



Electrokinetic Mechanisms and Synergistic Effect on Ion-Tuned Wettability in Oil-Brine-Rock Systems

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Abstract

Wettability alteration has been recognized as the dominant mechanism of ion-tuned waterflooding, where the ionic composition of injecting brine is modified to improve oil recovery. Yet mechanisms of ion-tuned wettability have not been fully understood, and there are ongoing debates over the effectiveness and relative contribution of each mechanism. In this paper, ion-tuned wettability in variable oil-brine-rock (OBR) systems over a wide range of ionic compositions is theoretically investigated, with focuses on two electrokinetic mechanisms, double layer expansion (DLE) and multicomponent ion exchange (MIE). Results indicate that the qualitative features of ion-tuned wettability in terms of DLE and MIE in various OBR systems with different surface properties can be divided into two typical types, depending on the electrical double layer (EDL) interaction being repulsive or attractive. With attractive EDL force, both DLE and MIE do not contribute to the water-wetness. While with repulsive EDL force, DLE only takes effect at relatively high concentration and MIE has a significantly larger impact at a low percentage of divalent cation. In addition, DLE and MIE can have a synergistic effect, where one mechanism alone has a negligible effect on wettability but two mechanisms combined have a big impact.

Article Highlights

- Wettability alteration in various oil-brine-rock systems share similar features and can be divided into two types.
- Double layer expansion (DLE) and multicomponent ion exchange (MIE) only take effect at a range of ionic compositions.
- The contribution of DLE and MIE cannot be simply separated and compared.

Keywords Ion-tuned wettability · Wettability alteration · Double layer expansion · Multicomponent ion exchange · Low-salinity waterflooding

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1 Introduction

The idea of modifying the ionic composition of injecting brine to improve oil recovery, known as ion-tuned waterflooding, has attracted much attention from researchers in recent decades. Among various proposed mechanisms of ion-tuned waterflooding, wettability alteration in the oil-brine-rock (OBR) system, known as ion-tuned wettability, has been recognized as the dominant one (Sheng 2014; Tian and Wang 2017; Bartels et al. 2019; Liu 2020). Other ion-tuned mechanisms including osmosis, interfacial viscoelasticity and fines migration do not have as substantial and solid experimental evidence and do not deny the ubiquitous contribution of wettability alteration. It is well established that wettability has a huge impact on the multiphase transport in porous media. In many works, it was generally assumed that more water-wet condition enabled additional oil recovery.

However, ion-tuned wettability itself is still complicated and not fully understood. Several mechanisms have been proposed and studied, of which double layer expansion (DLE) and multicomponent ion exchange (MIE) being the most discussed (Lager et al. 2008; Ligthelm et al. 2009). DLE favors lower salinity, which leads to the expansion of electric double layer (EDL) and enhanced EDL repulsion, making the system more water-wet. MIE emphasizes the significance of divalent cations, which can form cation bridges and ligand bonds between oil-brine and brine-rock interfaces. Such bridges and bonds make the system less water-wet. There was experimental evidence supporting those mechanisms as well as evidence against them (Haagh et al. 2017; Mugele et al. 2015; Xie et al. 2014; Lager et al. 2008; Mahani et al. 2015; Mahani et al. 2017a; Nasralla, Nasr-El-Din 2014; Xu et al. 2016; Tian et al. 2019). Debates over the contribution of each mechanism are ongoing, and it remains unclear what ionic composition leads to the most water-wet condition in a specific OBR system.

Many coreflooding experiments had been carried out to evaluate the effects of different ionic compositions on oil recovery (Agbalaka et al. 2009; Kafili Kasmaei and Rao 2015; Morrow et al. 1998; Nasralla et al. 2013), and higher oil recovery was sometimes considered an implication of stronger wettability alteration toward water-wet, which is sometimes questionable since experiments have shown that the optimal oil recovery did not necessarily occur in strongly water-wet condition (Jadhunandan and Morrow 1990, 1995; Morrow and Buckley 2011; Zhou et al. 2000), and unimproved oil recovery may correspond to strong wettability alteration as well. Xie et al. conducted a series of coreflooding experiments to compare the contributions of DLE and MIE (Xie et al. 2014). They found that, compared with formation brine, low-salinity brine with divalent cation achieved considerably higher recovery, but high-salinity brine without divalent cation did not. It was then concluded that DLE was a dominant mechanism and MIE was not. Nasralla and Nasr-El-Din studied the effects of brine pH and salinity on zeta potential, contact angle and oil recovery by experiment (Nasralla and Nasr-El-Din 2014). They found that lower pH weakened the EDL interaction and correspondingly the OBR system became more oil-wet and oil recovery was decreased. Therefore, they concluded that DLE was the primary mechanism.

Direct experimental studies on ion-tuned wettability are relatively lacking. Mugele et al. measured the contact angle in a decane-brine-mica system, with and without divalent Ca^{2+} (Mugele et al. 2015). Results suggested that the removal of divalent cations made the system more water-wet, in agreement with MIE. Haagh et al. directly compared the contributions of DLE and MIE to wettability alteration (Haagh et al. 2017). The contact angle of water was first measured in high-salinity brine with divalent cation in a simplified OBR system; then, the brine was diluted in different manners, with the concentration of divalent

cation kept constant or not. It was found that a decrease of total salinity without removal of divalent cation had a negligible effect on the contact angle, while the removal of divalent cation without a decrease of ionic strength altered the system to more water-wet. Thus MIE was more important than DLE in their study.

One of the most important reasons for those seemingly contradictory results of ion-tuned waterflooding and wettability is that the response to ion-tuned brine can differ a lot in different OBR systems. The properties of rock and oil have a big impact on ion-tuned wettability. It was also found that wettability did not always change monotonically with decreasing salinity, which suggested that the general trend of ion-tuned wettability could also change at different ionic compositions (Alotaibi et al. 2011; Buckley et al. 1997; Yu and Buckley 1997). Therefore, ion-tuned wettability can be better understood if variable OBR systems with different interface properties and a wide range of ionic compositions are considered. While experimental studies were usually limited to finite choices of ionic compositions and one specific OBR system due to the restriction of cost and time, theoretical approaches are much less affected by such restrictions. However, current theoretical studies directly on ion-tuned wettability are also lacking. Although surface complexation models were developed for oil-brine and rock-brine interfaces to predict the zeta potential with different ionic compositions (Bonto et al. 2019a, b; Brady et al. 2015; Song et al. 2017; Takeya et al. 2019, 2020), and the extended DLVO theory can be utilized to investigate the interaction between those two interfaces in an OBR system (Hirasaki 1991; Joekar-Niasar, Mahani 2016; Mahani et al. 2017b), they were rarely coupled to study ion-tuned wettability. When they were coupled, simplifications were often made that prevented the theoretical tool from studying more general cases. For example, the often adopted formula of EDL force under constant interfacial potential assumption without charge regulation requires 1:1 electrolyte and fails at a small distance (Sanaei et al. 2018), and the linearization of Poisson-Boltzmann equation only applies at low zeta potential. Comparison between charge regulation, constant potential boundary and constant charge boundary and the limitation of the latter two boundary conditions have been studied in detail in the work by Tian and Wang (2017).

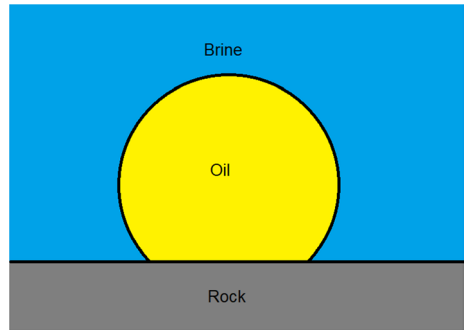
Therefore, this work aims to utilize the more advanced theoretical tool to investigate ion-tuned wettability in variable OBR systems over a wide range of ionic compositions, with emphasis on the mechanisms of DLE and MIE. The full nonlinear Poisson-Boltzmann equation is solved with various surface complexation models and triple-layer model of EDL; the EDL energy is calculated with charge regulation, and the extended DLVO theory and the augmented Young-Laplace equation are adopted to obtain the contact angle. Details of those methods will be introduced in Sect. 2, followed by results and discussion in Sect. 3, and finally the conclusion in Sect. 4.

2 Methods

In this section, the framework of our method and relevant equations are briefly introduced. For more details, please refer to our previous review papers on this topic (Liu and Wang 2020; Tian and Wang 2017).

The model OBR system in Fig. 1 is considered throughout this work. The thin brine film between the oil drop and the rock surface is the key to many mechanisms of wettability alteration like DLE and MIE. Interaction pressure Π between oil and rock across the brine film of thickness h_0 determines the contact angle of water (Hirasaki 1991):

Fig. 1 Diagram of the simplified OBR system



$$\cos \theta - 1 = \frac{1}{\sigma_{ob}} \left[\int_{h_0}^{\infty} \Pi(h) dh + h_0 \Pi(h_0) \right], \quad (1)$$

where σ_{ob} is the oil-brine interfacial tension. Π is also called the disjoining pressure and consists of three components: the Van der Waals pressure Π_{VDW} , the structural pressure Π_{STR} and the EDL pressure Π_{EDL} . According to our previous study (Liu, Wang 2020), the retardation and screening effect of the Van der Waals force can be safely ignored in this case, and the following classic form is adopted:

$$\Pi_{VDW}(h) = -\frac{A}{6\pi h^3}, \quad (2)$$

where $A = 1 \times 10^{-20} J$ is the Hamaker constant in a typical OBR system.

Hirasaki proposed an empirical form of structural pressure (Hirasaki 1991):

$$\Pi_{STR}(h) = A_s \exp\left(-\frac{h}{h_s}\right), \quad (3)$$

where $A_s = 1.5 \times 10^{10} Pa$ and $h_s = 0.05 nm$ are empirical parameters.

The EDL pressure is the ion-tuned part of the disjoining pressure, and its simplified form under the assumption of constant interfacial potential and 1:1 electrolyte was often adopted. However, the overlapping of EDLs can be strong across the water film so that the constant potential assumption fails and a mixture of monovalent and divalent cation in the brine has to be considered to study DLE and MIE together. Therefore, here the EDL energy is solved with full nonlinear Poisson-Boltzmann equation with charge regulation to cover more general cases:

$$\nabla^2 \phi = -\frac{eN_A}{\epsilon_0 \epsilon_r} \sum_i z_i c_i^\infty \exp\left(\frac{-z_i e \phi}{k_b T}\right), \quad (4)$$

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. The free energy needed to form two parallel EDLs at a distance h is:

$$F(h) = \int_{(0,0)}^{(\sigma_1(h), \sigma_2(h))} (\phi_1^e(\sigma'_1, \sigma'_2, h) - \phi_1^c(\sigma'_1)) d\sigma'_1 + (\phi_2^e(\sigma'_1, \sigma'_2, h) - \phi_2^c(\sigma'_2)) d\sigma'_2, \quad (5)$$

where $\sigma_i(h)$ ($i = 1, 2$) is the interfacial charge in equilibrium, ϕ_i^e is the interfacial potential obtained by Poisson-Boltzmann equation and electrostatic equilibrium condition and ϕ_i^c is the potential obtained by the surface complexation model. The increase of energy W_{EDL} due to the overlapping of EDLs is then $F(h) - F(\infty)$ and the EDL pressure can be calculated by the variation of W_{EDL} .

Given the surface complexation model at the oil-brine and rock-brine interfaces, the contact angle at different ionic compositions is solved by the same set of equations above. Therefore, the surface complexation model determines the response of a specific OBR system to the ion-tuned brine. In this work, our focus is on the qualitative features of the contact angle, since it has been found that the extended DLVO theory is quantitatively inaccurate but qualitatively correct: Uncertainties of the parameters in the van der Waals force and structural force can considerably alter the value of calculated contact angle at a specific ionic composition, but since those two forces are not affected by the change in ionic compositions, the contact angle alteration is still solely determined by the change in EDL energy, and the qualitative trend of ion-tuned wettability is unaffected by those uncertainties (Liu, Wang 2020). Therefore, we do a standardization of the calculated contact angle so that its qualitative trend is not affected but the overall value appears more reasonable by $\theta = \theta_0(\theta_{\max} + \pi/2)/2\theta_{\max}$, where θ_0 and θ are the contact angles, respectively, before and after standardization, θ_{\max} is the largest contact angle over all calculated ionic compositions in the current OBR system, and the value $\pi/2$ is chosen because the existence of a water film limits the calculated contact angle to be not larger than $\pi/2$. The flowchart of calculation is illustrated in Fig. 2. As our emphasis is laid on DLE and MIE, contributions of certain ion like sulfate are excluded and three types of ion are considered in the brine: Na^+ , Ca^{2+} and Cl^- , and correspondingly the reactions in Table. 1 are considered at the oil-brine and rock-brine interfaces (Kitamura et al. 1999; Takeya et al. 2019, 2020). Parameters in

Fig. 2 Flowchart of the calculation of contact angle

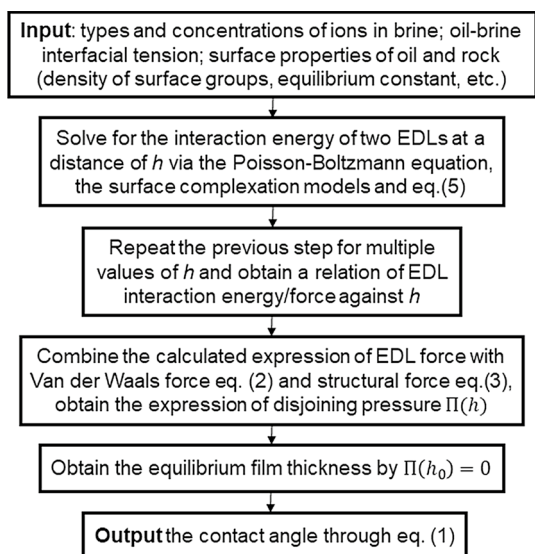


Table 1 Surface complexation models on the oil, sandstone and carbonate surfaces

Surface sites	Reaction	Equilibrium constant
Oil	$> \text{COOH} \rightleftharpoons > \text{COO}^- + \text{H}^+$	$\log K_0^{\text{ob}} = -5.6$
$\Gamma(> \text{COOH}) = 0.47 \text{ nm}^{-2}$	$> \text{COO}^- + \text{Na}^+ \rightleftharpoons > \text{COONa}$	$\log K_1^{\text{ob}} = 0$ (no reaction)
$\Gamma(> \text{NH}) = 0 \text{ nm}^{-2}$	$> \text{COO}^- + \text{Ca}^{2+} \rightleftharpoons > \text{COOCa}^+$	$\log K_2^{\text{ob}} = 0.8$
	$> \text{NH} + \text{H}^+ \rightleftharpoons > \text{NH}_2^+$	$\log K_3^{\text{ob}} = 5.5$
Sandstone	$> \text{SiOH} \rightleftharpoons > \text{SiO}^- + \text{H}^+$	$\log K_0^{\text{sb}} = -6.57$
$\Gamma(> \text{SiOH}) = 5 \text{ nm}^{-2}$	$> \text{SiO}^- + \text{Na}^+ \rightleftharpoons > \text{SiONa}$	$\log K_1^{\text{sb}} = -0.72$
	$> \text{SiO}^- + \text{Ca}^{2+} \rightleftharpoons > \text{SiOCa}^+$	$\log K_2^{\text{sb}} = -2.7$
Carbonate	$> \text{CO}_3\text{H} \rightleftharpoons > \text{CO}_3^- + \text{H}^+$	$\log K_0^{\text{cb}} = -7.3$
$\Gamma(> \text{CO}_3\text{H}) = 4.95 \text{ nm}^{-2}$	$> \text{CO}_3^- + \text{Na}^+ \rightleftharpoons > \text{CO}_3\text{Na}$	$\log K_1^{\text{cb}} = 0$ (no reaction)
$\Gamma(> \text{CaOH}) = 4.95 \text{ nm}^{-2}$	$> \text{CO}_3^- + \text{Ca}^{2+} \rightleftharpoons > \text{CO}_3\text{Ca}^+$	$\log K_2^{\text{cb}} = 0.85$
	$> \text{CaOH} + \text{H}^+ \rightleftharpoons > \text{CaOH}^+$	$\log K_3^{\text{cb}} = 15$

those surface complexation models like site density, equilibrium constant can be adjusted for investigations of different OBR systems, for example systems with clay minerals like kaolinite. Note that regardless of the surface being oil, sandstone or carbonate, the reactions are essentially the same:



where $> \text{A}$ is the “acid” site: $> \text{SiOH}$, $> \text{CO}_3\text{H}$, $> \text{COOH}$; and $> \text{B}$ is the “basic” site: $> \text{CaOH}$, $> \text{NH}$. Therefore, as long as no new type of surface site is involved, which is usually the case, and only Na^+ , Ca^{2+} and Cl^- are considered as in this study, the difference between OBR systems boils down to the difference in parameter value. Note that calcite dissolution is ignored because we require that the bulk brine composition should be an input parameter and also because its occurrence is not common in the cases studied.

The triple-layer model is adopted for the EDL structure (Kitamura et al. 1999; Takeya et al. 2019, 2020). If not otherwise specified, the following values of electrical capacities of the inner and outer parts of the Stern layer is used: at the oil-brine interface, $C_1^{\text{ob}} = 3.1 \text{ F} \cdot \text{m}^{-2}$, $C_2^{\text{ob}} = 2.25 \text{ F} \cdot \text{m}^{-2}$; at the sandstone-brine interface, $C_1^{\text{sb}} = 1.25 \text{ F} \cdot \text{m}^{-2}$, $C_2^{\text{sb}} = 0.2 \text{ F} \cdot \text{m}^{-2}$; at the carbonate-brine interface, $C_1^{\text{cb}} = 2.53 \text{ F} \cdot \text{m}^{-2}$, $C_2^{\text{cb}} = 0.695 \text{ F} \cdot \text{m}^{-2}$. The benchmark of our model is discussed in the appendix.

3 Results and Discussion

In this section, first an oil-brine-sandstone system and an oil-brine-carbonate system, parameters of which are given by Table. 1, are considered in subsections 3.1–3.3 to study the effect of DLE and MIE in those specific systems. Then the parameters are adjusted in subsection 3.4 for the investigation of different OBR systems.

Fig. 3 Contact angle in the oil-brine-sandstone system against brine concentration, without divalent cation at pH = 7. The trend is not monotonous

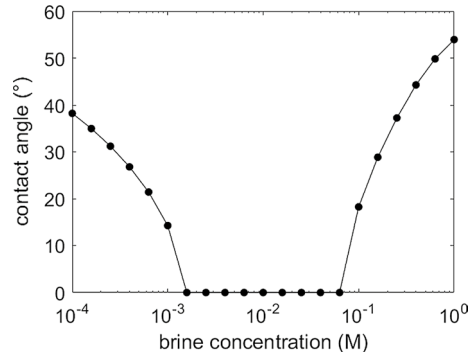
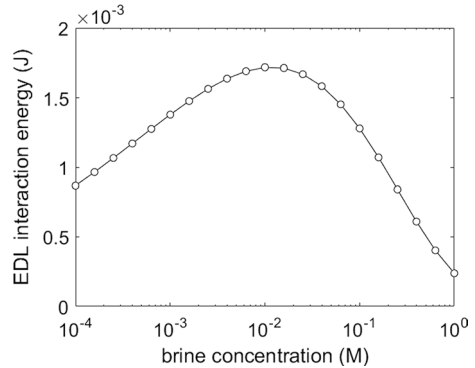


Fig. 4 EDL interaction energy in the oil-brine-sandstone system against brine concentration, without divalent cation at pH = 7



3.1 DLE Without MIE

To better understand DLE and MIE as mechanisms of wettability alteration, we first focus on only one mechanism by excluding the other. The contact angle of water is calculated in the oil-brine-sandstone system at pH = 7, with brine being NaCl solution at different concentrations, ranging from 10^{-4} M to 1 M. There is no MIE effect involved as there is no divalent cation. According to DLE, the contact angle should decrease as the concentration decreases because the EDL repulsion is enhanced.

However, as illustrated in Fig. 3, results indicate that the contact angle does not always decrease with lower concentration. The overall trend can be seen more clearly with Fig. 4 where the EDL interaction energy W_{EDL} is plotted, as the contact angle cannot be smaller than zero. With the dilution of the NaCl solution, W_{EDL} first increases, leading to a more water-wet condition in agreement with DLE, but when the concentration gets lower than around 10^{-2} M, it decreases and makes the system more oil-wet, in contradiction with DLE.

While it was found in some experiments that lower salinity did not always alter the wettability toward more water-wet (Alotaibi et al. 2011; Nasralla et al. 2013), it was often attributed to the impact of other mechanisms besides DLE. Yet in the current theoretical study, there is no other mechanism involved, suggesting that the DLE mechanism itself is challenged. Here we point out that this is because the expansion of EDLs due to low salinity does not necessarily enhance the EDL interaction. Start with the

often adopted expression of EDL interaction energy under constant potential assumption, considering two identically charged interfaces:

$$W_{EDL} = \kappa \epsilon_0 \epsilon_r (\sinh \kappa h)^{-1} ((1 + \sinh \kappa h - \cosh \kappa h)) \phi^2, \quad (9)$$

where $\kappa = \sqrt{2e^2 N_A I / \epsilon_0 \epsilon_r k_b T}$ is the Debye parameter, the reciprocal of which proportional to the characteristic thickness of EDL. It can be seen that the EDL thickness always increases as the ionic strength $I = \sum_i z_i^2 c_i / 2$ decreases. If the interfacial potential does not change with salinity, with unit potential Eq. (9) gives the relation between W_{EDL} and monovalent brine concentration, as in Fig. 5, which shows that the expansion of EDLs at low salinity actually weakens the EDL interaction when the concentration is lower than around 1 M. It is the increase of the interfacial potential $|\phi|$ with dilution that compensates for the weakening effect of EDL expansion and enables W_{EDL} to continue growing. Yet according to Eq. (9), such compensation is bound to break down at low enough concentration, as the interfacial potential approaches a finite value but the rest of the product approaches zero, eventually leading to a decrease of W_{EDL} and less water-wet condition.

When charge regulation is considered as in our study, the analysis becomes less straightforward. We merely explain why it is possible for W_{EDL} to decrease at low salinity in the supplement material.

Note that all the discussion above is based on the fact that both interfaces have the same sign of charges and the EDL interaction is repulsive. This is true for the oil-brine-sandstone system where both oil and sandstone surfaces are negatively charged. Carbonate, however, can often be positively charged in brine. The carbonate model we adopt is validated to be positively charged at pH=7, and the corresponding contact angle in the oil-brine-carbonate system, shown in Fig. 6, increases as the concentration decreases. Such trend is expected from the mechanism of DLE as the EDL interaction is now attractive and the expansion of EDLs enhances the interaction, thus making the system more oil-wet. In a sense, this agrees with the DLE mechanism as the EDL interaction is enhanced. However, there can be misunderstandings as DLE is usually viewed as a mechanism that contributes to the water-wetness. Here we emphasize that the charging condition needs to be taken into consideration when discussing the impact of EDL expansion. Following the original definition of the DLE mechanism that it enhances the EDL repulsion, it can be concluded that in this case where the interfaces are oppositely charged, there is no DLE effect as the EDL interaction is not repulsive.

Fig. 5 EDL interaction energy calculated by Eq. (9). The trend is not monotonous

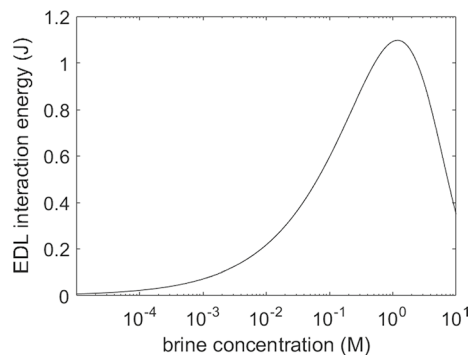
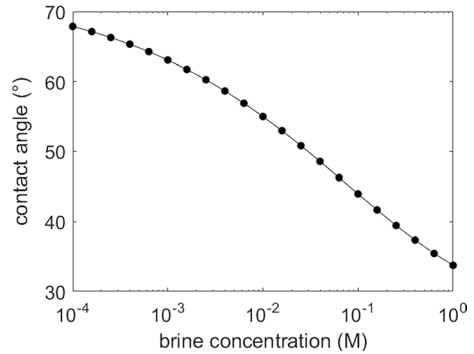


Fig. 6 Contact angle in the oil-brine-carbonate system against brine concentration, without divalent cation at pH=7



3.2 MIE Without DLE

To study the effect of MIE without DLE, the ionic composition of brine is varied in such manner that the concentrations of both Ca²⁺ and Na⁺ are changed while the concentration of the anion is kept constant at 0.01 M. Defining the percentage of Ca²⁺ as 2c(Ca²⁺)/c(Cl⁻), the contact angle in the oil-brine-sandstone system at pH=7 is shown in Fig. 7. According to MIE, the removal of Ca²⁺ should break the attractive bonds between oil and rock and make the system more water-wet. The result indeed shows a monotonic trend of contact angle against the percentage of Ca²⁺, but the impact of removing Ca²⁺ on wettability alteration is almost negligible at high Ca²⁺ percentage, for example when the percentage changes from 1 to 0.6, in contrast to its significant impact at low Ca²⁺ percentage, when the percentage changes from 0.2 to 0. This seemingly unexpected behavior can be explained by simple analysis. Divalent cation tends to accumulate near negatively charged interfaces because of its higher valence, indicated by the Boltzmann distribution:

$$c(Ca^{2+}) = c(Ca^{2+})^{bulk} \cdot \exp(-2e\phi/kT) \tag{10}$$

The accumulated Ca²⁺ near the interfaces then promotes its binding to the surface sites, increasing the positive charge of the interface. As a result, the repulsive force is weakened and the system becomes less water-wet. At the same time, the zeta potential becomes less negative due to the accumulation of Ca²⁺, which in turn prevents the accumulation of newly added Ca²⁺. To sum up, at low Ca²⁺ percentage, the

Fig. 7 Contact angle in the oil-brine-sandstone system against percentage of divalent cation, with anion concentration kept at 0.01 M at pH=7

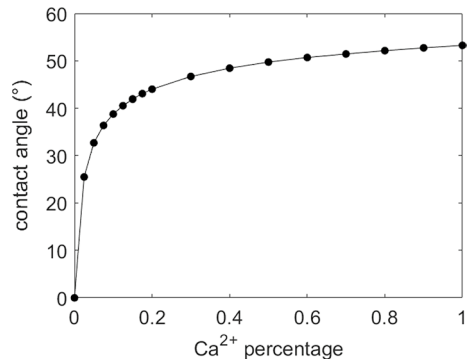


Fig. 8 Zeta potential in the oil-brine-sandstone system against percentage of divalent cation, with anion concentration kept at 0.01 M at pH=7

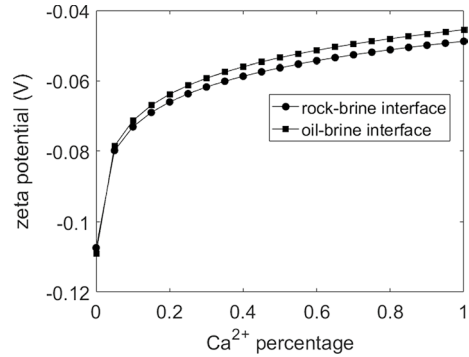
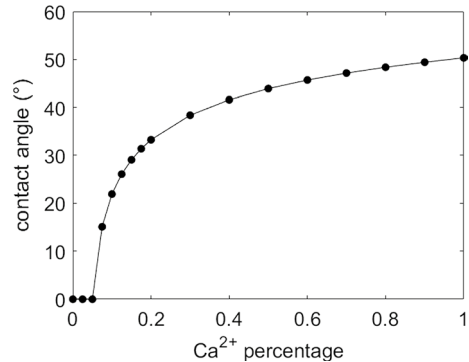


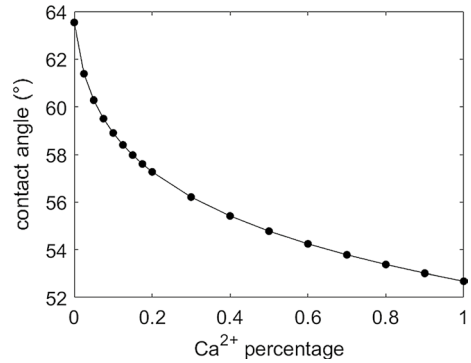
Fig. 9 Contact angle in the oil-brine-sandstone system against percentage of divalent cation, without cation binding to surface sites and with anion concentration kept at 0.01 M at pH=7



interfaces are more negatively charged, leading to high accumulation of the added Ca^{2+} and correspondingly larger impact on wettability. At high Ca^{2+} percentage, the previous accumulation of Ca^{2+} makes the interfaces less negatively charged, leading to low accumulation of newly added Ca^{2+} and smaller impact on wettability. Figure 8 of interfacial potential against Ca^{2+} percentage agrees with the analysis. Note that in the current study no ligand bond is formed; therefore, the attractive bonds related to Ca^{2+} are essentially electrostatic. Even if Ca^{2+} does not bind to the surface sites at all, its accumulation near the interfaces still contributes to the electrostatic attractive force and should have similar effect on wettability, as validated in Fig. 9. The above finding implies that, in order for MIE to take effect, divalent cation has to be almost totally excluded. Merely lowering the concentration of Ca^{2+} may have a negligible impact as low Ca^{2+} percentage has nearly as much capability to alter the wettability as high Ca^{2+} percentage.

When one of the interfaces is positively charged without divalent cation, as in the oil-brine-carbonate system, the accumulation of Ca^{2+} near the one negatively charged interface no longer weakens the repulsive force; instead, it may weaken the attractive force and make the system more water-wet as Ca^{2+} percentage increases. This is indeed the case in our oil-brine-carbonate system at pH=7, presented in Fig. 10. Following the definition of MIE that the removal of divalent cations breaks the attractive bonds they form, it can be concluded that there is no MIE effect when the two interfaces are always oppositely charged, as there is no cation bridge or ligand bond related to divalent cations.

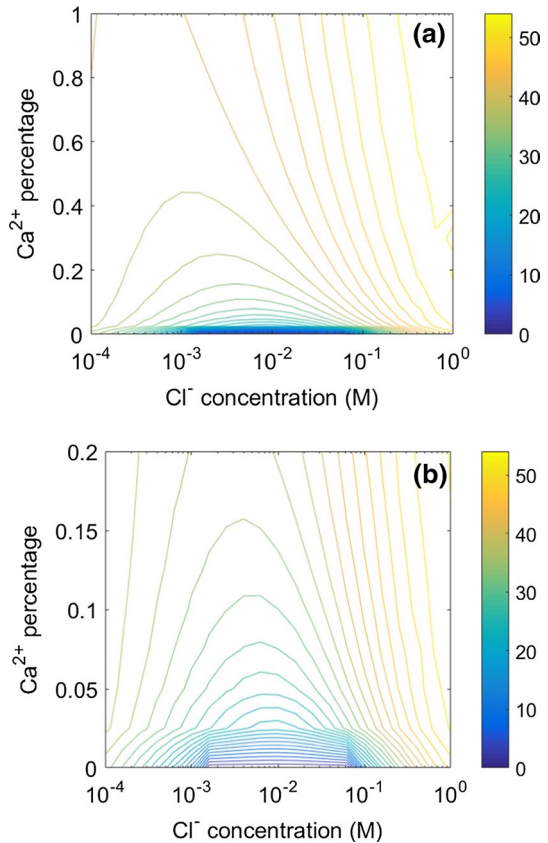
Fig. 10 Contact angle in the oil-brine-carbonate system against percentage of divalent cation, with anion concentration kept at 0.01 M at pH=7



3.3 Comparing DLE and MIE: The Synergistic Effect

To investigate the combined effect of DLE and MIE, first the contact angle is calculated over a wide range of not only anion concentration but also Ca²⁺ percentage at pH=7. The distribution of contact angle in the oil-brine-sandstone system is plotted in Fig. 11. It can be seen that the features of DLE and MIE previously found in Sect. 3.1 and 3.2 without

Fig. 11 **a** Contact angle distribution in the oil-brine-sandstone system at different ionic composition at pH=7; **b** local enlarged version of **a** at Ca²⁺ percentage lower than 0.2



divalent cation or at a specific anion concentration of 0.01 M, still hold at other Ca^{2+} percentage or anion concentration: at low enough concentration DLE no longer contributes to the water-wetness, and MIE has significantly larger impact at low Ca^{2+} percentage. In order to directly compare the contribution of DLE and MIE to wettability alteration by ion-tuned brine, the process of altering the ionic composition is imagined to consist of two steps: removing Ca^{2+} while keeping the anion concentration constant, so that only MIE takes effect, and lowering the anion concentration while keeping the concentration of Ca^{2+} constant, so that only DLE takes effect. Note that the order of the steps can be reversed. The comparison is limited to the concentration range where DLE still contributes to the water-wetness. We consider the process where ionic composition changes from $c(\text{Cl}^-) = 1\text{ M}, 2c(\text{Ca}^{2+}) = 0.01\text{ M}$ to $c(\text{Cl}^-) = 0.01\text{ M}, 2c(\text{Ca}^{2+}) = 0\text{ M}$. If DLE is chosen to first take effect, then after DLE it is altered to $c(\text{Cl}^-) = 2c(\text{Ca}^{2+}) = 0.01\text{ M}$. If MIE is chosen to first take effect, then after MIE it is altered to $c(\text{Cl}^-) = 1\text{ M}, 2c(\text{Ca}^{2+}) = 0\text{ M}$. A more common treatment of dilution by pure water from $c(\text{Cl}^-) = 2c(\text{Ca}^{2+}) = 1\text{ M}$ to $c(\text{Cl}^-) = 2c(\text{Ca}^{2+}) = 0.01\text{ M}$ is also considered. The change of contact angle by DLE and MIE in each step is shown in Fig. 12. Results indicate that the contribution of DLE and MIE to wettability alteration is path-dependent and cannot be simply separated. Regardless of the mechanism in the first step being DLE or MIE, one mechanism alone has little effect on the wettability, but after the second step the wettability is considerably altered. This can be interpreted as a synergistic effect of DLE and MIE: In this case, only two mechanisms combined can have a big impact on wettability. Previous seemingly contradictory results of the relative contribution of DLE and MIE can possibly be explained by such a synergistic effect. If divalent cation is first removed from high-salinity brine, followed by dilution, then DLE will be found to be more important. Otherwise, if divalent cation is removed after a decrease of total salinity, then MIE will be considered dominant.

The synergistic effect of DLE and MIE corresponds to the saturation of high total salinity and high Ca^{2+} percentage in terms of their capability to make the system less water-wet. At high salinity, the more positive interfacial potential and the weak overlapping of EDLs both prevent the accumulation of further added Ca^{2+} . At high Ca^{2+} percentage, the effect of weakening the EDL repulsion by high salinity is limited because the EDL interaction is already weak and cannot be weaker than zero.

As for the case where one interface is positively charged, it has already been presented that both DLE and MIE do not contribute to the water-wetness. Here the contact angle distribution in the oil-brine-carbonate system at $\text{pH} = 7$ is illustrated in Fig. 13 to show that such behavior is not unique to a specific concentration or Ca^{2+} percentage.

Fig. 12 The contact angle at several different ionic compositions, which indicate the contribution of DLE and MIE

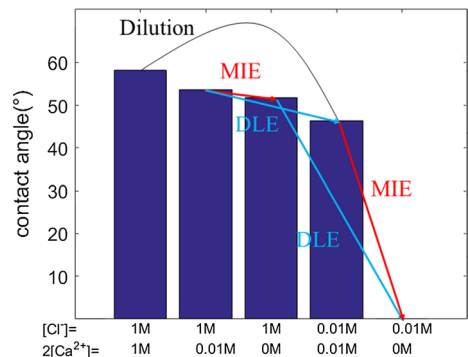
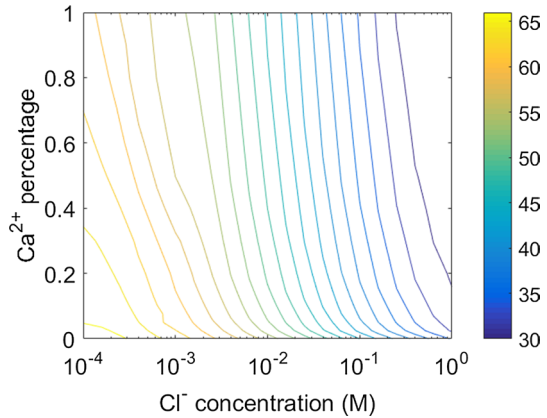


Fig. 13 Contact angle distribution in the oil-brine-carbonate system at different ionic composition at pH=7



3.4 Impact of Different Surface Properties and pH

Previous results are limited to the specific OBR systems with surface properties given in Table. 1 at pH=7. When the components of sandstone, carbonate or oil change, its surface property can have considerable variation. In order to validate the generality of previous findings, in this subsection, modified OBR systems with different surface complexation models and at different pH are studied. As discussed in the method section, the difference between OBR systems boils down to the difference in parameter value. Surface site density, equilibrium constant and pH are modified in a wide range to mimic different physical conditions, and a few other parameters like electrical capacity in the triple-layer model and the Hamaker constant in the van der Waals force are also modified to check the impact of uncertainties of the theoretical model. For those modified systems, the contact angle distribution with anion concentration and Ca^{2+} percentage is calculated, as in subsection 3.3.

Here only some representative results are presented, the rest can be found in the supplement material. Results over a wide range of physical parameters indicate that the behavior of DLE and MIE in various OBR systems can be roughly classified into two typical types according to the direction of the EDL interaction and the charging condition of the interfaces. When the EDL interaction is strongly attractive, which generally means the interfaces are oppositely charged, the OBR system behaves similarly to the previous oil-brine-carbonate system. When the EDL interaction is strongly repulsive, which generally means the interfaces are both negatively charged since oil is rarely positively charged in brine, the OBR system behaves similarly to the oil-brine-sandstone system. Therefore, the most important impact of the various physical parameters lies in how the charging conditions are affected.

The contact angle distribution in the same oil-brine-sandstone system at other pH is shown in Fig. 14. From the generalized reactions in Eqs. (6, 7), it can be seen that lower pH shifts the interface toward more positively charged, but as there is no “basic” site on this specific oil or sandstone surface, the sign will not be reversed. As a result, at lower pH the EDL repulsion is weakened and the whole system shifts toward more oil-wet, but the distributions are still qualitatively alike in terms of the previous findings: At low enough concentration dilution increases the contact angle, MIE has more significant impact at low Ca^{2+} percentage, and DLE and MIE have a synergistic effect. Another difference worth noting is that as the overall contact angle increases at lower pH, the contour becomes sparser. This is

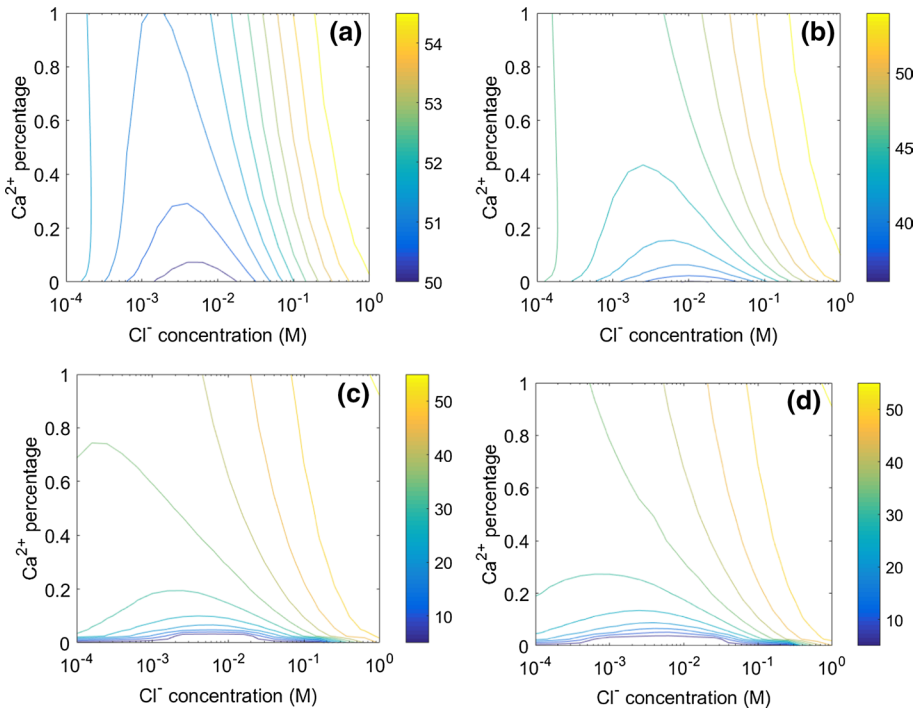


Fig. 14 Contact angle distribution in the oil-brine-sandstone system at different ionic composition at other pH. **a** pH=5; **b** pH=6; **c** pH=8; **d** pH=9. It can be seen that they share similar features with the pH=7 case, but the overall wettability shifts toward more water-wet at higher pH

because the contact angle has an upper limit where the EDL repulsion equals zero. Similar explanations apply for the shift toward more water-wet and denser contour at higher pH. To sum up, because the change of pH in this case do not reverse the charging condition, similar qualitative behaviors of wettability alteration remain in spite of quantitative differences. This applies to the change of other parameters as well, as long as the charging condition stays, which can be seen in the following and in the supplement material.

If the change of physical parameters reverses the charging condition, however, then the qualitative behaviors of wettability alteration also change. The contact angle distribution in the oil-brine-sandstone system with the surface site density of oil modified is illustrated in Fig. 15. According to a review paper, the common range of acid and basic site density of oil is, respectively, $0.5\text{--}2.5\text{ nm}^{-2}$ and $0\text{--}2\text{ nm}^{-2}$ (Bonto et al. 2019c). Our previous calculation where $\Gamma(> \text{COOH}) = 0.47\text{ nm}^{-2}$, $\Gamma(> \text{NH}) = 0\text{ nm}^{-2}$ approximately corresponds to one extreme case; thus, here we consider the other three extreme cases. The charging condition of oil is only reversed for the $\Gamma(> \text{COOH}) = 0\text{ nm}^{-2}$, $\Gamma(> \text{NH}) = 0.5\text{ nm}^{-2}$ case, and results indeed show that the contact angle distribution behaves similar to the oil-brine-carbonate system, where the interfaces are also oppositely charged. The other two cases share similar qualitative features with the oil-brine-sandstone system.

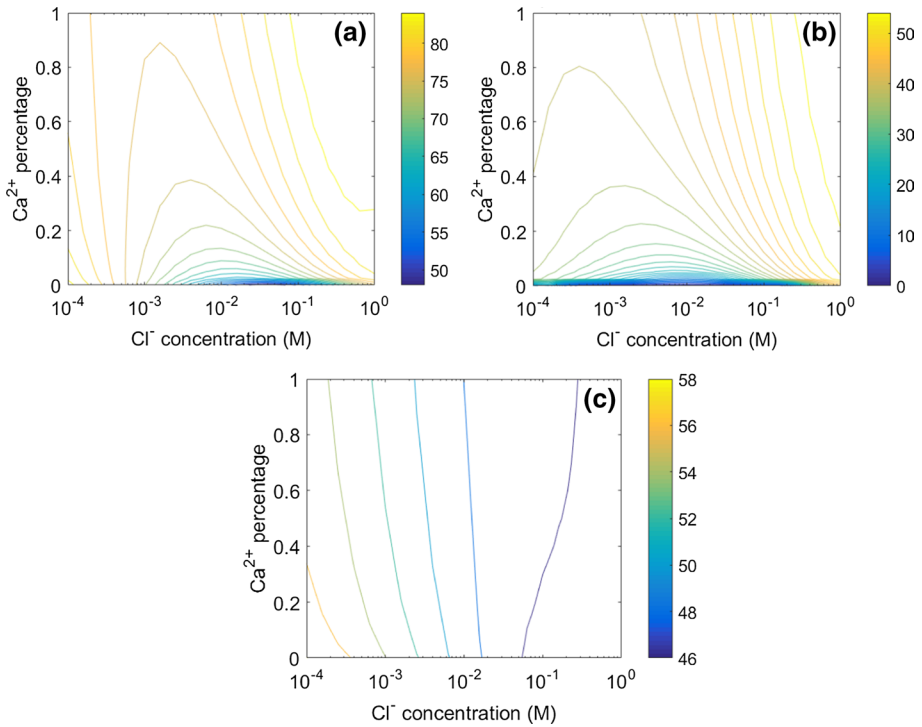


Fig. 15 Contact angle distribution in the oil-brine-sandstone system at different ionic composition at pH=7, with surface sites density of oil modified to be **a** $\Gamma(>\text{COOH})=2.5 \text{ nm}^{-2}$, $\Gamma(>\text{NH})=0.5 \text{ nm}^{-2}$; **b** $\Gamma(>\text{COOH})=2.5 \text{ nm}^{-2}$, $\Gamma(>\text{NH})=0 \text{ nm}^{-2}$; **c** $\Gamma(>\text{COOH})=0 \text{ nm}^{-2}$, $\Gamma(>\text{NH})=0.5 \text{ nm}^{-2}$

In addition to the two typical types of contact angle distribution depending on the EDL interaction being distinctively attractive or repulsive, there is also the possibility that a system behaves in between these two, which means the EDL interaction is only weakly attractive or repulsive and may change direction at different ionic compositions. Ignoring the binding of cation to the surface sites and given $\Gamma(>\text{AH}) = \Gamma(>\text{B})$, it can be derived that a neutrally charged interface requires $K_A = K_B \cdot 10^{-2\text{pH}}$. For the previous oil-brine-carbonate system at pH=7, by keeping $K_A = 10^{-7.3}$ and gradually decreasing K_B , it can be seen in Fig. 16 how the qualitative features of the OBR system go from the typical oil-brine-carbonate system to the in between case and eventually to the typical oil-brine-sandstone system. To conclude, results in this subsection show that the qualitative findings previously obtained from two specific OBR systems are general for various OBR systems as long as the reactions can be described by Eqs. (6, 7, 8).

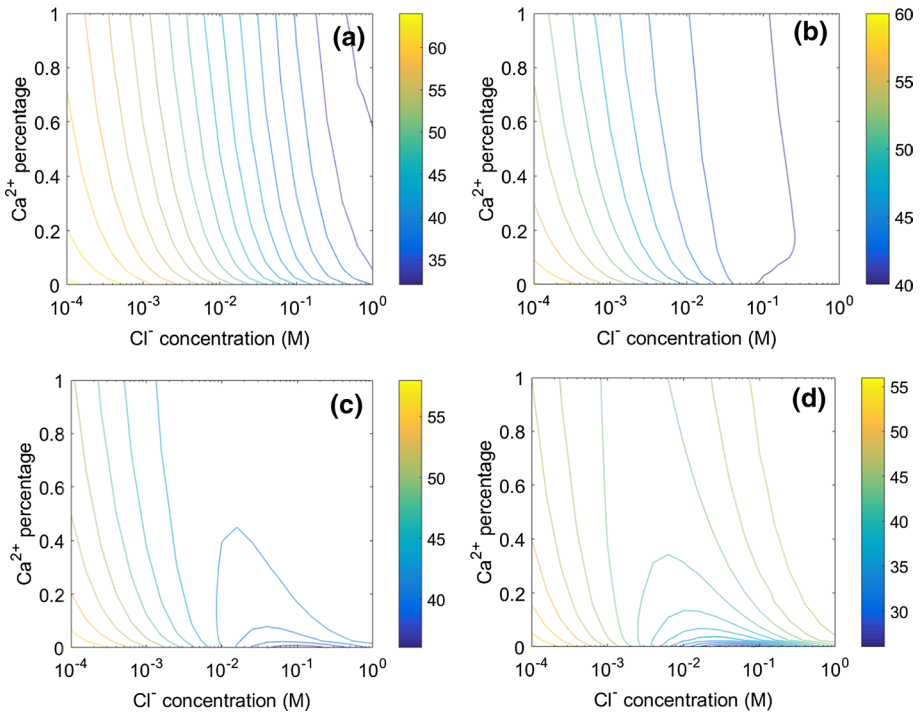


Fig. 16 Contact angle distribution in the oil-brine-carbonate system at different ionic composition at pH=7, with $\log K_B$ modified to be **a** 9; **b** 7; **c** 6; **d** 5

4 Conclusion

This paper studies the ion-tuned wettability in various OBR systems over a wide range of ionic compositions theoretically with focus on two electrokinetic mechanisms, DLE and MIE, thanks to the advanced theoretical tools of solving the complete nonlinear Poisson-Boltzmann equation and obtaining the EDL energy under charge regulation. It is found that there are two typical types of qualitative responses to ion-tuned brine for an OBR system, depending on the EDL interaction being attractive or repulsive. DLE and MIE mechanisms only take effects when EDL force is repulsive, and in which case, DLE contributes to the water-wetness within a relatively high concentration range, and MIE requires nearly complete removal of divalent cation to have a big impact. DLE and MIE can have a synergistic effect in that either DLE or MIE alone has a little effect on wettability but DLE and MIE together have a significant influence. It is worth noting that results in this work cannot be interpreted quantitatively as the extended DLVO theory has been found to be quantitatively inaccurate (Liu, Wang 2020). Current qualitative findings contribute to a better understanding of ion-tuned wettability, provide possible explanations for previous contradictory results and offer new insight for wettability alteration models in ion-tuned waterflooding simulations.

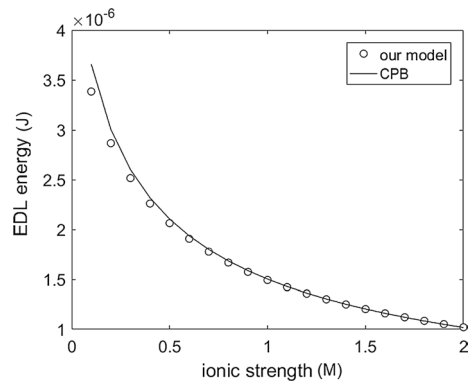
Appendix: On Benchmarks of Current Theoretical Tools

Direct benchmark of our method against experiment is difficult as there is a lack of experimental data. Both the surface properties and the contact angle result in a specific OBR system need to be known, but they were rarely studied at the same time in previous works. Therefore, the benchmark is given indirectly here.

In this work, we focus on the qualitative behaviors, so the method only needs to be proven qualitatively correct. The contact angle theoretically computed under the constant potential or charge boundary condition, which does not require the knowledge of the surface properties, has been validated to qualitatively agree with experiment in multiple works (Alshakhs and Kavscek 2016; Sadeqi-Moqadam et al. 2016; Sanaei et al. 2018). Here we show that as long as the constant potential assumption still applies, which means weak EDLs overlapping, the charge regulation boundary in our method obtains the same EDL energy, and thus, the same contact angle as the constant potential boundary, as illustrated in Fig. 17.

In addition, since our method involves various parameters in the surface complexation models, by modifying those parameters the contact angle results can always be fitted so that they agree with experiments. Although different experimental data will lead to different fitting parameters, in Sect. 3.4 it is shown that our qualitative conclusions are not affected by the difference in parameters, as long as they are within a realistic range. Here the parameters we adopt in the surface complexation models are validated against previous works, as illustrated in Fig. 18. To sum up, (1) the qualitative validations against experiments of the existing "simpler" methods, (2) the ability of our method to be reduced to those "simpler" methods when relevant assumptions made in the "simpler" methods apply, (3) and the ability of our charging models to obtain correct interfacial potential and charge, together provide an indirect validation of our own method. Therefore, it can be safely concluded that the qualitative findings by our method are reliable.

Fig. 17 EDL energy computed by our model and by CPB (constant potential boundary) in the oil-brine-sandstone system without divalent cation at pH = 7. At a relatively high ionic strength where the EDL interaction is weak, our model obtains the same result as CPB



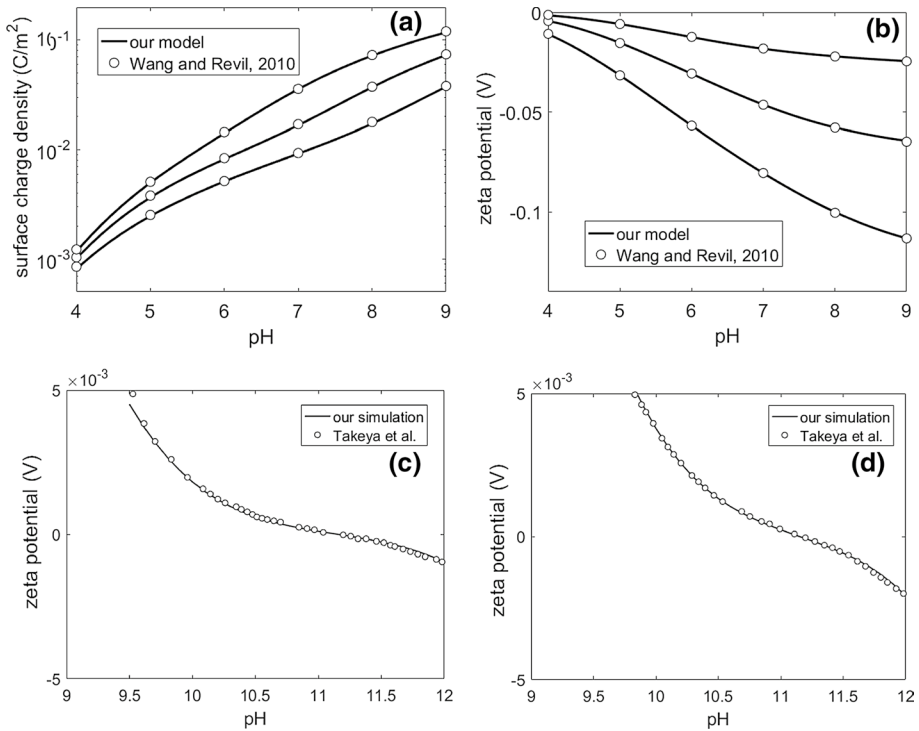


Fig. 18 Validations of the surface complexation models against previous works. **a** Charge density of the sandstone-brine interface; **b** zeta potential of the sandstone-brine interface; **c** zeta potential of the carbonate-brine interface at brine concentration of 0.1 M; **d** zeta potential of the carbonate-brine interface at brine concentration of 0.02 M

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Availability of Data and Materials The original data are not available publicly online but can be provided by the authors for interested researchers.

Code availability The source code is not available publicly online but can be provided by the authors for interested researchers.

Compliance with Ethical Standards

Conflicts of interest There are no conflicts of interest.

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