

## Original article

# Analysis of wettability alteration in low salinity water flooding using a zeta potential-based model

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### Abstract:

This study introduces a zeta potential-based model which connects low salinity water flooding oil recovery to the reservoir wettability. The model assumed that the reservoir wettability is controlled by the electrostatic forces that exist between rock-brine and oil-brine interfaces. Therefore, it links the wettability to the zeta potentials present at the corresponding interfaces. Using the model, various literature oil recovery data were simulated and then statistically compared the trend of the oil recovery factor with the trend of the wettability indicator values. The Pearson correlation coefficient was used for the statistical analysis. The results from the suggested model were compared with the outputs computed from other pre-existing models for wettability alteration. The simulation outcome indicated that a strong relationship exists between reservoir wettability and the zeta potentials produced at the rock-brine and oil-brine interfaces. The Pearson correlation coefficient calculated for the suggested model exceeded 0.7 for all the experimental cases simulated. However, most of the other pre-existing models showed weak relationships between the wettability indicator values and the oil recovery factor, with some models producing the Pearson correlation coefficient below 0.2. This study highlights the role of zeta potentials at the rock-brine and oil-brine interfaces on the wettability alteration during low salinity water flooding. The suggested model can be utilized in the decision making and implementation of low salinity water flooding works.

## 1. Introduction

Low salinity water flooding (LSWF) is one of the enhanced oil recovery strategies utilised to increase the oil recovery factor. This recovery technique has gained considerable attention, and many related research studies have been conducted over the past years. Laboratory experiments have demonstrated that higher oil recovery is achieved with LSWF than the oil produced with conventional water flooding (Mehraban et al., 2021). The observed LSWF oil recovery factor is attributed to wettability alteration (Dang et al., 2013; Jackson et al., 2016; Li and Hu, 2019; Boampong et al., 2022a), where the reservoir is shifted from its initial oil-wet condition towards water-wet condition. Experimental studies suggest that the wettability alteration is evidenced by a change in the oil and water relative permeability curves to one favourable for high

oil recovery (Mahmud, 2022). Thus, while the oil relative permeability is increased, the water relative permeability is reduced during the LSWF process. However, the underlying mechanisms underpinning the wettability alteration process are not well understood. Various studies are conducted to investigate the connection between LSWF oil recovery and changes in the reservoir wettability, and this includes the application of numerical models to simulate the LSWF process (Hiorth et al., 2010; Etemadi et al., 2017; Bonto et al., 2019; Korrani and Jerauld, 2019; Bonto et al., 2020; Tetteh et al., 2022). In numerical modelling, the wettability alteration is modelled via a change in the oil and water relative permeabilities. Therefore, two sets of relative permeability curves are implemented which define the initial and final reservoir states. During a timestep, the relative permeability curves are

interpolated using wettability interpolant. This results in the water-oil relative permeability curves that are consistent with the current state of the reservoir. The wettability alteration is thus measured by the correlation between the wettability indicator and the oil recovery. Thus, the mechanism suggested to induce the wettability alteration is indicated by the wettability indicator (Boampong et al., 2022c).

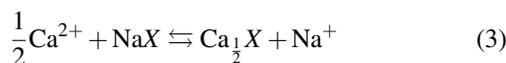
It is worth mentioning that different wettability indicators are found in the literature, however, the predictive capabilities of some of the proposed models are disputed as they failed to accurately calculate the experimental LSWF oil recovery trends. Jerauld et al. (2008) were among the first investigators to propose a model to investigate the LSWF process. The authors indicated that the wettability alteration observed from LSWF is related to the salinity or the ionic strength of the reservoir brine (Jerauld et al., 2008; Korrani and Jerauld, 2019). They suggested that the reservoir is shifted towards water-wet condition when the salinity or the ionic strength of the brine is decreased. Therefore, they proposed a wettability indicator that used the ionic strength or salinities of low-salinity and high-salinity brine as the threshold for the interpolation. The ionic strength and salinity are calculated:

$$\text{ionicstrength} = 0.5 \sum C_i z_i^2 \quad (1)$$

$$\text{salinity} = \sum C_i \quad (2)$$

where  $C_i$  denotes concentration (mol/L) of ionic species  $i$  and  $z_i$  is the charge of ionic species  $i$ . Interestingly, the proposed models disregard the impacts of brine properties (e.g., pH), oil composition, temperature, and mineralogy on the wettability. However, the wettability alteration is not exclusively caused by the salinity of the brine, but rather, it is related to the geochemical reactions that take place inside the reservoir (as the brine is injected). The interactions between the rock, oil, and brine which regulate the wettability are more complex. As a result, describing the LSWF by ionic strength (a single parameter) is inadequate (Bonto et al., 2019). Furthermore, results reported by some researchers showed no relationship between salinity and oil recovery (Fathi et al., 2011; Chandrasekhar et al., 2016).

Other researchers also linked LSWF wettability alteration to equivalent fraction of adsorbed specific ion on the mineral surface (Omekeh et al., 2012; Dang et al., 2013). Equivalent fraction is defined as the amount of the selected ion that can be exchanged at the mineral surface (Dang et al., 2013). The reservoir is water-wet when the equivalent fraction of the chosen ion is increased (Omekeh et al., 2012; Dang et al., 2013). The formulation of this wettability indicator is attributed to the ion exchange mechanism suggested by Lager et al. (2008). In this mechanism, the rock is considered as an exchange, where ions from the aqueous phase can displace the ions on the exchanger. Example of ion exchange reaction is given below:



The equivalent fraction of ion  $i$  is then calculated as:

$$[\text{EQFRA}]_i = \frac{n_i}{n_t} \quad (4)$$

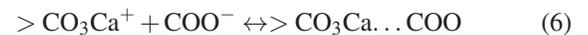
where  $[\text{EQFRA}]_i$  signifies equivalent fraction of ionic species  $i$ ,  $X$  denotes the exchanger, and  $mX$  is the adsorbed ionic species on the rock surface.  $n_i$  corresponds to the moles of sites of the adsorbed ionic species and  $n_t$  is the total moles of sites. It is worth mentioning that ion exchange models do not incorporate a lot of information about the interactions that occur at the rock-brine interface (Sø et al., 2012). Additionally, the interactions between the oil phase and the brine and/or rock are not taken into account, by the ion exchange model. As a result, this model may not be reliable in predicting the LSWF process.

Another widely used wettability indicator in the modelling of LSWF is the bond product sum, BPS, suggested by Brady et al. (2012). According to the authors, the BPS is calculated:

$$\begin{aligned} \text{BPS} = & [> \text{CO}_3 \text{Ca}^{+1.75}] [\text{COO}^-] + [> \text{CO}_3 \text{Mg}^{+1.75}] [\text{COO}^-] \\ & + [> \text{CaOH}_2^{0.25}] [\text{COO}^-] + [\text{CO}_3^{-0.25}] [\text{NH}^+] \\ & + [\text{CaCO}_3^{-1.75}] [\text{NH}^+] + [\text{CaSO}_4^{-1.75}] [\text{NH}^+] \\ & + [\text{COOCa}^+] [\text{CO}_3^{-0.25}] + [\text{COOCa}^+] [\text{CaCO}_3^{-1.75}] \\ & + [\text{COOCa}^+] [\text{CaSO}_4^{-1.75}] + [\text{COOMg}^+] [\text{CO}_3^{-0.25}] \\ & + [\text{COOMg}^+] [\text{CaCO}_3^{-1.75}] + [\text{COOMg}^+] [\text{CaSO}_4^{-1.75}] \end{aligned} \quad (5)$$

The value of the computed BPS corresponds to the wetting condition of the porous medium, and the reservoir is considered water-wet when the estimated bond product sum is lower. On the other hand, oil-wet condition is produced when the BPS is high. However, the model solely relies on the concentrations of surface species and ignores the influence of the water-film thickness that separates the oil from the rock surface. Meanwhile, previous studies have shown that the interaction between the oil and the rock surface is controlled by the thickness of the water-film (Jackson et al., 2016; Boampong et al., 2022a, 2022c).

Qiao et al. (2016) proposed another model which uses the adsorbed carboxylic oil component to model the LSWF. The concentration of carboxylate bonds identified on the rock surface was related to the change in the reservoir wettability. The reservoir becomes oil-wet when much of the carboxylic oil species is adsorbed on the rock surface. Qiao et al. (2016) mentioned that the injection of LSWF releases some of the carboxylic oil components which shifts the reservoir to water-wet state. Eq. (6) shows the mineral-brine-oil reactions, leading to the oil adsorption.



where  $> \text{CO}_3 \text{Ca} \dots \text{COO}$  is the adsorbed carboxylic oil component on the rock surface.  $> \text{CO}_3 \text{Ca}^+$  denotes the rock surface species and  $\text{COO}^-$  is the oil surface species. Decreasing the concentration of the  $> \text{CO}_3 \text{Ca} \dots \text{COO}$  makes the reservoir water-wet. The proposed model, however, has more adjustable parameters and lacks consistency (Bonto et al., 2019). Furthermore, the model ignored the interactions of the basic oil component with the rock surface. Meanwhile, studies have shown that the reservoir wettability can be influenced by the base component (Zhang and Austad, 2005).

Evje and Hiorth (2010), Kazemi et al. (2015), and Kleppe and Khaleadiusti (2018) proposed a wettability indicator using calcite dissolution. According to the authors, calcite dissolution releases some adsorbed oil components, and this makes the reservoir water-wet. Consequently, the suggested wettability indicator is coupled to the dissolved calcite amount. Nonetheless, neither Kazemi et al. (2015) nor Evje and Hiorth (2010) validated their model using experimental data. Furthermore, there was no improvement in the oil recovery when surface reactions were excluded from the model (Kazemi et al., 2015). Similar findings were reported by Kleppe and Khaleadiusti (2018) and Boampong et al. (2022c) who noted a negligible amount of dissolved calcite during the injections of low salinity water.

To accurately simulate the LSWF process, a model that takes into account, the individual ions, and quantifies how they interact with the mineral surface is essential (Hiorth et al., 2008). A wettability indicator involving surface species amounts and zeta potentials ( $\zeta$ -potentials) was recently proposed by Bonto et al. (2019, 2020), however, it was specifically designed for chalk reservoirs. Furthermore, the authors assumed that the wettability alteration is controlled by the acid-base interactions. The work of Boampong et al. (2022c) included the impacts of ion binding interactions and calcite dissolution on the wettability alteration. Some investigators, on the other hand, had employed the concentration of aqueous ions to explore the wettability alteration mechanism, while other studies used the Deryaguin-Landau-Verwey-Overbeek (DLVO theory) to model LSWF process (Alshakhs and Kovscek, 2016; Xie et al., 2017; Taheriotaghsara et al., 2021; Tetteh et al., 2022; Zivar et al., 2022).

It is evident that the complexity of the geochemical reactions involving rock, oil, and brine was not considered by some of the existing models in estimating the reservoir wettability. The models ignored one or more of the influential factors in predicting the wetting state of the reservoir, including oil composition effects, brine composition effects, and mineralogical effects. As such, some of these models failed to predict the experimental LSWF oil recovery factor performed in different reservoir conditions. In this study, the validity of a newly proposed wettability indicator (Boampong et al., 2022a) is evaluated under a variety of experimental conditions so that conclusions can be drawn about its applications for LSWF process. It is hypothesized that crude oil adsorption and reservoir wettability are primarily controlled by the electrostatic force existing at the oil-brine and the rock-brine interfaces. It is worth noting that the model incorporated factors, including brine composition, salinity, pH, oil composition, mineralogy, and temperature, that are suggested to impact the rock-brine-oil interactions. The reliability of the proposed model was analysed statistically, using the Pearson correlation coefficient.

## 2. Methodology

### 2.1 Modelling of rock-brine-oil interface reactions

The carbonate-brine and oil-brine interface reactions were calculated using a triple layer model (TLM) developed in a

previous work (Boampong et al., 2022a, 2022b, 2022c). This model was built in the PHREEQC simulator (Parkhurst, 1995) using the charge-distribution multisite complexation model (CD-MUSIC). The model assumes that the oil phase has two active sites, acidic and basic sites that can interact with the aqueous species. Acid site ( $N_{\text{COOH}}$ ) and base site ( $N_{\text{NH}}$ ) densities were calculated from the total acid number (TAN) and total base number (TBN) of the oil, respectively (Eftekhari et al., 2017):

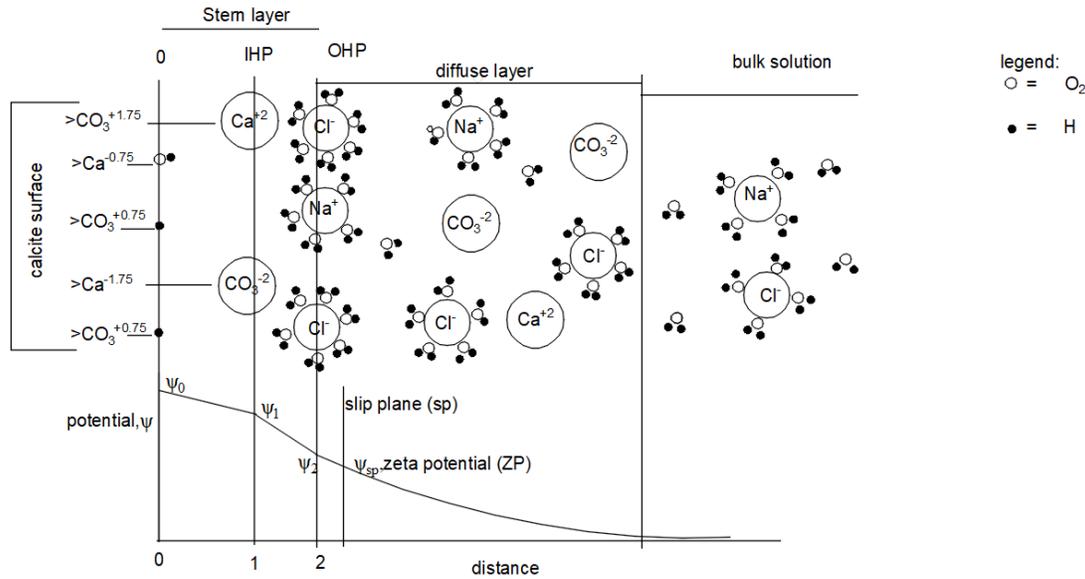
$$N_{\text{COOH}} \left( \frac{\text{no. sites}}{\text{nm}^2} \right) = 0.602 \times 10^6 \times \text{TAN} \left( \frac{\text{mgKOH}}{\text{g} \cdot \text{oil}} \right) \times \frac{1}{1000 \times \text{oil}_{sp} \times \text{MW}_{\text{KOH}}} \quad (7)$$

$$N_{\text{NH}} \left( \frac{\text{no. sites}}{\text{nm}^2} \right) = 0.602 \times 10^6 \times \text{TBN} \left( \frac{\text{mgKOH}}{\text{g} \cdot \text{oil}} \right) \times \frac{1}{1000 \times \text{oil}_{sp} \times \text{MW}_{\text{KOH}}} \quad (8)$$

where  $\text{oil}_{sp}$  corresponds to the oil specific surface area ( $\text{m}^2/\text{g}$ ),  $\text{MW}_{\text{KOH}}$  is the molecular weight of KOH ( $\text{g}/\text{mol}$ ), and  $0.602 \times 10^6$  is a conversion factor (from  $\text{mol}/\text{m}^2$  to  $\text{no. sites}/\text{nm}^2$ ). Two calcite sites were considered when modelling the interactions at the carbonate-brine interface:  $>\text{Ca}$  and  $>\text{CO}_3$  sites. Fractional charge of 0.25 was used for the carbonate sites ( $>\text{Ca}^{+0.25}$ ,  $>\text{CO}_3^{-0.25}$ ) (Stipp, 1999). In contact with the aqueous phase, the carbonate sites become hydrated and produce new complexes ( $>\text{CaOH}^{-0.75}$ ,  $>\text{CO}_3\text{H}^{+0.75}$ ). The model used site-density of  $4.95/\text{nm}^2$  for each of the calcite lattice ions, consistent with literature (Heberling et al., 2011; Li et al., 2016). Moreover, the specific surface area was set to  $1.0 \text{ m}^2/\text{g}$ , for both the oil and rock surfaces (Boampong et al., 2022a). Protonation/deprotonation reactions were assumed to occur at the 0-plane and the adsorption of the counterions were modelled at the Helmholtz planes (Li et al., 2016; Bonto et al., 2019). The adsorbed ions contribute to the surface charge density of the planes. Therefore, the charge of the adsorbed ion is deposited at the plane, except the complex ions (e.g.,  $\text{SHO}_4^{-2}$ ), whose charges are distributed between the 0-plane and 2-plane (Hiemstra and Riemsdijk, 1996). Fig. 1 shows the schematic diagram describing the solid-solution interface reactions as modeled by the triple layer model (Boampong et al., 2022a). The model estimated  $\zeta$ -potential with the assumption that slip plane coincides with the outer Helmholtz plane (Li et al., 2016). Therefore, the potential at the outer Helmholtz plane, as computed by the PHREEQC simulator, is equivalent to the  $\zeta$ -potential (Li et al., 2016; Bonto et al., 2019; Takeya et al., 2019). The rock-brine-oil interface reaction parameters used for the TLM are shown in Table 1. Boampong et al. (2022a) gives detail description of the model.

### 2.2 The wettability indicator

As previously mentioned, the proposed wettability indicator, referred to as adhesion number is calculated from the electrostatic force in the porous medium (Boampong et al., 2022a):



**Fig. 1.** Schematic of the electrical double layer at the rock-brine interface. Three layers describe the Stern layer: 0-plane where protonation and deprotonation reactions occur; 1-plane and 2-plane where counter-ions are adsorbed. The electrical potential decreases away from the rock surface (Boampong et al., 2022a).

$$\begin{cases} \beta = \exp \left[ \frac{F(|\psi_{ob}| + |\psi_{rb}|)}{RT} \right] \times (-1)^n, \text{ for } (\psi_{ob} \times \psi_{rb}) \neq 0 \\ \beta = 0, \text{ for } (\psi_{ob} \times \psi_{rb}) = 0 \end{cases} \quad (9)$$

where  $n = 2$  for  $(\psi_{ob} \times \psi_{rb}) > 0$ ,  $n = 1$  for  $(\psi_{ob} \times \psi_{rb}) < 0$ ,  $\beta$  corresponds to adhesion number (the wettability indicator),  $\psi_{ob}$  is oil-brine interface  $\zeta$ -potential (in volts, V),  $\psi_{rb}$  denotes rock-brine interface  $\zeta$ -potential (V).  $F$  denotes Faraday constant (96,485 C/mol),  $R$  corresponds to universal gas constant (8.314 J/mol), and  $T$  is absolute temperature in K. The above equation was developed using the concept of electrostatic adsorption energy, which is the electrostatic work done (or work released) in moving charge(s) from the bulk solution to a surface of potential  $\psi$  (Hiemstra and Van Riemsdijk, 1996; Bonto et al., 2019). This electrostatic work done is equivalent to  $\exp(F\psi/RT)$  (Hiemstra and Van Riemsdijk, 1996). The oil-brine and rock-brine interfaces were assumed to interact with each other (Bonto et al., 2019). Therefore, the electrostatic work required to separate the two interfaces (repulsive work) or bring them towards each other (attractive) can be computed. Derivation of Eq. (9) is detailed in Boampong et al. (2022a).

It is important to note that  $R$  and  $T$  in Eq. (9) are constants. Therefore, the adhesion number is controlled by the  $\zeta$ -potentials produced at the oil-brine and rock-brine interfaces. It should be noted that the value of the adhesion number gives an indication of the wetting condition of the reservoir. Positive adhesion number is obtained when both the oil-brine and the rock-brine interface  $\zeta$ -potentials are of the same polarity, and this corresponds to repulsive electrostatic force. The reservoir at this state is called water-wet. When the corresponding interfaces attain opposite  $\zeta$ -potentials (opposite polarities), a negative adhesion number is produced, indicating an oil-wet system. However, when the adhesion number is zero, which

occurs when either of the  $\zeta$ -potentials is zero, the reservoir is neutral or intermediate wet. Boampong et al. (2022a) reported simulation results performed with the proposed wettability indicator. However, their work focused on LSWF oil recovery data performed with diluted brines. In this study, the model is extended to complex LSWF conditions such as variable temperature, brine composition, and oil composition, which were not considered in Boampong et al. (2022a). Furthermore, the model is compared with other pre-existing models in the current study. This will enable us to evaluate the validity and applicability of the proposed model.

### 2.3 Statistical evaluation of the wettability indicator

The experimental oil recovery results of Zhang and Austad (2006), Chandrasekhar and Mohanty (2013), and Fathi et al. (2011) were used to evaluate and compare the predictive capability of the proposed model with other pre-existing models. The authors performed LSWF studies under different conditions and assessed the viability of the recovery method by varying some experimental parameters. For instance, Zhang and Austad (2006) investigated the impacts of oil composition, brine composition, and temperature on the LSWF oil recovery factor. The authors used two different oils which have different acid number and base number to conduct the experiment. The composition of the brine was varied by increasing the  $\text{SO}_4^{2-}$  ion concentration or removing NaCl from the brine. Moreover, the studies were performed at 70, 100, and 130 °C. Chandrasekhar and Mohanty (2013), however, performed their experiments at the same temperature and used the same oil type. Meanwhile, the injection brine was altered by either decreasing its salinity or increasing the  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  ions concentration in the brine. The experimental method of

**Table 1.** Adsorption reactions used for the study (Boampong et al., 2022a, 2022c, 2022b).

Interface	Reaction	log(K) 25 °C
Oil-brine	$\text{COOH} \leftrightarrow \text{COO}^- + \text{H}^+$	-4.80
	$\text{NH}^+ \leftrightarrow \text{N} + \text{H}^+$	-3.92
	$\text{COOH} + \text{Ca}^{2+} \leftrightarrow \text{COOCa}^+ + \text{H}^+$	-3.10
	$\text{COOH} + \text{Mg}^{2+} \leftrightarrow \text{COOMg}^+ + \text{H}^+$	-3.58
	$\text{COOH} + \text{Na}^+ \leftrightarrow \text{COONa} + \text{H}^+$	-4.20
	$>\text{CaOH}^{-0.75} + \text{H}^+ \leftrightarrow >\text{CaOH}_2^{+0.25}$	11.80
	$>\text{CaOH}^{-0.75} + \text{CO}_3^{2-} \leftrightarrow >\text{CaCO}_3^{-1.75} + \text{OH}^-$	1.25
Rock-brine	$>\text{CaOH}^{-0.75} + \text{SO}_4^{2-} \leftrightarrow >\text{CaSO}_4^{-1.75} + \text{OH}^-$	2.47
	$>\text{CaOH}_2^{+0.25} + \text{Cl}^- \leftrightarrow >\text{CaOH}_2 \dots \text{Cl}^{-0.75}$	-1.10
	$>\text{CO}_3^{+0.75} \leftrightarrow \text{CO}_3^{-0.25} + \text{H}^+$	-3.54
	$>\text{CO}_3^{+0.75} + \text{Ca}^2 \leftrightarrow >\text{CO}_3\text{Ca}^{+1.75} + \text{H}^+$	-2.90
	$>\text{CO}_3\text{H}^{+0.75} + \text{Mg}^{2+} \leftrightarrow >\text{CO}_3\text{Mg}^{+1.75} + \text{H}^+$	-2.90
	$>\text{CO}_3^{-0.25} + \text{Na}^+ \leftrightarrow >\text{CO}_3 \dots \text{Na}^{+0.75}$	-1.15

Fathi et al. (2011) was similar to that of Zhang and Austad (2006). These studies suggested wettability alteration as the underlying mechanism behind the observed oil recoveries. Hence, the models can be applied to simulate their reported data. It is important to highlight that the models to be tested (the proposed model and the literature models discussed in the introduction section of this study) are based on different mechanisms, therefore, simulating the oil recovery data with the same relative permeability curves can lead to unexpected outcomes. Consequently, the reported final oil recovery is utilised, where trend of the estimated wettability indicator is matched to the trend of the final oil recovery factor. Although this method is a qualitative approach, it can be used to predict how well the models will perform when used to simulate LSWF oil recovery. Similar method has been employed by Bonto et al. (2020), where their proposed model was compared with others, using the remaining oil saturation.

Pearson's correlation coefficient,  $r$ , was used to assess the relationship between the wettability indicator and the oil recovery factor. The Pearson's correlation coefficient measures the linear correlation between two variables. The value of the correlation coefficient range between -1 and 1. A stronger correlation between the variables is indicated by a higher absolute value of the correlation coefficient. A correlation coefficient of zero, however, implies that no relationship exists between the two variables. Considering two variables,  $x$  and  $y$ , the correlation coefficient is calculated from Eq. (10):

$$r = \frac{n \sum x_i y_i - \sum x_i \sum y_i}{\sqrt{n \sum x_i^2 - (\sum x_i)^2} \sqrt{n \sum y_i^2 - (\sum y_i)^2}} \quad (10)$$

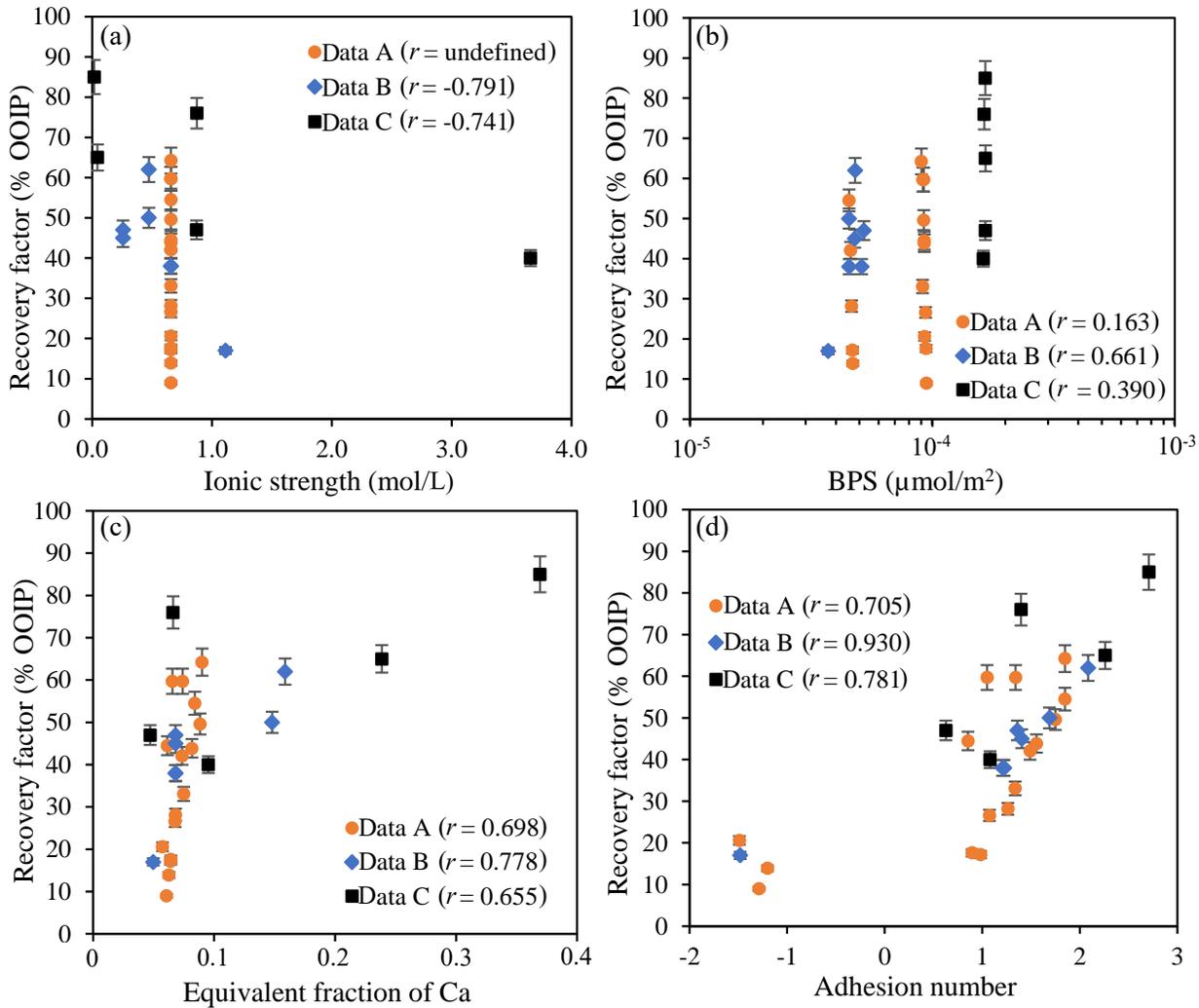
where  $x_i$  and  $y_i$  denotes the sample data points and  $n$  corresponds to the total number of data points. In this study, the values of  $x$  and  $y$  correspond to the values of the wettability indicator and the final oil recovery factor. Therefore, the

absolute value of  $r$  determines the correlation between the wettability indicator and the LSWF oil recovery.

### 3. Results and discussion

Fig. 2(a) shows results of the correlation between ionic strength and the oil recovery factor. For simplicity, the experimental data modelled are denoted as data A, data B, and data C. Data A is the oil recovery factor obtained from Zhang and Austad (2006), data B is the oil recovery factor obtained from Fathi et al. (2011), while Chandrasekhar and Mohanty (2013) oil recovery factor is denoted as data C. The authors of data A performed the experiments using brines with the same ionic strength but varying ionic composition. Moreover, they used different oils, and varied the experimental temperature. As a result, different oil recovery factors were obtained from the various experiments. As previously mentioned, ionic strength model does not consider geochemical reactions in the calculation of the wettability indicator. However, wettability alteration is significantly impacted by the rock-brine-oil reactions which are controlled by various factors (temperature, oil composition, brine composition, mineral composition salinity, pH). Therefore, this wettability indicator (ionic strength) could not account for the variations in the oil recoveries. Meanwhile, the ionic strength model showed good correlation with the oil recovery as it can be seen in data B and data C, the calculated  $r$  values exceeded 0.74. It should be noted that the experiments for data B and data C were performed by using brines with different ionic strengths. Hence, the model showed good results. It can be argued, based on the simulation results that, the reservoir wettability can be altered by changing some parameters (e.g., temperature, brine composition, oil composition) while keeping the ionic strength constant.

The simulation findings demonstrated that no significant correlation exists between BPS and oil recovery. The computed



**Fig. 2.** Relationship between wettability alteration indicators and experimental oil recovery. (a) The correlation between ionic strength and oil recovery factor, (b) correlation between bond product sum and oil recovery factor, (c) relationship between equivalent fraction and oil recovery factor and (d) correlation between adhesion number and oil recovery factor. Data A is the oil recovery factor from Zhang and Austad (2006) while data B is the oil recovery factor from Fathi et al. (2011). Data C, however, is the oil recovery factor from Chandrasekhar and Mohanty (2013). Error bars were calculated assuming  $\pm 5\%$  error (Zhang and Austad, 2005; Bonto et al., 2020).

$r$  for the BPS and the oil recovery factor range between the values of 0.163 and 0.661 for all the experimental cases modelled (Fig. 2(b)). This signifies weak correlation between BPS and LSWF oil recovery factor. As previously mentioned, BPS calculates wettability alteration directly from the surface species, without considering the impact of water-film on the oil adsorption process. This might have led to the observed outcome, where BPS was unable to predict the oil recovery trend accurately. However, equivalent fraction and adhesion number showed good correlation with the oil recovery factor. In contrast to adhesion number, which produced  $r$  values between 0.71 and 0.93, equivalent fraction provided  $r$  values between 0.66 and 0.78. This implies that the proposed model can capture LSWF mechanism and perform better than some existing models. It should be noted that while the equivalent fraction model ignored the effects of oil and mineral com-

position, the suggested model incorporated these parameters on the wettability alteration calculation. Accordingly, adhesion number showed better correlation with the oil recovery factor compared with equivalent fraction. The simulation output suggests that LSWF oil recovery is predominantly caused by the  $\zeta$ -potential obtained at the interfaces. Our findings are consistent with some experimental results. For instance, Sari et al. (2017) noted a strongly water-wet state from their contact angle experiment. According to their findings, the measured  $\zeta$ -potential values were consistent with the observed contact angle values. The authors measured the same polarities of  $\zeta$ -potentials at the oil-brine and rock-brine interfaces, and they asserted that a repulsive double layer force exists in the reservoir rock which shifted the reservoir to a water-wet state. Similar outcomes were reported by Mahani et al. (2015). The experimental results of Jackson et al. (2016) shown that

low salinity brines which generated the same polarities of  $\zeta$ -potentials produced more oil. In contrast, brines which generated opposite polarities of  $\zeta$ -potentials at the oil-brine and rock-brine interfaces could not produce additional oil.

It has been suggested that repulsive interactions between the interfaces contribute to a positive disjoining pressure in the porous media (Myint and Firoozabadi., 2015). Thus, a repulsive force generated from the interface  $\zeta$ -potentials can produce a positive disjoining pressure which stabilises the thin water-film between the oil and rock surface. This shifts the reservoir towards water-wet condition and increase the oil recovery factor (Jackson et al., 2016; Al Maskari et al., 2020; Boampong et al., 2022a, 2022c; Tetteh et al., 2022). Our study confirms the role of  $\zeta$ -potential in the wettability alteration process. It showed that  $\zeta$ -potential is an important parameter in the LSWF oil recovery, and that  $\zeta$ -potential should be considered when planning LSWF projects. For instance, in planning LSWF projects, the low salinity brines should be designed such that the geochemical reactions result in the generation of identical  $\zeta$ -potentials at the interfaces (same polarities) to generate a more water-wet reservoir (Jackson et al., 2016; Boampong et al., 2022a).

#### 4. Conclusion

In this study, a wettability alteration model based on the oil-brine and the rock-brine interface  $\zeta$ -potentials was proposed to simulate the LSWF oil recovery process. The wettability indicator values obtained by the model were statistically compared with the trend of the reported oil recovery factor, using the Pearson correlation coefficient. The outcome of the proposed model was also compared with the results of some pre-existing models. The study observed that some literature models could not accurately predict the experimental oil recovery factors simulated. Most of the pre-existing models produced correlation coefficient values below 0.2, indicating weak relationships between the wettability indicator and the LSWF oil recovery factor. However, the Pearson correlation coefficient obtained from the proposed model exceeded 0.7, signifying a strong correlation between the suggested wettability indicator and the LSWF oil recovery factor. The study demonstrated that LSWF oil recovery is essentially driven by the electrostatic forces produced from the oil-brine and rock-brine interface reactions, and these reactions are influenced by various parameters including temperature, salinity, ionic strength, pH, mineralogy, and oil composition. Consequently, the design of LSWF projects should incorporate brines that generate similar polarities of  $\zeta$ -potentials at the rock-brine and oil-brine interfaces.

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#### Conflict of interest

The authors declare no competing interest.

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#### References

- Al Maskari, N. S., Almobarak, M., Saeedi, A., et al. Influence of pH on acidic oil-brine-carbonate adhesion using atomic force microscopy. *Energy & Fuels*, 2020, 34(11): 13750-13758.
- Alshakhs, M. J., Kovscek, A. R. Understanding the role of brine ionic composition on oil recovery by assessment of wettability from colloidal forces. *Advances in Colloid and Interface Science*, 2016, 233: 126-138.
- Boampong, L. O., Rafati, R., Sharifi Haddad, A. A calibrated surface complexation model for carbonate-oil-brine interactions coupled with reservoir simulation-Application to controlled salinity water flooding. *Journal of Petroleum Science and Engineering*, 2022a, 208(A): 109314.
- Boampong, L. O., Rafati, R., Sharifi Haddad, A. Evaluation of sour gas-low salinity water-flooding in carbonate reservoirs-A numerical simulation approach. *Petroleum Research*, 2022b. (in Press)
- Boampong, L. O., Rafati, R., Sharifi Haddad, A. Modelling of carbonate rock wettability based on surface charge and calcite dissolution. *Fuel*, 2022c, 331: 125856.
- Bonto, M., Eftekhari, A. A., Nick, H. M. A calibrated model for the carbonate-brine-crude oil surface chemistry and its effect on the rock wettability, dissolution, and mechanical properties. Paper SPE 193865 Presented at the SPE Reservoir Simulation Conference, Galveston, Texas, 10-11 April, 2019.
- Bonto, M., Eftekhari, A. A., Nick, H. M. Wettability indicator parameter based on the thermodynamic modeling of chalk-oil-brine systems. *Energy & Fuels*, 2020, 34(7): 8018-8036.
- Brady, P. V., Krumhansl, J. L., Mariner, P. E. Surface complexation modeling for improved oil recovery. Paper SPE 153744 Presented at the SPE Improved Oil Recovery Symposium, Tulsa, Oklahoma, 14-18 April, 2012.
- Chandrasekhar, S., Mohanty, K. K. Wettability alteration with brine composition in high temperature carbonate reservoirs. Paper SPE 166280 Presented at the SPE Annual Technical Conference and Exhibition, New Orleans, Louisiana, 30 September-2 October, 2013.
- Chandrasekhar, S., Sharma, H., Mohanty, K. K. Wettability alteration with brine composition in high temperature carbonate rocks. Paper SPE 181700 Presented at the SPE Annual Technical Conference and Exhibition, Dubai, UAE, 26-28 September, 2016.
- Dang, C. T., Nghiem, L. X., Chen, Z. Modeling low salinity waterflooding: Ion exchange, geochemistry and wettability alteration. Paper SPE 166447 Presented at the SPE Annual Technical Conference and Exhibition, New Orleans, Louisiana, 30 September-2 October, 2013.

- Eftekhari, A. A., Thomsen, K., Stenby, E. H., et al. Thermodynamic analysis of chalk-brine-oil interactions. *Energy & Fuels*, 2017, 31(11): 11773-11782.
- Etemadi, A., Khodapanah, E., Tabatabaei-Nejad, S. A. Modelling low-salinity waterflooding: Effect of divalent cations and capillary pressure. *Journal of Petroleum Science and Engineering*, 2017, 149: 1-8.
- Evje, S., Hiorth, A. A mathematical model for dynamic wettability alteration controlled by water-rock chemistry. *Networks and Heterogeneous Media*, 2010, 5(2): 217-256.
- Fathi, S. J., Austad, T., Strand, S. Water-based enhanced oil recovery (EOR) by "smart water": Optimal ionic composition for EOR in carbonates. *Energy & Fuels*, 2011, 25(11): 5173-5179.
- Heberling, F., Trainor, T. P., Lützenkirchen, J., et al. Structure and reactivity of the calcite-water interface. *Journal of Colloid and Interface Science*, 2011, 354(2): 843-857.
- Hiemstra, T., Van Riemsdijk, W. H. A surface structural approach to ion adsorption: The charge distribution (CD) model. *Journal of Colloid and Interface Science*, 1996, 179(2): 488-508.
- Hiorth, A., Cathles, L. M., Kolnes, J., et al. Chemical modelling of wettability change in carbonate rocks. Paper Presented at the Wettability Conference, Abu Dhabi, UAE, 27-28 October, 2008.
- Hiorth, A., Cathles, L. M., Madland, M. V. The impact of pore water chemistry on carbonate surface charge and oil wettability. *Transport in Porous Media*, 2010, 85: 1-21.
- Jackson, M. D., Al-Mahrouqi, D., Vinogradov, J. Zeta potential in oil-water-carbonate systems and its impact on oil recovery during controlled salinity water-flooding. *Scientific Reports*, 2016, 6: 37363.
- Jerauld, G. R., Lin, C. Y., Webb, K. J., et al. Modeling low-salinity waterflooding. *SPE Reservoir Evaluation & Engineering*, 2008, 11(6): 1000-1012.
- Kazemi, A. K., Fu, W., Sanaei, A., et al. Mechanistic modeling of modified salinity water-flooding in carbonate reservoirs. Paper SPE 175102 Presented at the SPE Annual Technical Conference and Exhibition, Houston, Texas, 28-30 September, 2015.
- Kleppe, R., Khalediadusti, K. Studying the potential of calcite dissolution on oil liberation from rock surfaces during single-well-chemical-tracer tests by coupling a multiphase flow simulator to the geochemical package. *Journal of Petroleum & Environmental Biotechnology*, 2018, 9(1): 1000359.
- Korrani, A. K. N., Jerauld, G. R. Modeling wettability change in sandstones and carbonates using a surface-complexation-based method. *Journal of Petroleum Science and Engineering*, 2019, 174: 1093-1112.
- Lager, A., Webb, K. J., Black, C. J. J., et al. Low salinity oil recovery-An experimental investigation. *Petrophysics*, 2008, 49: 28-35.
- Li, S., Hu., S. A brief review of the correlation between electrical properties and wetting behaviour in porous media. *Capillarity*, 2019, 2(3): 53-56.
- Li, S., Leroy, P., Heberling, F., et al. Influence of surface conductivity on the apparent zeta potential of calcite. *Journal of Colloid and Interface Science*, 2016, 468: 262-275.
- Mahani, H., Keya, A. L., Berg, S., et al. Insights into the mechanism of wettability alteration by low-salinity flooding (LSF) in carbonates. *Energy & Fuels*, 2015, 29(3): 1352-1367.
- Mahmud, W. N. Impact of salinity and temperature variations on relative permeability and residual oil saturation in neutral-wet sandstone. *Capillarity*, 2022, 5(2): 23-31.
- Mehraban, M. F., Ayatollahi, S., Sharifi, M. Experimental investigation on synergic effect of salinity and pH during low salinity water injection into carbonate oil reservoirs. *Journal of Petroleum Science and Engineering*, 2021, 202: 108555.
- Myint, P. C., Firoozabadi, A. Thin liquid films in improved oil recovery from low-salinity brine. *Current Opinion in Colloid & Interface Science*, 2015, 20(2): 105-114.
- Omekeh, A., Friis, H. A., Fjelde, I., et al. Modeling of ion-exchange and solubility in low salinity water flooding. Paper SPE 154144 Presented at the SPE Improved Oil Recovery Symposium, Tulsa, Oklahoma, 14-18 April, 2012.
- Parkhurst, D. L. User's guide to PHREEQC, a computer program for speciation, reaction path, advective-transport, and inverse geochemical calculation. U.S. Geological Survey, 1995.
- Qiao, C., Johns, R., Li, L. Understanding the chemical mechanisms for low salinity water-flooding. Paper SPE 180138 Presented at the SPE Europec Featured at 78<sup>th</sup> EAGE Conference and Exhibition, Vienna, Austria, 30 May-2 June, 2016.
- Sari, A., Xie, Q., Chen, Y., et al. Drivers of low salinity effect in carbonate reservoirs. *Energy & Fuels*, 2017, 31(9): 8951-8958.
- Sø, H. U., Postma, D., Jakobsen, R., et al. Competitive adsorption of arsenate and phosphate onto calcite; experimental results and modeling with CCM and CD-MUSIC. *Geochimica et Cosmochimica Acta*, 2012, 93: 1-13.
- Stipp, S. L. S. Toward a conceptual model of the calcite surface: Hydration, hydrolysis, and surface potential. *Geochimica et Cosmochimica Acta*, 1999, 63(19-20): 3121-3131.
- Taheriotaghsara, M., Bonto, M., Nick, H. M., et al. Estimation of calcite wettability using surface forces. *Journal of Industrial and Engineering Chemistry*, 2021, 98: 444-457.
- Takeya, M., Shimokawara, M., Elakneswaran, Y., et al. Predicting the electrokinetic properties of the crude oil/brine interface for enhanced oil recovery in low salinity water flooding. *Fuel*, 2019, 235: 822-831.
- Tetteh, J. T., Barimah, R., Korsah, P. K. Ionic interactions at the crude oil-brine-rock interfaces using different surface complexation models and DLVO theory: Application to carbonate wettability. *ACS Omega*, 2022, 7(8): 7199-7212.
- Xie, Q., Brady, P. V., Pooryousefy, E., et al. The low salinity effect at high temperatures. *Fuel*, 2017, 200: 419-426.
- Zhang, P., Austad, T. The relative effects of acid number and

- temperature on chalk wettability. Paper SPE 92999 Presented at the SPE International Symposium on Oilfield Chemistry, The Woodlands, Texas, 2-4 February, 2005.
- Zhang, P., Austad, T. Wettability and oil recovery from carbonates: Effects of temperature and potential determining ions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2006, 279(1-3): 179-187.
- Zivar, D., Ishanov, A., Pourafshary, P. Insights into wettability alteration during low-salinity water flooding by capacitance-resistance model. *Petroleum Research*, 2022, 7(4): 500-510.