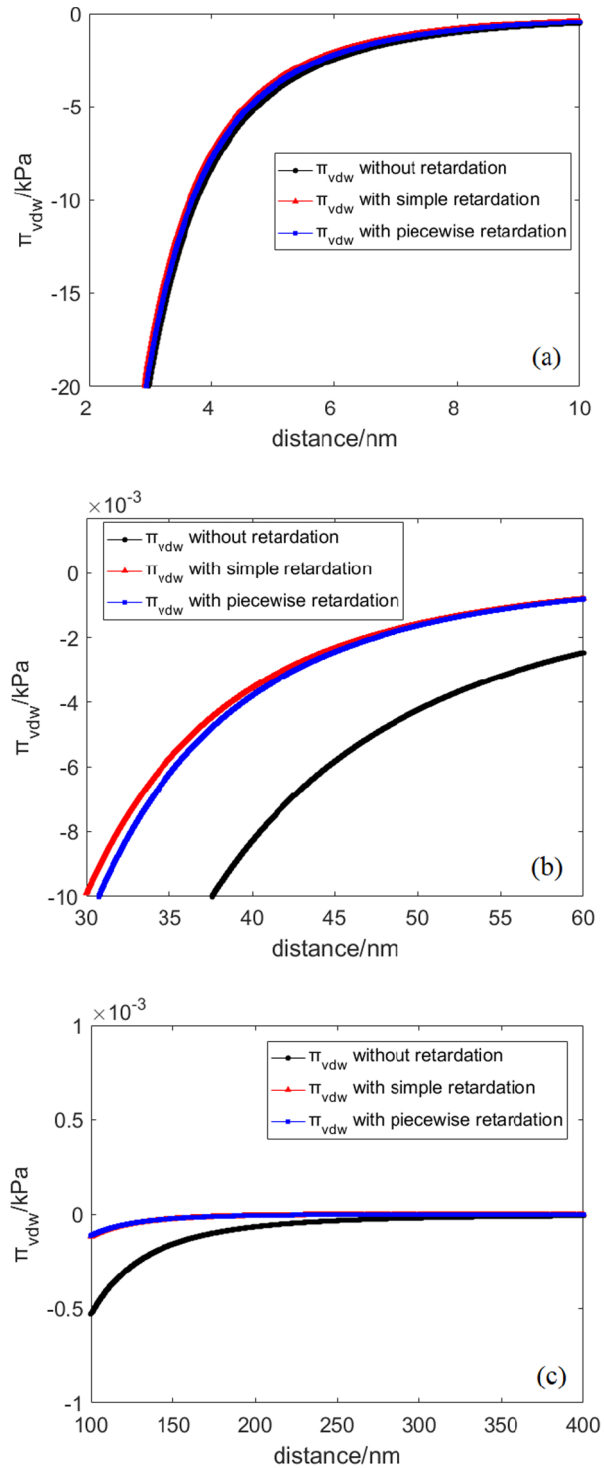


Fig. 6. The van der Waals force with simple retardation, with piecewise retardation and without retardation at (a) small, (b) medium and (c) large separations.

captures the retardation at transitional region and also the non-retarded interaction at small and large separations. The contact angle is calculated for different expressions of van der Waals force and results are shown in Fig. 7. The contact angles are very close for all cases, indicating that the retardation effect has few influences on the prediction of wettability.

3.4.4. Van der waal force: electrolyte screening effect

The electrostatic contribution of the van der Waals force will be

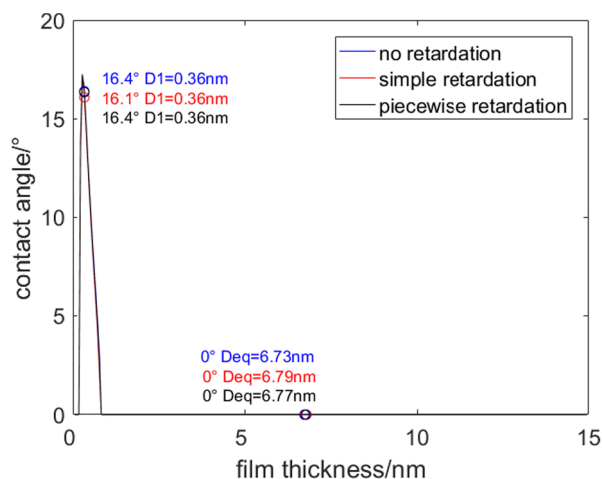


Fig. 7. The contact angle against film thickness curve, calculated with different considerations of the retardation effect. The equilibrium value is indicated by markers.

screened in electrolyte solutions, as indicated by Eq. (18), which was not considered in most works on the prediction of the contact angle. Sadeqi et al. calculated the contact angle with and without electrolyte screening and found that ignoring the screening effect could lead to considerable deviation [74]. However, we do similar calculations for two charging cases: $\phi_1 = \phi_2 = -0.04 V$ and $\phi_1 = -\phi_2 = -0.04 V$, and find that electrolyte screening effects have few influences on the predicted contact angle: (Fig. 8)

This contradiction stems from the different forms of screening factors. In Sadeqi et al.'s work, a different form from Eq. (18) was adopted [74]:

$$A = A_{v=0} e^{-2\kappa D} 2\kappa D + A_{v > 0}. \quad (28)$$

Another charging case is calculated: $\phi_1 = \phi_2 = -0.08 V$ and $n = 0.001 M$, and it is found that with the screening of Eq. (28), the contact angle change is much more evident, as Fig. 9 shows. We argue that Eq. (18) is more reasonable because the electrolyte screening effect should vanish without ions, namely when $\kappa \rightarrow 0$. This is the case with Eq. (18) but not with Eq. (28), which in fact has the strongest screening effect at $\kappa = 0$. Therefore, it is concluded that the electrolyte screening effect can be safely ignored in wettability calculation.

3.4.5. Van der Waal force: Uncertainty of the Hamaker constant

The Hamaker constant depends on the properties of oil, brine and rock all and is in principle different for different OBR systems, generally among the range between $5 \times 10^{-11} J$ and $1.5 \times 10^{-11} J$. Yet it was often chosen to be $1 \times 10^{-11} J$ without validations against experiments. We compare three choices of the Hamaker constant: $5 \times 10^{-11} J$, $1 \times 10^{-11} J$ and $1.5 \times 10^{-11} J$, and calculate the contact angle in three charging conditions: $\phi_1 = \phi_2 = -0.04 V$, $\phi_1 = -\phi_2 = -0.04 V$ and $\phi_1 = \phi_2 = -0.08 V$. For the $\phi_1 = \phi_2 = -0.08 V$ case, the bulk ion concentration is $n = 0.001 M$.

Results are shown in Fig. 10. The choice of Hamaker constant within the range $5 \times 10^{-11} J$ – $1.5 \times 10^{-11} J$ can lead to differences in the contact angle as large as 20°, and the deviation is larger when the system is more water-wet. Therefore, an accurate value of the Hamaker constant is crucial for a reliable prediction of contact angle.

3.4.6. Structural force: Uncertainty of empirical parameters

The form of Eq. (19) for the structural force is purely empirical, and for the two empirical parameters, most studies used the same value as that Hirasaki proposed 30 years ago [88], which was not validated against experiments. There were a few studies that chose a different form or different set of parameters, which could lead to considerable

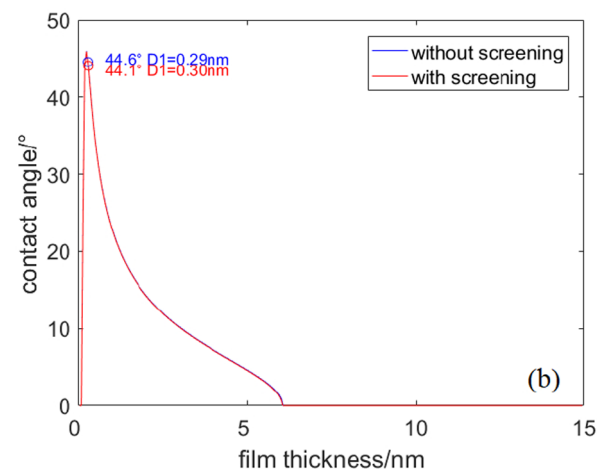
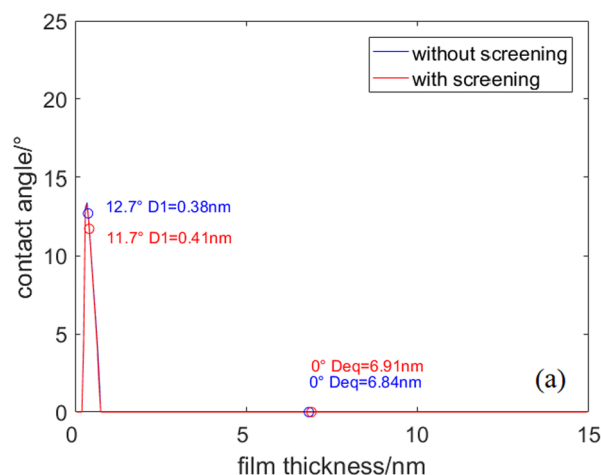


Fig. 8. The contact angle against film thickness curve, calculated with or without electrolyte screening effect considered. The equilibrium value is indicated by markers. (a) electric potential of both boundaries equals $-0.04 V$; (b) potential at one boundary is changed to $0.04 V$ compared with (a).

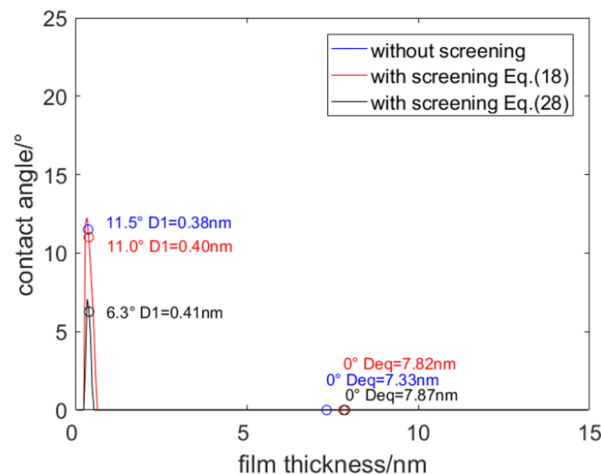


Fig. 9. The contact angle against film thickness curve, calculated with different forms of electrolyte screening effect. The equilibrium value is indicated by markers. It can be seen that with Eq. (28) the change of contact angle is more evident.

variation in results [117–119]. Here we compare three sets of empirical parameters for Eq. (19). The first is the same as in Hirasaki's earliest work and most works on wettability alteration, $A_s = 1.5 \times 10^{10} Pa$ and $D_s = 0.05 nm$. The second is used by some other researchers,

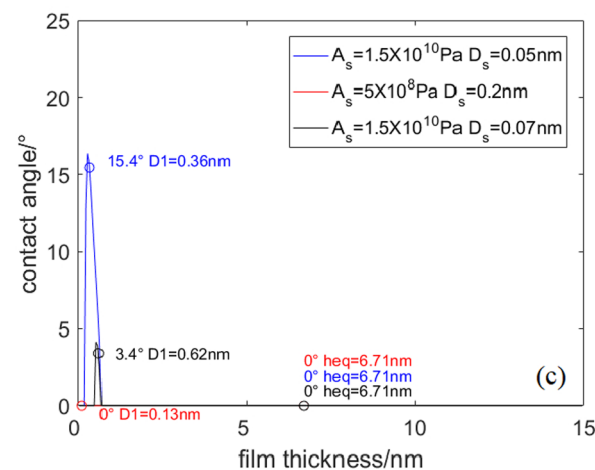
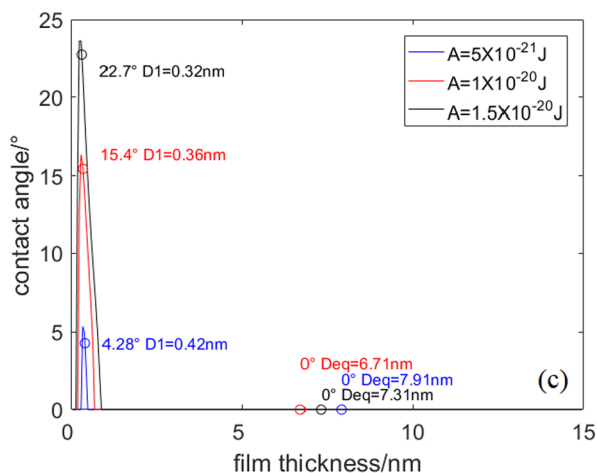
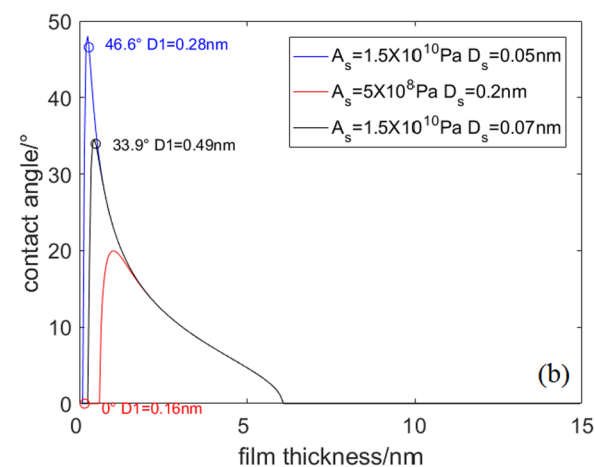
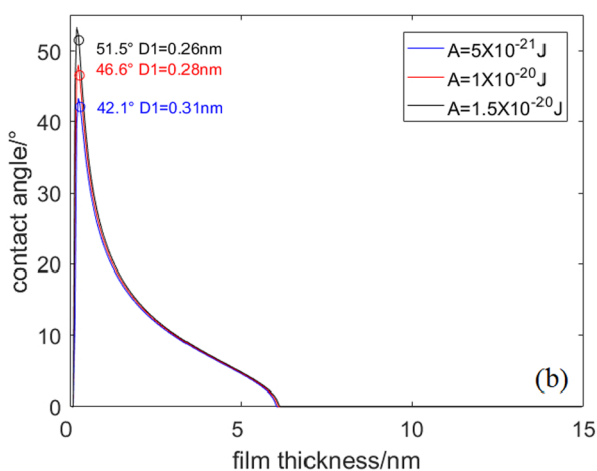
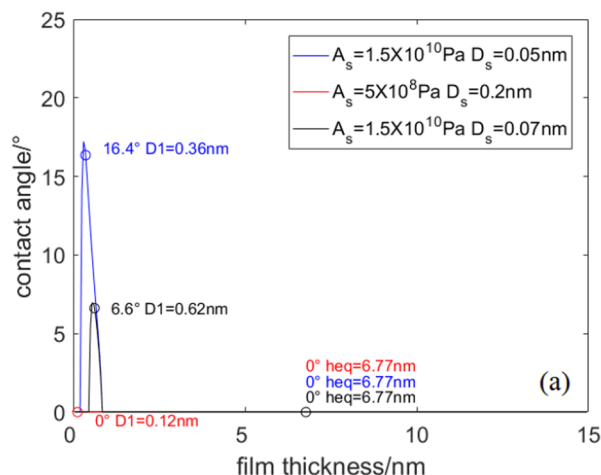
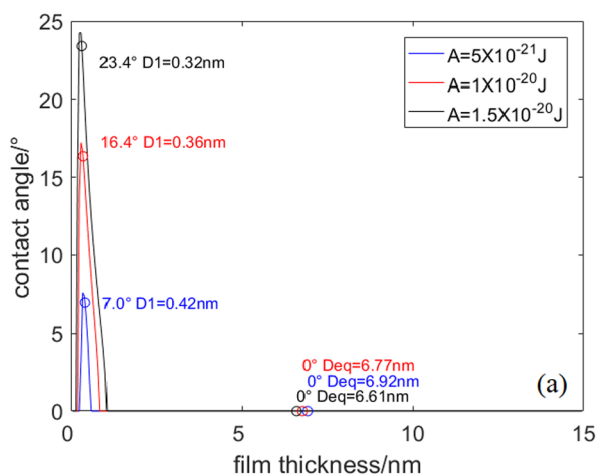


Fig. 10. The contact angle against film thickness curve, calculated with different values of Hamaker constant. The equilibrium value is indicated by markers. (a) electric potential of both boundaries equals -0.04 V; (b) potential at one boundary is changed to 0.04 V compared with (a); (c) electric potential of both boundaries equals -0.08 V, and bulk ion concentration is lowered to 0.001 M.

Fig. 11. The contact angle against film thickness curve, calculated with different empirical parameters in the structural force. The equilibrium value is indicated by markers. (a) electric potential of both boundaries equals -0.04 V; (b) potential at one boundary is changed to 0.04 V compared with (a); (c) electric potential of both boundaries equals -0.08 V, and bulk ion concentration is lowered to 0.001 M.

$A_s = 5 \times 10^8 Pa$ and $D_s = 0.2 nm$ [118]. The last one is modified a little from Hirasaki's parameters, $A_s = 1.5 \times 10^{10} Pa$ and $D_s = 0.07 nm$. Contact angles for those three sets of parameters are calculated under three charging conditions the same as those in Section 3.4.5.

As Fig. 11 illustrates, the choice of empirical parameters has a huge impact on the contact angle. Solely increasing D_s by 0.02 nm can cause contact angle deviation as much as 10° . The other set of empirical parameters used by some researcher seems to make the system fully water-wet with a contact angle of 0° , even when Hirasaki's parameters obtain a contact angle of 46.6° . It can be concluded that no prediction on wettability is quantitatively reliable unless the empirical parameters in structural force are validated against experiments.

3.4.7. Change of capillary pressure

The capillary pressure in Eq. (22) is usually considered as a known parameter and kept constant in wettability alteration calculations. However, the change of contact angle and oil-brine interfacial tension both influence the capillary pressure. Contact angles for three capillary pressures are calculated to see its impact: $P_c = 2 kPa$, $20 kPa$ and $200 kPa$ (Fig. 12.).

The results show that for capillary pressure difference large as two orders of magnitude, the variation in contact angle is rather small. Therefore, the value of capillary pressure is not important in wettability calculations. Note that the capillary pressure does have an impact on the meta-stable film thickness, and for the $P_c = 200 kPa$ case the meta-stable condition no longer exists.

3.4.8. Summary

It is evident that the extended DLVO theory cannot work when certain mechanisms like MIE are in play because it does not include the chemical interaction. However, even if there is no interaction beyond the range of the theory, the evaluation in this section shows that the current model is unable to obtain a good quantitative contact angle that agrees with experiments. Neglect of Stern layer, uncertainty of the Hamaker constant and empirical parameters in structural force can all lead to non-negligible deviations of contact angle. Considering that in most wettability alteration studies the largest contact angle change is within 20° , the deviation could totally invalidate the results. Therefore, if quantitative prediction of wettability alteration is expected, more precise model needs to be developed, especially for the empirical parameters.

In addition, the factors evaluated in this section are only part of the limitations of the current theory. For EDL interaction alone, the finite size of ions [120–123], the ion-ion correlation [124], the variation of relative permittivity due to polarization [121,125,126], the roughness

of the oil-brine and the brine-rock interfaces [127–129] and so on are all factors that may have considerable impact on the results but are usually ignored. Even the surface complexation model for EDL interaction alone is one very complicated and debated issue. Therefore, a quantitatively accurate prediction of contact angle is extremely hard and requires a much more detailed examination of all relevant factors.

4. Impact of wettability alteration on oil recovery

In many studies on mechanisms of wettability alteration, it was assumed that altering the OBR system to a more water-wet condition was better for oil recovery, which was not necessarily the case as some experiment works suggested [6,19,22,130]. Figuring out how wettability alteration impacts multiphase flow and oil recovery is a crucial part of predicting the responses of LSW and is no less complicated than wettability alteration itself. This section reviews the impact of wettability alteration on oil recovery, by first discussing the optimal wettability for oil recovery beyond core scale, then the pore-scale multiphase flow mechanisms at pore scale, and finally the coupling of wettability alteration and multiphase flow.

4.1. Overview of optimal wettability for oil recovery

Before talking about the optimal wettability for oil recovery, one needs to clarify what 'wettability' means and what is the goal of enhanced oil recovery. Although the contact angle is the most common and direct description of wettability, measuring the contact angle distribution in a core sample can be expensive and troublesome. Instead, a wettability index called the Amott-Harvey index is usually adopted to describe the wettability of an OBR system at core scale. The index is obtained by the Amott test where a couple of spontaneous and forced imbibition experiments of water and oil are done [131]. Before the test, the core sample should be prepared at a water saturation S_{wi} identical to the reservoir by flooding or centrifuging. The Amott test consists of four steps in order: spontaneous imbibition of water, forced imbibition of water, spontaneous imbibition of oil and forced imbibition of oil. The amount of water or oil imbibed in each step is measured and the Amott-Harvey index is given by:

$$\text{Index} = \frac{\text{Spontaneous water imbibition}}{\text{Total water imbibition}} - \frac{\text{Spontaneous oil imbibition}}{\text{Total oil imbibition}} \quad (29)$$

By definition, the Amott-Harvey index is between -1 and 1 , with more positive value corresponding to more water-wet. It qualitatively agrees with the contact angle, but as shown in Zhao et al.'s simulation work [36], an index near zero can correspond to a wide range of contact angles, for example from 70° and 110° . Besides, it cannot capture the heterogeneous distribution of contact angles in a core sample. Therefore, it might not be a good quantitative measurement of wettability, especially for a neutral system.

The goal of enhanced oil recovery is also a significant issue. In most works, the overall result of more oil produced or less residual oil trapped in reservoirs is considered an improvement by LSW, with few emphases on the amount of brine injected. However, some researchers suggested that from an economic perspective a 'faster' oil recovery was more important because the same amount of oil could be produced with less brine injected [108,132]. Fig. 13 is an extreme example to illustrate those two opinions. Oil is produced much faster when brine 1 is injected and the maximum recovery is reached with a relatively small amount, while brine 2 can recover more oil if the amount injected is sufficient large. Therefore, the first opinion favors brine 2 and the second opinion prefers brine 1. In reality, the amount of brine injected before oil recovery saturates generally does not vary too much for different brines, thus in this work a better or improved oil recovery means more oil produced or less residual oil after enough amount of brine is injected.

The optimal wettability for oil recovery can also depend on the

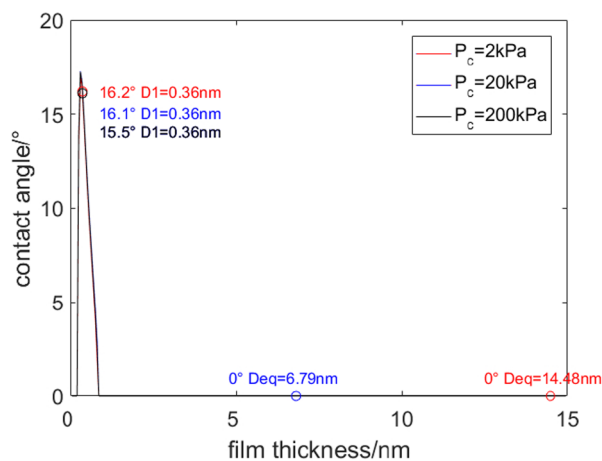


Fig. 12. The contact angle against film thickness curve, calculated with different capillary pressure. The equilibrium value is indicated by markers. Results show that capillary pressure has a negligible influence on contact angle.

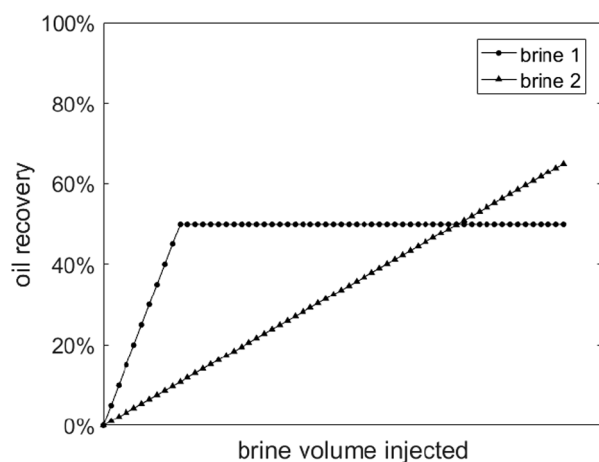


Fig. 13. A diagram to show the different opinions of better oil recovery. More oil can be produced by brine 2 in the long term, but brine 1 recovers oil much faster with much less brine injected. The x-axis has no scalar, just showing the trend of curves and qualitative comparison between the two curves.

specific waterflooding process. It has been pointed out that the dynamics in secondary mode LSW where low salinity brine is injected from the beginning is significantly different from that in tertiary mode where low salinity brine is injected after high salinity waterflooding and the optimal wettability could be different for those two modes [133–136]. The optimal wettability in secondary mode should be of more interest because multiple works have shown that the secondary mode was superior to the tertiary mode [135,137,138].

Some early waterflooding experiments found that the more water-wet the sample was, the more oil was produced [19]. This agrees with the physical intuition that in more water-wet OBR systems oil tends to detach from the rock surface and water imbibition rates will be faster, leading to better oil recovery. However, since the 1990s, lots of experiments showed that maximum oil recovery occurred at weakly water-wet or neutral conditions [6,19,20,22,130,139]. It was suggested that this had to do with the pore-scale flow behavior, which will be discussed in detail in the next section. It has gradually become a consensus that the optimal wettability for oil recovery is weakly water-wet [21,36,135,140,141] and has not been challenged by experiments so far.

However, this conclusion is not elaborate enough to help the prediction of LSW. The wettability was described by the Amott-Harvey index in almost all of the coreflooding experiments, which was around zero at weakly water-wet conditions. As is put out before, the index close to zero corresponds to a wide range of contact angles, often wider than the range of wettability alteration by LSW. Therefore, the contact angle before and after LSW may correspond to the same wettability index and no assertion can be made on which is better. In addition, the wettability index was usually measured after waterflooding, which might be different from the *in situ* wettability during waterflooding. Alhammedi et al. did waterflooding experiments and measured the *in situ* contact angle distributions by X-ray micro-tomography [21]. The average contact angles for the three samples in their experiments were 77°, 94° and 104° and maximum oil recovery was obtained at 94°. However, the oil in those three samples was different and the viscosity of different oils varied a lot (0.135 mPa·s, 0.39 mPa·s, 2.02 mPa·s), so it was not very convincing to relate the difference in oil recovery solely to the wettability change. Christensen and Tanino studied the dependence of oil recovery upon contact angle in mixed-wet limestone by doing coreflooding experiments under different wetting conditions established by tuning the acid content of the oil [142]. They found that the optimal wettability of oil contacted surface for recovery was near-neutral over typical duration of waterflooding, but it gradually shifted to more oil-wet as more brine was injected. Note that the physical

picture is a little different in their work as they investigated a mixed-wet sample where only the wettability of the oil-contacted surface was altered. In addition, the contact angle was not measured *in situ*, but separately on another substrate using the sessile drop methods. Further experiments are required in order to understand the relation between oil recovery and the contact angle.

Besides, there is discrepancy between experiments and simulations in terms of the optimal wettability. The direct simulation of waterflooding at pore scale only emerges in the recent decade. In 2010, Zhao et al. used pore network modeling to study the effect of wettability on oil recovery by calculating the relative permeability curve and doing Buckley–Leverett analysis for samples of different wettability [36]. They found that oil recovery increased as the system became more oil-wet and the relation was monotonic. This contradiction with experiments was noted in their work and they proposed that this could be due to the wettability distribution, as later in their oil recovery versus oil-wet fraction curve, it showed that the oil recovery first increased then decreased as the oil-wet fraction increased. However, this could not explain why the oil recovery versus wettability index curve in their work was not in agreement with experiment. Gharbi and Blunt did similar pore network modeling to study the effect of oil-wet fraction but chose a different parameter to characterize the waterflooding efficiency [140]. They suggested that the higher the water saturation when the oil and water relative permeabilities were equal, the more efficient the waterflooding. In this sense they found that the mixed-wet condition was better than oil-wet or water-wet. Note that both of these studies did not simulate the oil recovery directly but obtain it through theoretical analysis based on the relative permeability curve. In Kallel et al.'s pore network modeling study, it was found that the residual oil decreased as the system became more oil-wet, thus the optimal wettability would be oil-wet [143]. In recent years, more and more researchers began to use lattice Boltzmann method (LBM) to simulate waterflooding as it can capture more realistic core structure. Several LBM studies modeled the relative permeability curve under different wetting conditions in OBR systems, but did not directly consider the oil recovery [144,145]. Akai et al. modeled the coreflooding process using LBM, and their results showed that the maximum oil recovery occurred in the most water-wet case [146]. It seems that the few simulation works that agreed with experiment conclusion was Aziz et al.'s recent study [135], where the volume of fluid method was used to simulate the pore-scale two-phase flow. They compared the oil recovery in secondary mode LSW when the contact angle was altered from 140° to 60° and from 140° to 30°, and found that the contact angle of 60° was better for producing oil, not the oil-wet 140° or water-wet 30°. They also found that for the tertiary mode, 30° was superior to 60°, and they proposed that this disagreement was due to the stagnant region in the tertiary mode, where the transport was dominated by diffusion instead of flow. The detailed mechanisms will be discussed in the next section and readers can also refer to their original paper [135].

To sum up, experiments in recent decades have come to the consensus that weakly water-wet conditions are the best for oil recovery, but the range of weakly water-wet is too large to help predict the responses of LSW and the relation between oil recovery and contact angles is not clear. Simulation in theory can help investigate such relation, but so far most simulation works have obtained contradictory results with experiments, where the optimal wettability could be either water-wet or oil-wet.

4.2. Pore-scale flow mechanisms in different wetting conditions

Besides observing the overall responses of oil recovery to wettability alteration, researchers have also sought to investigate the impact of wettability on pore-scale flow behaviors to explain the results and better understand LSW. One of the most discussed pore-scale effects of wettability alteration is the change of capillary pressure. Capillary pressure in water-wet OBR systems tends to drive the oil–water

interface to move towards the oil side, thus enhances the imbibition of water. It was validated by experiments that the imbibition rate was the fastest in strongly water-wet samples [20,147,148] and that was one primary reason that water-wet was viewed as the best for oil recovery before the 1990 s. However, experiments in recent decades suggested that weakly water-wet was the best for oil recovery instead of water-wet. From the capillary pressure point of view, it was proposed that in water-wet samples, the capillary pressure in small pores was so large that water mostly imbibed small pores while in less water-wet conditions a few large pores could also be imbibed, thus final oil recovery was increased. This imbibition feature was observed in experiments and simulations [141,149–151].

Another well-known mechanism that hinders oil recovery in strongly water-wet systems is the snap-off or entrapment of oil [152]. In narrow pore throat, oil tends to form neck menisci with thin water wetting films due to the water-wet rock surface. During waterflooding, the neck meniscus often becomes unstable and breaks, leaving part of oil disconnected and immobile. Mohanty et al. studied the detailed physics of the snap-off process at pore-level [153] and such phenomenon has been observed in multiple experiment and simulation works [151,154–157]. In less water-wet pores, the snap-off process is inhibited, therefore less oil is entrapped and the residual oil saturation is decreased [154,155,158]. It is worth mentioning that some works found that individual oil ganglia could rebuild the connectivity and be mobilized by capillary waves generated by snap-off [159,160]. Yet still, snap-off is characteristic of strongly water-wet systems and generally leads to more residual oil.

The above mechanisms can explain why strongly water-wet is not good for oil recovery, but not why neutrally-wet is better than oil-wet. In fact, results of several simulation works showed that oil recovery increased as the system became more oil-wet [36,143]. The waterflooding behavior in oil-wet pores is relatively less understood. Many studies suggested that oil films would form on oil-wet rock surfaces and such films could maintain the connectivity of the oil phase during waterflooding. Therefore, oil recovery would continue after water breakthrough by slow drainage from those oil films and the overall oil recovery would be increased, in contrast to the water-wet case where maximum oil recovery occurred near breakthrough [161]. Such theory would predict the best oil recovery occur in the most oil-wet system. While the existence of oil films and their connectivity were confirmed by X-ray micro-tomography [150,162], experiments generally found bad recovery in very oil-wet samples. This could be caused by the low conductance of oil films [161,163–165] and the duration of experiments. Although theoretically more oil could be produced by drainage from connected oil films in oil-wet systems, the recovering rate is usually low compared with more water-wet cases, and the advantage of oil-wet samples may only be revealed after sufficient time. The current finding of weakly water-wet being the best for oil recovery might just be a special case for a certain time scale. Again, we see the importance of taking time scale into account when talking about what wettability is better for oil recovery.

Wettability heterogeneity can also have an effect on oil recovery. While the overall influences of wettability distribution on relative permeability and oil recovery has been paid attention to in many studies [143,144,166,167], investigation on the pore-scale impact is relatively lacking. A recent simulation work by Aziz et al. studied the pore-scale mechanism caused by wettability heterogeneity during tertiary mode LSW [135]. The wettability distribution in their work was caused by different ways of transport in flowing regions and stagnant regions: the flowing region was advection controlled and quickly replaced with low salinity water, while the stagnant region was diffusion controlled and salinity changed very slowly, leading to more water-wet conditions in the flowing region. Such distribution of wettability caused the oil–water interface near high salinity region to pull back from the oil side, and in some new regions water pushed oil forward. They found that the overall consequence of the redistribution of oil and water was a

decrease of oil recovery, because the reach of LSW was limited by the flexible redistribution process.

4.3. Discussion on the coupling of wettability alteration and multiphase flow

Current knowledge of the impact of wettability on oil recovery is still insufficient for the prediction of LSW. Pore-scale simulation is a useful tool to directly investigate the responses of LSW, but as have been reviewed in Section 4.1, simulation studies so far have not been able to obtain consistent results with experiments. In addition to the intrinsic limitations of specific simulation methods, one of the primary causes of the discrepancy could be that the coupling of wettability alteration and multiphase flow is not handled correctly. As a matter of fact, most simulation works of LSW did not consider the process of wettability alteration at all, instead they simply simulated cases of different wettability. This approach brings about inconsistencies in several ways. First of all, the value of contact angle change by LSW in simulation studies was usually chosen manually or by some simple relation against salinity without consideration of wettability alteration in real OBR systems reviewed in Section 3.3, therefore the results were not indicative of the real responses of LSW. Secondly, in addition to fluid flow, ion transport would also need to be considered if formation brine was present. The mixing of brine would lead to wettability heterogeneity that was ignored in many studies. Thirdly, the time needed for wettability alteration to occur was generally neglected, which could cause considerable change on the sweeping behavior of the water front. It is for the best if a study on the prediction of LSW considers the coupled wettability alteration and multiphase flow simultaneously.

A notable paradox related to the coupling of wettability alteration and multiphase flow is about the optimal wettability after alteration by low salinity brine, which is different from the optimal wettability for oil recovery discussed earlier. Although experiments suggested that weakly water-wet conditions were better than water-wet as they led to the lowest residual oil likely due to the suppression of snap-off, a few researchers argued that altering to a more water-wet condition during LSW was better for oil recovery [108]. This is not a contradictory but complementary opinion. The main idea is that a neutrally wet or mixed-wet condition will first be reached in the wettability alteration process towards a water-wet condition during LSW. While the rock contacting the bulk brine has been altered to water-wet, wettability at the oil side of the oil–water interface remains unaltered, thus when the oil front moves it actually experiences a mixed-wet condition and snap-off can be suppressed. The further wettability alteration from mixed-wet to water-wet will not lead to more trapped oil because the oil front has already passed. In the contrary, the oil recovery may be further increased by oil detachment in water-wet conditions. While direct experimental evidence for this opinion is currently lacking, it is worth taking into consideration when doing LSW simulations. Lots of simulations works were not able to examine this phenomenon because no wettability alteration process was actually considered.

5. Conclusion and perspectives

To conclude, this paper reviews LSW mechanisms in a manner that focuses on improving the predictability of LSW responses, with special attention paid to wettability alteration because it has been accepted as the most important mechanism. In addition to introduction of various wettability alteration mechanisms, this work also shows how each mechanism can be quantitatively considered and how the contact angle can be calculated in a typical OBR system. The need of more quantitative predictions of wettability is emphasized because the relation between wettability and oil recovery can be more complicated than expected and the impact of wettability alteration on oil recovery is reviewed as well, at both core scale and pore scale. The current models for the extended DLVO theory often adopted to predict contact angles are evaluated, and it is found that they cannot give a reliable prediction

of contact angle. Neglect of the Stern layer, uncertainty of the Hamaker constant and empirical parameters in the structural force are some of the factors proved to cause non-negligible deviation. In addition, chemical interactions are not included in the model. All of those issues need to be resolved if accurate prediction of wettability alteration is expected and solely improving the model for one interaction like EDL interaction is not adequate.

Experiments has found the maximum oil recovery generally occurs in weakly water-wet to neutrally-wet conditions but this conclusion is not elaborate enough to help prediction of LSW because the wettability was described by a core-scale index in most studies and the corresponding range of contact angles is quite large. Simulations in theory are able to investigate the relation between contact angle and oil recovery, but so far many simulation works have failed to achieve agreement with experiments and obtained contradictory results with each other. One primary reason for the discrepancy can be that the coupling of wettability alteration and multiphase flow is not handled correctly. Further simulation works on LSW are suggested to couple more realistic process of wettability alteration into modeling, including the ion transport, the formation of liquid film, the time needed for alteration and so on.

Last but not least, the field scale should be concerned when it comes to the ultimate goal of practical oil production. Though this work is mostly focused on the pore scale, further field scale studies can benefit from improved pore-scale models where wettability alteration and multiphase flow are correctly coupled, by multi-scale techniques linking those two scales, like the generalized multi-scale finite element method [168], pore-field-iteration method [169] and so on.

Author contributions

Moran Wang conceived and promoted this work. Fanli Liu did the literature review and produced the simulations. Fanli Liu wrote the paper and Moran Wang gave revisions to the text.

Declaration of Competing Interest

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

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