A Surface Complexation Model of Alkaline-SmartWater Electrokinetic Interactions in Carbonates

Moataz Abu-Al-Saud[*], Amani Al-Ghamdi, Subhash Ayirala, and Mohammed Al-Otaibi

Saudi Aramco, EXPEC Advanced Research Center, Dhahran, Saudi Arabia

Abstract. Understanding the effect of injection water chemistry is becoming crucial, as it has been recently shown to have a major impact on oil recovery processes in carbonate formations. Various studies have concluded that surface charge alteration is the primary mechanism behind the observed change of wettability towards water-wet due to SmartWater injection in carbonates. Therefore, understanding the surface charges at brine/calcite and brine/crude oil interfaces becomes essential to optimize the injection water compositions for enhanced oil recovery (EOR) in carbonate formations. In this work, the physicochemical interactions of different brine recipes with and without alkali in carbonates are evaluated using Surface Complexation Model (SCM). First, the zeta-potential of brine/calcite and brine/crude oil interfaces are determined for Smart Water, NaCl, and Na_2SO_4 brines at fixed salinity. The high salinity seawater is also included to provide the baseline for comparison. Then, two types of Alkali (NaOH and Na_2CO_3) are added at 0.1 wt% concentration to the different brine recipes to verify their effects on the computed zeta-potential values in the SCM framework. The SCM results are compared with experimental data of zeta-potentials obtained with calcite in brine and crude oil in brine suspensions using the same brines and the two alkali concentrations. The SCM results follow the same trends observed in experimental data to reasonably match the zeta-potential values at the calcite/brine interface. Generally, the addition of alkaline drives the zeta-potentials towards more negative values. This trend towards negative zeta-potential is confirmed for the Smart Water recipe with the impact being more pronounced for Na_2CO_3 due to the presence of divalent anion carbonate $(CO_3)^{-2}$. Some discrepancy in the zeta-potential magnitude between the SCM results and experiments is observed at the brine/crude oil interface with the addition of alkali. This discrepancy can be attributed to neglecting the reaction of carboxylic acid groups in the crude oil with strong alkali as NaOH and Na_2CO_3. The novelty of this work is that it clearly validates the SCM results with experimental zeta-potential data to determine the physicochemical interaction of alkaline chemicals with SmartWater in carbonates. These modeling results provide new insights on defining optimal SmartWater compositions to synergize with alkaline chemicals to further improve oil recovery in carbonate reservoirs.

1. Introduction

Water ionic composition in the waterflooding process plays a crucial role in oil recovery for carbonate formations [1]. The chemistry of injected water strongly affects the reservoir wettability, which has been proven and observed in numerous laboratory and field studies for both carbonates and sandstones [2-4]. Modifying the water chemistry to alter the rock wettability is known as SmartWater or low salinity [5]. However, the root causes of this wettability alteration effect, which takes place at the pore-level, remain poorly understood especially for carbonates [6]. This lack of fundamental understanding of root causes of wettability alteration has resulted in conflicting studies, where some studies have observed an increase in oil recovery while other cases have not shown an increment in oil recovery [7]. Various pore-scale mechanisms have been proposed to delineate the wettability alteration process in carbonates. Some of these plausible mechanisms include electric double layer [4],

in-situ soap generation (saponification effect) [8], and multi-ion exchange [9]. The surface charges of carbonate/brine and crude oil/brine are altered in such pore-scale processes, which affects the zeta-potential measurements used in understanding the rock wettability [10,11].

Recently, the synergy between tailored water salinity and enhanced oil recovery (EOR) has gained a lot of attraction [12]. For polymer EOR, it has been shown that the use of tailored salinity (SmartWater) reduces the polymer consumption used to increase the injected water viscosity [13]. For surfactant-based EOR, it has been observed that decreasing the water salinity increases the effect of surfactant on crude oil/brine through efficiently reducing the interfacial tension [14]. It is well-known that surfactants are adsorbed on carbonate rock surfaces. Therefore, a large amount of chemical surfactant is consumed before the chemical reaches the crude oil/brine

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[*] Corresponding author: moataz.abualsaud@aramco.com

interface. To minimize surfactant adsorption on carbonate rock surfaces, alkaline is added to the injected water [15]. The alkaline chemical reacts with both crude oil/brine and calcite/brine interfaces. The reaction of alkali and naphthenic acid in crude oil generates in-situ soap that locally reduces the interfacial tension of the crude oil/brine interface. For the calcite surface, the adsorption of alkali changes the electric charges balance on the calcite/brine interface which alters the carbonate wettability towards more water-wet state [15]. Therefore, understanding the electrokinetics of brine with alkaline chemicals in carbonates is crucial to define the optimal water compositions for improving oil recovery.

There are several electrokinetic studies involving zeta-potentials that have reported the synergy effect of water salinity, crude oil, and alkaline in carbonates for crude oi/brine [17, 18] and calcite/brine interfaces [15, 16]. To the best of our knowledge, the role of individual ions in different brine compositions in the presence of alkaline chemicals for both the calcite/brine and crude oil/brine interfaces has not been previously studied using a surface chemistry model and lab measurements. In this work, we study the electrokinetics of with various brine recipes interacting with crude oil and calcite with and without alkali chemicals using a surface complexation model (SCM). We validate the modeling results with zeta-potentials of calcite/brine and crude oil/brine interfaces measured in the lab.

The outline of this work is as follows; a brief summary of the experimental setup for zeta-potential measurement is presented in section 2, followed by the surface complexation model (SCM). Then, the results of the SCM and lab measurements are shown in section 3. The conclusion and summary are included in section 4.

2. Materials and Methods

2.1. Experiment

Rock sample:
Pure calcium carbonate is used to represent the calcite rock sample. The purity of the calcite disk sample is measured using x-ray diffraction (XRD), which is composed of 99 wt. % of CaCO₃ as shown in **Figure 1**. The calcite purity confirms that there are no mineral impurities interfering with the ion adsorption on the calcite surface. The calcite disk is manually grinded using a granite mill for 30 minutes at atmospheric conditions far from contaminants to avoid surface impurities.
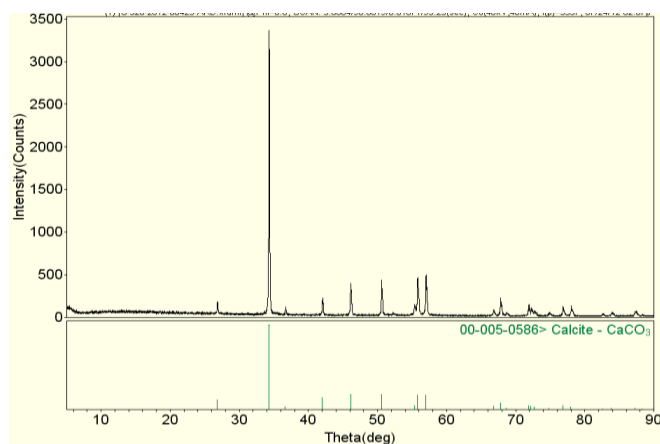

Figure 1: X-ray diffraction (XRD) diffractograms of calcite disk with reference patterns of pure calcite compound. The x-ray wavelength is 1.54 Å.

Brine and Crude Oil Properties:
Synthetic brine ionic compositions are prepared by adding different salts to deionized water. The ionic composition of the considered brine samples is listed in **Table 1**. The crude oil properties are shown in **Table 2**.

Alkaline chemicals:
Two types of Alkali (NaOH and Na₂CO₃) are added at 0.1 wt% concentration (1000 ppm) relevant to each brine recipe. Typically, alkali chemicals increase the brine pH level, which causes calcium and magnesium ions to precipitate as Ca(OH)₂ and Mg(OH)₂ respectively. Therefore, the addition of alkali to seawater is not considered to avoid precipitation, as seawater contains a high ionic concentration of hardness ions such as Mg^{2+} and Ca^{2+}. **Table 3** lists the equilibrium pH level of different brines including alkali chemicals. The brine pH is measured after reaching equilibrium with alkaline and calcite suspensions without manually adjusting the pH level.

Zeta-potential measurement:
The measurement of zeta-potential is conducted using phase analysis light scattering technique (zeta PALS) applied to calcite in brine and crude oil emulsion in brine samples. 0.2 g of grinded pure calcite particles were thoroughly mixed with 50 cm³ of different brines for a minimum of 48 hours to ensure suspension and equilibrium are achieved. The ratio of solid/liquid and liquid/liquid is fixed throughout the experiment to guarantee consistency in the reported values. The brine pH level is not manually adjusted. The oil droplets and calcite particles size distribution in different brines is determined using optical microscopy, similar to the approach in [19]. The average calcite particle size distribution is estimated to be around 10 μm, while the average oil droplet size is between 14-35μm. Sonification is used to avoid calcite particle aggregation or crude oil coalescence in brine suspensions. The zeta-potential values are determined using Smoluchowski approximation based on the electrophoretic mobility of brine suspensions. Each zeta-potential measurement is

repeated three times to ensure consistent results. The measurement variation for each reported zeta-potential value is within 3 mV. Additional details on the sample preparation and experimental zeta-potential measurement procedures can be found in [19].

Table 1. The composition of different synthetic brines used in this study.

Brine samples (concentration mg/L)				
	Seawater	**SmartWater**	**NaCl**	**Na₂SO₄**
Ions				
Na^+	18,300	1824	2266	1865
Cl^-	32,200	3220	3495	-
Ca^{2+}	650	65	-	-
Mg^{2+}	2,110	211	-	-
SO_4^{-2}	4,290	429	-	3896
$HCO3-$	120	-	-	-
Total dissolved Solids, ppm	57,670	5,761	5,761	5,761
pH	7.45	7.4	6.3	6.11

Table 2. Crude Oil Properties

API	27.1
Acid Number mg KOH/g	0.47
Base Number mg KOH/g	0.04
Saturates (%)	50.6
Asphaltenes (%)	1.6
Resins (%)	20.7
Aromatics (%)	27.1

Table 3. Equilibrium pH values of calcite suspension in different electrolytes containing alkali.

Type of electrolyte	pH CaCO₃	pH CaCO₃ (NaOH 0.1 wt.%)	pH CaCO₃ (Na₂CO₃ 0.1 wt.%)
Na₂SO₄	9.85	12	10
NaCl	9.4	11.33	10
SmartWater	8.6	11.7	10
Seawater	7.45	-	-

2.2 Surface Complexation Model

The surface complexation model (SCM) describes the equilibrium state of ion adsorption based on specified surface reactions. The surface reactions of ions give rise to surface electric charges. For calcite/brine/crude-oil system, the adsorption of ions on crude-oil/brine and calcite/brine interfaces determine the surface charges and the corresponding zeta-potentials. The SCM has been employed to gain insight on the effect of electrokinetics on wettability in the context of brine chemistry in carbonates [20,21,24,25]. Brady *et al.* [21] used SCM

based on surface reactions proposed in [22,23] to predict zeta-potentials for both rock/brine and brine/crude-oil interfaces in sandstone and carbonate rocks. However, the SCM has not been validated with experimental zeta-potential measurements. Mahani *et al.* [24] studied the electrokinetics of carbonate-based rocks with different water salinities using SCM. The SCM results were qualitatively validated with different carbonate/brine zeta-potential measurements. Song *et al.* [25] applied SCM and reported quantitative agreement with experimental zeta-potential measurements of synthetic calcite and multiple brine recipes. The SCM surface reactions are based on the model proposed in [26], which includes different SCM reactions compared to the models in [21,24]. The SCM work of Song *et al.* [25] has been recently extended to include surface reactions of organic and inorganic impurities occurring in natural carbonates [27]. In this work, we use SCM with surface reactions similar to the approach in [25] to predict zeta-potentials for pure calcite and different brine recipes with and without alkali chemicals. In addition, we determine brine/crude oil zeta-potentials by modeling SCM reactions at the brine/crude oil interface. **Tables 4 and 5** list the surface reactions and the corresponding equilibrium constants for both calcite and crude oil surfaces. The non-integer surface charge values of $> CaOH^{-0.75}$ and $> CO_3H^{+0.75}$ hydrated calcite sites is due to the structure of calcite crystal. The ionic bonding between Ca and O atoms from $(CO_3)^{-2}$ gives an effective charge of +1/3 for Ca atoms [26]. In this model, a charge of +1/4 is assumed for Ca atoms, following the approach in [25,26]. The crude oil surface reactions are similar to the models used in [20,21,28]. The SCM equations are solved using PHREEQC software [29], whereby the double layer model is specified. In the model, the concentration of adsorbed surfaces complexes (adsorbed ions) determines the total surface charge as follows:

$$\sigma = \frac{F}{SA}\Sigma z_i c_i, \qquad (1)$$

where σ is the surface charge density (C/m²), F is the Faraday constant (96493.5 C/mol), S is the surface material mass (g), A is the specific surface area (m²/g), z_i is the ionic electric charge, and c_i is the adsorbed ion concentration (mol). The surface charge and surface-potential are related through the Gouy-Chapman model [29]:

$$\sigma = (8000\epsilon_o\epsilon_w RTI)^{1/2} \sinh\left(\frac{\nu F\Psi.}{2RT}\right), \qquad (2)$$

where ϵ_o is the vacuum permittivity $\left(\frac{C^2}{mJ}\right)$, ϵ_o is the water relative permittivity, Ψ is the surface-potential (V), R is the gas constant $\left(\frac{J}{mol\,K}\right)$, T is the temperature (K), I is the brine ionic strength (mol/l), and ν is the electrolyte ionic charge which is assumed to be unity in PHREEQC [29]. The bulk concentration of ions interacts with the adsorbed ions at the surface due to coulombic forces. Hence, the apparent equilibrium constants are considered to include the effect of bulk concentration of the ions. The apparent

and intrinsic equilibrium constants (listed in Tables 4 and 5) are described through the Boltzmann distribution [29]:

$$K_{app} = K_{int} \exp\left(\frac{Z_c F \Psi.}{RT}\right), \qquad (3)$$

where Z_c is the net change of the surface charge at the surface due to surface reaction. The zeta-potential ζ can be approximated from the surface-potential based on the linearized Debye-Huckel theory [25], which is valid for $|\Psi| \leq 25$ mV [30]:

$$\zeta = \psi \exp(-\kappa d_s), \qquad (4)$$

where κ is the inverse Debye length-scale, and d_s is the slipping plane distance from the outer Helmholtz plane. For brines with ionic-strength of 0.1 mol/l (the considered brine recipes except for sea water), the slipping distance d_s is 0.33 nm [25, 26], while the Debye length κ^{-1} is 0.97 nm. For the seawater case (ionic strength of 1.1 mol/l), d_s is 0.1 nm ($d_s = 0.1/c^{0.5}$ [26]), while κ_{sw}^{-1} is 0.29 nm. The site density for calcite surface is 4.95 sites/nm² [26, 27], while the crude oil surface has a site density of 0.47 sites/nm² [28]. The calcite specific surface area is 1 m²/g [26], while the crude oil specific area is 0.5 m²/g [28]. Additional details of the above SCM equations are elaborated in [29,31].

Table 4. Surface Complexation Reactions and Parameters for the Calcite Surface.

Calcite Surface Reaction	Equilibrium Constant ($\log_{10} K_{int}$)
$> CaOH^{-0.75} + H^+ \leftrightarrow > CaOH_2^{+0.25}$	0.4
$> CO_3H^{+0.75} + OH^- \leftrightarrow > CO_3^{-0.25} + H_2O$	0.5
$> CaOH^{-0.75} + Ca^{2+} \leftrightarrow > CaOH..Ca^{+1.25}$	1.53
$> CaOH^{-0.75} + Mg^{2+} \leftrightarrow > CaOH..Mg^{+1.25}$	1.15
$> CO_3H^{+0.75} + SO_4^{2-} \leftrightarrow > CO_3H..SO_4^{-1.25}$	1.5
$> CO_3H^{+0.75} + CO_3^{2-} \leftrightarrow > CO_3H..CO_3^{-1.25}$	2.23
$> CO_3H^{+0.75} + HCO_3^- \leftrightarrow > CO_3H..HCO_3^{-0.25}$	0.09
$> CaOH^{-0.75} + Na^+ \leftrightarrow > CaOH..Na^{+0.25}$	0.22
$> CO_3H^{+0.75} + Cl^- \leftrightarrow > CO_3H..Cl^{-0.25}$	0.65

Table 5. Surface Complexation Reactions and Parameters for the Crude Oil Surface.

Crude Oil Surface Reaction	Equilibrium Constant ($\log_{10} K_{int}$)
$-COOH \leftrightarrow -COO^- + H^+$	6
$-N + H^+ \leftrightarrow -NH^+$	4
$-COOH + Ca^{+2} \leftrightarrow -COOCa^+ + H^+$	-4
$-COOH + Mg^{+2} \leftrightarrow -COOMg^+ + H^+$	-4.3
$-COOH + Na^+ \leftrightarrow -COONa + H^+$	-4

3. Results and Discussion

Figures 2 to 7 compare the SCM and experimental measurements of the zeta-potential values for different brine recipes with and without alkali. First, the zeta-potentials for brine/calcite interface are analyzed, followed by the brine/crude oil interface. The intrinsic

equilibrium constants are varied in the SCM to match the measured zeta-potentials. The number of fitting parameters is equal to the number of surface reaction equations (nine equations for calcite/brine interface, and five equations for the crude oil/brine interface). The site density and specific surface area of the considered surfaces are fixed (see **Section 2.2**). For the brine/calcite interface (**Figures 2-4**), the SCM results follow the trends observed in experimental data, and quantitatively agree with the lab zeta-potential measurements especially for NaCl, SmartWater, and Na₂SO₄ brines. For the seawater case without alkali, the SCM underestimates the zeta-potential as can been seen in **Figure 2**. When NaOH alkaline is added to the brine recipes, the change in zeta-potential values of calcite/brine interface is almost negligible and in agreement with the experimental zeta-potential measurements as illustrated in **Figure 3** (within 2.5 mV difference). The addition of (OH)⁻ ions increases the negative charge, and decreases the adsorption of H⁺ protons while adding Na⁺ ions increase the charge positivity resulting in an insignificant total change in the surface charge. For the Na₂CO₃ alkaline, the SCM calcite/brine zeta-potentials decrease for the considered brine recipes as displayed in **Figure 4**. This decrease in zeta-potential values is mainly due to the presence of divalent anion carbonate $(CO_3)^{-2}$, which forms a surface complex on the calcite surface with a -1.25 charge as illustrated in reaction 6 in **Table 3**. Calcite precipitation/dissolution has not been considered in SCM, which is likely to contribute to the slight discrepancy observed in the SmartWater recipe case in **Figure 4**. The intrinsic equilibrium constants (fitting parameters) in **Table 4** are in agreement with the work of Song et al. [25] except for the Cl⁻ ion which has the largest discrepancy. The SCM confirms that the total surface charge and zeta-potential of calcite/brine interface strongly depend on the divalent ions (Ca^{2+}, Mg^{2+}, CO_3^{2-}, and SO_4^{2-}) due to large intrinsic equilibrium constants compared to the other ions. The SCM predicts that the most effective ion in pushing the calcite surface charge to a negative value is the divalent anion carbonate $(CO_3)^{-2}$, which has the largest equilibrium constant.

For the crude oil/brine interface cases, the SCM zeta-potential results qualitatively match the experimental observations. The predicted zeta-potentials are in general negatively charged as shown in **Figure 5**, which agree with the experimental results. The equilibrium constants in **Table 5** agree with the values reported in the literature [21,28] (the discrepancy in the equilibrium constants are within a value of one for each reaction). At pH > 7 (greater than the isoelectric point for crude oil/brine interface with a similar acid number [32]), the carboxylic acids in crude oil are not completely protonated (reaction 1 in **Table 5**). Also, the protonation of nitrogen bases (reaction 2 in **Table 5**) is not sufficient to switch the crude oil surface to a positive charge. When alkali is added to the brine recipe (**Figures 6 and 7**), the variation in SCM zeta-potentials is less than 2 mV. The zeta-potentials slightly increase in the positive side, especially for NaOH alkaline. This slight increase is not expected as the protonation activity decreases with the increase of the brine pH level.

However, the reactions in SCM predict that the adsorption of Mg^{2+} and Ca^{2+} (reactions 3 and 4) slightly compensates for the decrease in H^+, which results in a small increase in the zeta-potential. Based on the model predictions of calcite/brine and brine/crude oil zeta-potentials, the Na_2SO_4 brine with Na_2CO_3 alkaline provides the largest interface negative charges (**Figures 4 and 7**). The modeling results support the conclusion drawn from the experiments that the Na_2SO_4 brine with Na_2CO_3 alkaline is the preferable brine recipe to synergize with anionic surfactants due to its large negative zeta-potential. This large negative zeta-potential increases the water-wetness towards carbonate reservoir [16] and reduces the anionic surfactant retention [15]. Further improvement and refinement in the SCM will be considered as this is a starting point for ongoing research in electrokinetic modeling. Such improvements include using an SCM triple-layer model, non-linear diffuse double layer model to infer zeta-potential from the surface-potential, and adding dissolution/percipation reactions for the calcite/brine interface. Also, including the crude oil chemistry (acid/base numbers) to be part of the surface site density [33] of nitrogen base and carboxylate groups will improve the SCM for the crude oil/brine interface.
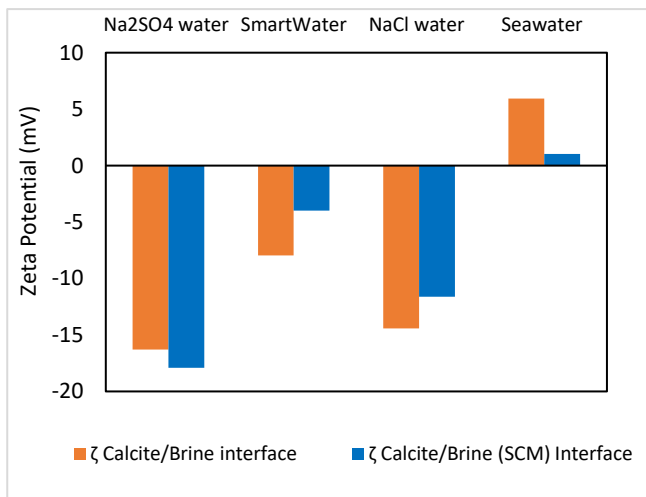

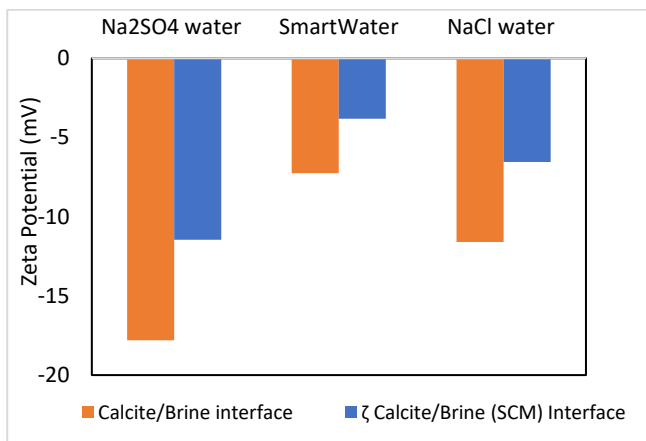**Figure 2:** Experimental and SCM ζ- potential values at the calcite/brine interface

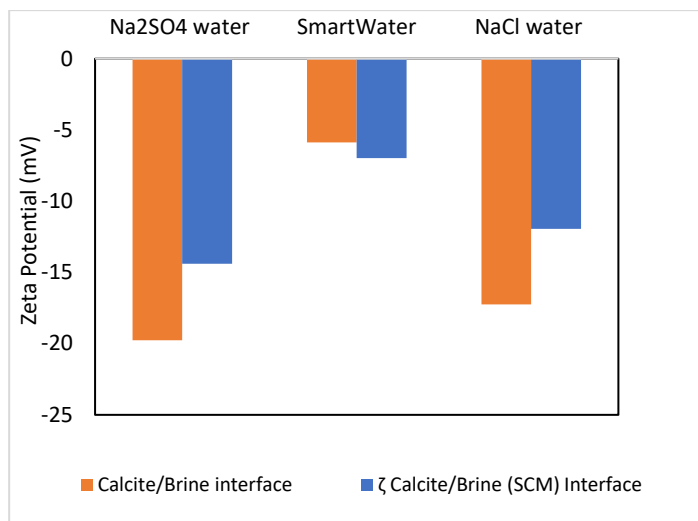**Figure 3:** Experimental and SCM ζ- potential values at the calcite/brine interface. Brine is containing 0.1 wt.% NaOH.

Figure 4: Experimental and SCM ζ- potential values at the calcite/brine interface. Brine is containing 0.1 wt.% Na_2CO_3.
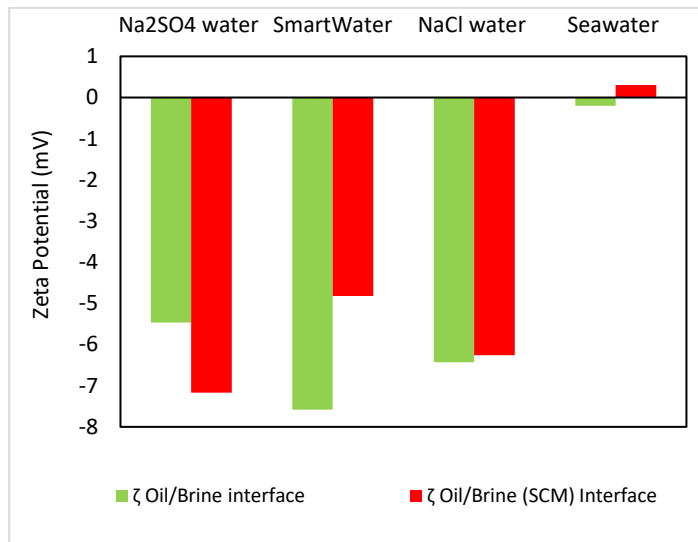

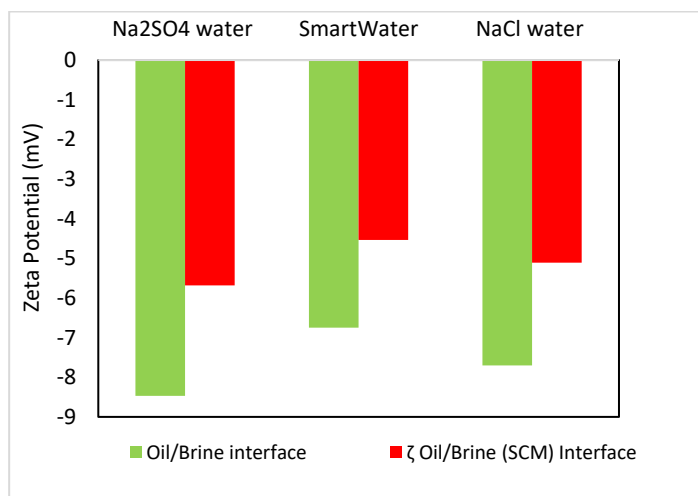**Figure 5:** Experimental and SCM ζ- potential values at oil/brine interface.

Figure 6: Experimental and SCM ζ- potential values at oil/brine interface. Brine is containing 0.1 wt.% NaOH.
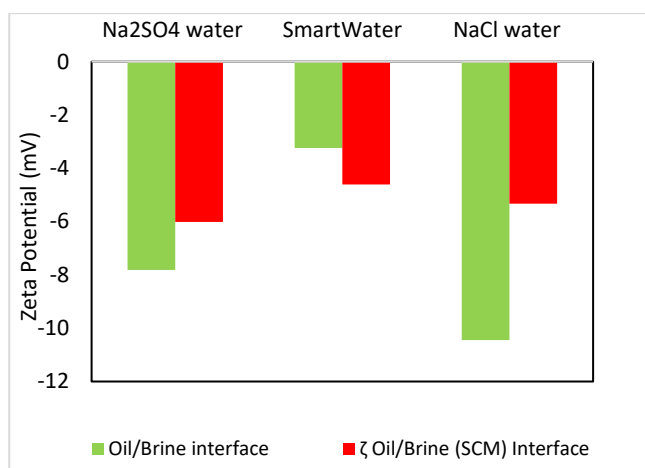
Figure 7: Experimental and SCM ζ- potential values at oil/brine interface. Brine is containing 0.1 wt.% Na_2CO_3.

4. Conclusions

This work explores the electrokinetic interactions of different brine recipes with and without alkali in carbonates using Surface Complexation Model (SCM). Various SCM calculations of brine/calcite and crude oil/brine zeta-potentials are conducted to evaluate the synergy between different brine recipes and alkali chemicals. The proposed SCM predicts zeta-potential results that are consistent with the experimental measurements for choosing the Na_2SO_4 brine with Na_2CO_3 alkaline to be the most suitable alkaline-based recipe due to its large negative zeta-potentials. In alkaline/surfactant EOR process, the negative electrokinetic calcite charge repels the anionic surfactant causing a reduction in surfactant retention. The modeling of zeta-potential results quantitatively agree with the experiments for the calcite/brine interface. For the crude oil/brine interface, the SCM zeta-potential results reasonably match the experimental measurements. Further correlation of the carboxylic acid group and nitrogen base crude oil active surface sites with the acid/base number is required [33] to quantitatively predict accurate zeta-potentials and gain additional insights on the electrokinetics of crude oil surfaces.

Acknowledgements

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