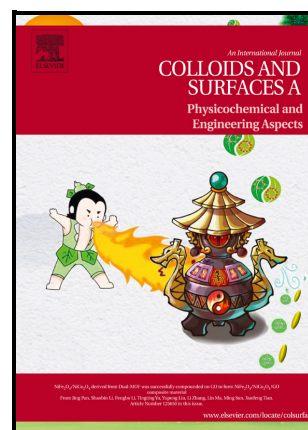# Journal Pre-proof

Triple-Layer Surface Complexation Modelling: Characterization of Oil-Brine Interfacial Zeta Potential Under Varying Conditions of Temperature, pH, Oil Properties and Potential Determining Ions

Motaz Saeed, Prashant Jadhawar, Yingfang Zhou, Rockey Abhishek

Triple-Layer Surface Complexation Modelling: Characterization of Oil-Brine Interfacial Zeta Potential Under Varying Conditions of Temperature, pH, Oil Properties and Potential Determining Ions

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Abstract

Low salinity water flooding (LSWF) is a popular enhanced oil recovery technique. Among factors that affect the performance of LSWF, geochemical interaction at the oil-brine interface and the associated enterokinetic properties plays a prominent role. This work presents a triple-layer surface complexation model for predicting the zeta potential of the oil-brine interface. We improve upon previous modelling studies by incorporating the effects of (1) temperature variation, (2) basic (-NH) oil surface group interactions (3) adsorption of sodium ions on outer and inner Helmholtz planes and (4) the presence of sulphate ions in brine. Model validation against published experimental data shows model accuracy between 66-99 %. The model displays higher accuracies at lower salinities (making it particularly suited for LSWF applications), intermediate pH and higher total acid number. In addition, a correlation between (-NH) site density and total acid/base numbers is proposed. A sensitivity study performed utilizing the developed model showed that higher sulphate concentration in the brine and elevated temperature makes the zeta potential at the oil-brine interface more negative. In addition, the sensitivity study indicates that a higher concentration of basic polar oil compounds is less favourable as it may result in less water-wet conditions in the reservoir.

Graphical abstract
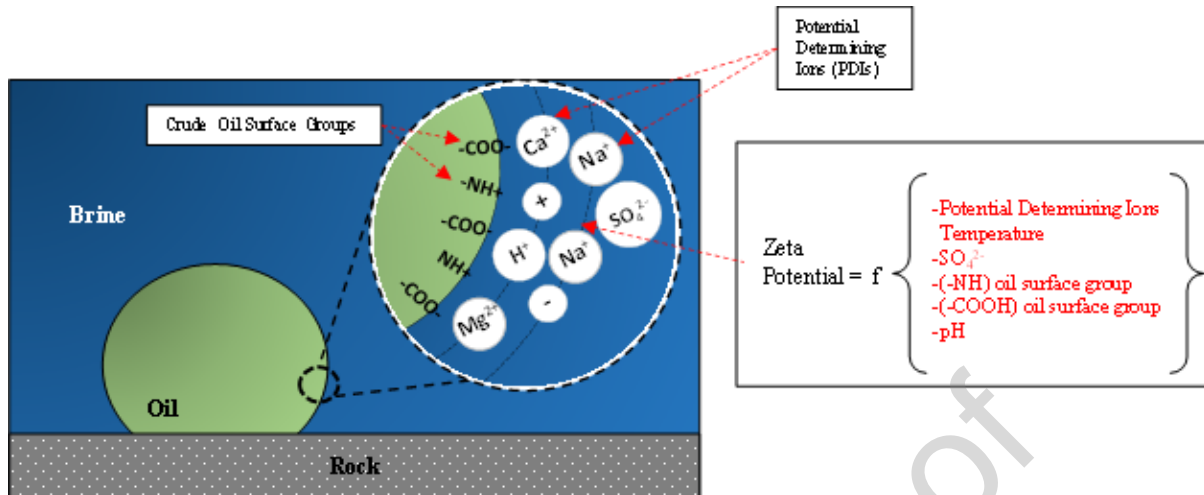
Keywords: Oil - Brine Interface, Zeta Potential, Surface Complexation Modelling, Electric Triple Layer, Low Salinity waterflooding, Wettability Alteration

1   Background

Low salinity waterflooding (LSWF) has been identified as an improved oil recovery method and has been the focus of many studies in the last 15 years. However, the exact mechanism behind it is not well defined [1]. A number of LWSF mechanisms have been suggested including multi-component ion exchange (MIE), fines migration, release of mixed wet particles, local increase in pH, osmotic pressure, expansion of double layer and Alkaline like effect among others [2 – 7]. Some researchers suggested that the incremental oil recovery is a result of wettability alteration from oil-wet to water-wet [5,8]. This wettability alteration process is mainly controlled by the oil-brine and rock-brine interactions. The focus of this work is to develop an oil-brine (OB) interface model to account for the geochemical and electrostatic interactions occurring at the interface. This model can then be used to predict the respective electrokinetic properties through the triple-layer surface complexation modelling.

Wettability alteration depends on several factors including the initial wetting conditions, oil composition, water composition and rock mineralogy. These factors govern the adhesion of crude oil to the rock surface. The adhesion mostly occurs through the bridges formed by the attachment of polar components present in the oil, mainly the carboxylic (-COOH) and amine (-NH) components, to the clay present on sandstone rock surfaces (refer to Figure 1). These clays act as pinning points to the oil on the sandstone rock surface as observed by Mahani et al. [9]. When these bridges are broken and reduced in the reservoir, more oil is allowed to migrate and be recovered. The breakage process occurs through different geochemical

reactions that are triggered by lowering the salinity of the injected water, especially through the reduction of divalent cations abundance in brine. This leads to a decrease in the zeta potential and surface potential at the oil-brine and rock-brine interfaces. As a result, the thickness of the electric double-layer (EDL) increases, overcoming the Van Der Waal attraction forces resulting in an increase in the disjoining pressure and facilitating the release of the organic materials [10, 11, 12].

1.1 Surface complexation modelling

Surface complexation modelling (SCM) is used in describing the systems where species in aqueous phases form complexes while interacting with functional groups that are present at solid surfaces. SCM utilises thermodynamics in quantifying the geochemical interactions and adsorption that occur at the crude oil-brine-rock (COBR) system [10 - 14]. This is done by describing two interfaces that contain functional groups: rock-brine interface and oil-brine interface, and the ions that are present in the aqueous phase as exchange species. The functional groups that are present on sandstone rock surfaces, such as aluminium and silicon oxides (Al:SiO-), are dependent on the clay type abundant in the formation and rock mineralogy. Carboxylic (-COOH), and nitrogen (-NH) groups are believed to be the functional groups present on the oil surface [15 - 18]. The quantification of the reactions that occur on these interfaces allows the calculation of forces prevalent in the electrical double layer and properties in the COBR system. DLVO theory, named after Derjaguin, Landau, Verwey, and Overbeek, describes the disjoining pressure acting between two surfaces comprising three main forces: electrical double-layer forces, Van der Waal attraction forces and structural forces. The summation of these forces dictates the stability of the system that includes the two interacting layers depicted by the oil/brine interface and the brine/rock interface as shown in Figure 1 [11]. Many researchers have used diffuse double layer SCM in modelling wettability alteration through low/modified salinity waterflooding [19 – 27].
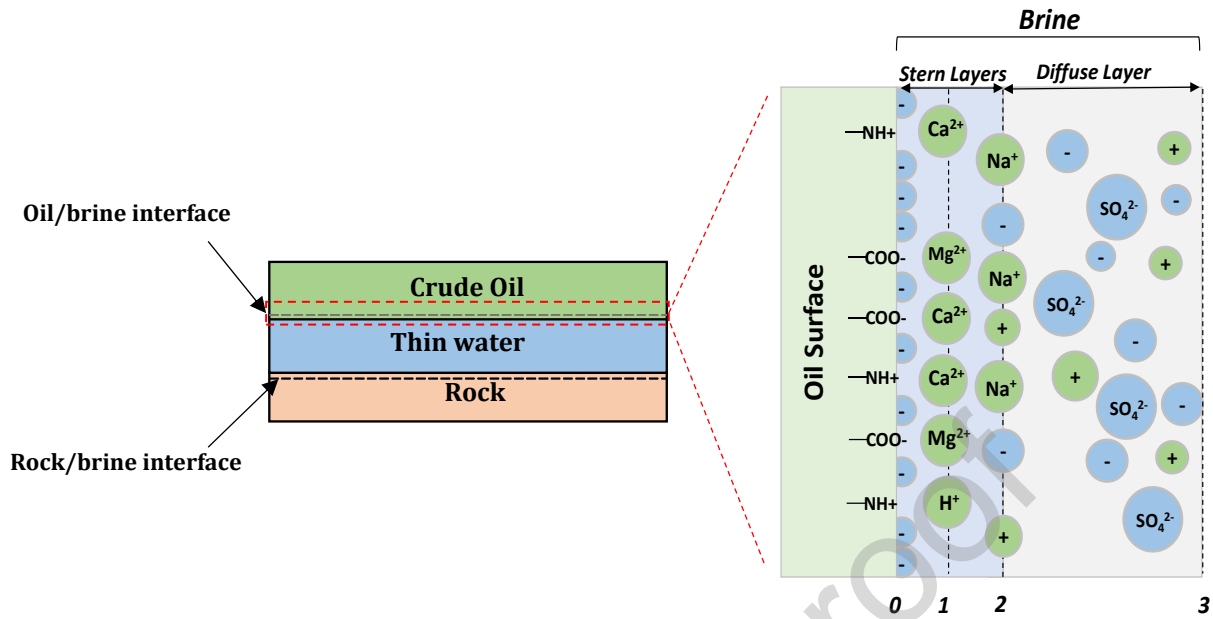
Figure 1: (left) Representation of thin water film between oil/brine and rock/brine interfaces (modified after Korrani and Jerauld [13]), (right) Representation of the oil-brine electrical interfacial layer

1.2 Triple-layer surface complexation modelling

The electrical interfacial layer models are the different representations of the layers and planes within an electrical double-layer [28], comprising four electrostatic planes i.e. 0-,1-,2- and 3-plane (Figure 1). These planes represent the constraints of three different adsorption layers. The inner and outer Helmholtz layers present between the 0- and 1-plane and the 1- and 2- plane, consequently. The inner and outer Helmholtz layers are also termed the stern layers. The 2- and 3-planes represent the limits for the diffuse layer part of the double-layer.

Triple-layer models (TLM) enable the modelling of both the inner and outer-sphere complexes depending on the size of the adsorbed ions and their affinities to adsorb to the adsorption planes, allow the distribution of the charge of an adsorbed ion between two consecutive planes. Moreover, the TLM is capable of placing the adsorption planes at different distances by altering capacitance values depending on the adsorbed ion sizes [29, 30]. This has made the TLM a robust model successful in describing the adsorption of different species at different conditions, especially pH, ionic strength and adsorbate concentrations [30].

Takeya et al. [31, 32] developed a triple-layer surface complexation model (TLM) to study the oil and brine interactions during LSWF using the charge-distribution multisite surface complexation model (CD-MUSIC) of PHREEQC software. Adsorption of ionic species on

two different planes, surface potential (at the 0-plane) and zeta potentials at the 2-plane were estimated from the model and then compared to their experimentally measured zeta potential values to calibrate and validate the constructed model. Their modelling studies assumed that basic conditions prevail inside the reservoir, hence, only carboxylic (-COOH) group is present on the oil surface. A good match was found between the results of their proposed model and the experimental results. Their modelling work was, however, conducted at one specific temperature of 50° C, with the limitation of pH values above 7. Since no basic sites are considered, their model would not be able to capture the possibly positive zeta potentials at low pH values. These limitations of the model developed in the work of Takeya et al. [31, 32] are addressed in our proposed oil-brine TLM.

Liu and Wang [33] proposed an oil-brine TLM which considered acidic and basic oil surface groups, as well as Ca^{2+} adsorption on the oil surface. Their model did not show how the surface site densities for both (-COOH) and (-NH) surface groups were calculated. In addition, their model did not consider the adsorption of any other ion other than Ca^{2+} on the oil surface. These limitations were also addressed in our current work. Triple layer surface complexation modelling was also utilised in simulating the interactions at the carbonate rock-brine interface and sandstone rock-brine interfaces for wettability characterization applications [33 - 37].

1.3   Oil surface groups

The crude oil composition affects the wetting properties of the crude oil-brine system. The presence of acidic carboxylic groups (-COOH) and basic amine groups (-NH) in the crude oil results in the development of charge at the oil surface due to the ionization of these groups. Experimental investigations of Yang et al. [16, 17] concluded that only 2% of total asphaltene content is responsible for the stabilization of the oil-in-water emulsion at the oil-brine interface area, suggesting that only a small part of total asphaltene should be considered in the site density calculation of oil surface groups. Ruiz-Morales and Mullins [38] studied the molecular orientation of asphaltenes at the oil-water interface. Their dissipative particle dynamics (DPD) simulations concluded that the coarse asphaltene molecules aggregate at the oil-water interface, while nanoaggregates move towards the bulk solution. Although both the carboxylic groups and nitrogen groups are believed to be present at the oil-brine interface, most of the studies so far were mostly focused on carboxylic groups as opposed to basic groups. Andersen et al. [39] experimentally investigated the effect of the carboxylic

compound on the interfacial properties of the oil-brine interface, concluding that the carboxylic acids species (e.g., fatty acids, resins, or asphaltenes) are concentrated at the interface. They also suggested that the acids can be removed from the oil-brine interface through ion exchange with resins. In another work, Guo et al. [15] observed that asphaltene fractions in oil-water emulsions contained more polar, larger carboxylic acidic components more than any other component, further suggesting that acidic groups are more dominant in crude oil than basic groups. Moreover, the experimental studies of oil-water emulsions by Havre et al. [40] concluded that the naphthenic acids govern the stability of oil-water interface and are closely related to the pH and electrical double-layer effects of the COBR system.

The motivation for this work was to develop a triple-layer surface complexation model that can overcome the limitations of the past models, especially triple-layer models, such as lack of modelling (-NH) oil surface group, sodium ion adsorption on outer Helmholtz plane (OHP), temperature effect on zeta potential and sulphate effect on the oil surface charge. In the following section, we describe in detail the methodology followed to overcome the limitations of the previously published models.

2   Model development

A triple-layer surface complexation model was developed using the CD-MUSIC module of the geochemical code PHREEQC^{TM} [41] to thoroughly investigate the oil-brine interactions through surface complexation reactions while incorporating the following parameters: (1) first and second Helmholtz layers capacitances, (2) association equilibrium constants and, (3) specific surface area, surface groups site density and the charge distribution. The CD-MUSIC model in PHREEQC was executed using the Donnan approach for the oil-brine interfacial evaluation in this work. More details on the Donnan theory and application can be found in [42, 43]. The model was then validated using the data sets of experiments of 16 different crude oils from nine different published experimental studies collected from the literature. Sensitivity analysis was also performed to evaluate the effects of -NH surface group, Na$^+$ adsorption to carboxylate group, SO$_4^{2-}$ reaction with the oil surface groups, and temperature on the predicted zeta potential.

In the triple-layer model, the relationship between the charge and potentials at the different electrostatic planes is governed by the Poisson-Boltzmann equation (Eq. 1) as well as the capacitance of the two stern layers (see Eq. 2 and Eq. 3) (inner and outer Helmholtz layers).

$$\frac{d^2\psi}{dx^2} = -\frac{F}{\varepsilon\varepsilon_0}\sum_{i=0}^{N} z_i(\rho_i(x) - \rho_i^0) \qquad \text{Eq. 1}$$

$$\sigma_0 = (\Psi_0 - \Psi_1)C_1 \qquad \text{Eq. 2}$$

$$\sigma_0 + \sigma_1 = (\Psi_1 - \Psi_2)C_2 = -\sigma_2 \qquad \text{Eq. 3}$$

Where ψ is the potential in mV, x is the distance away from the surface in meters, F is the Faraday constant (96485.3 C/mol), ρ is the ionic concentration in mol/m^3, σ is the charge density in C/m^2 and C_1 and C_2 are the capacitances of the inner and outer Helmholtz layers with the units F/m^2. Subscripts 0, 1 and 2 denote the planes 0, 1 and 2 of the electrical interfacial layer as depicted in Figure 1. The capacitance of each layer is governed by the dielectric constant (F/m) of the electrolyte as well as the distance between the planes i.e. sizes of the adsorbed ions and is given by:

$$C = \frac{\varepsilon_0\varepsilon_r}{d} \text{Eq. 4}$$

Where d is the thickness of the layer in meters, ε_0 is the dielectric constant of free space, ε is the relative dielectric constant. The thickness of each layer is determined by the size of assumed adsorbed ions.

The charged oil surface is assumed to have both acidic (-COOH) and basic (-NH) surface groups. Calcium, magnesium, sodium, hydroxyl and hydrogen ions, the potential determining ions that affect the zeta potential and adsorb at different electrostatic planes, were used in the evaluation of oil-brine interactions. CD-MUSIC module of PHREEQC is employed to capture these ionic species adsorptions occurring at different electrostatic planes away from the charged surface. The charge distribution of these surface species at the different planes in the proposed model is visualized in Figure 1. The divalent cations associated with the carboxyl group form inner-sphere complexes with their charges on the 1-plane, as the first layer is a surface plane for the adsorption of H$^+$, OH$^-$, and strongly bound ions such as divalent cations Mg^{2+} and Ca^{2+}, whereas the sodium ion assumed to form an outer-sphere complex with its charge distributed between the 1- and 2-planes [29, 44]. The number of sites of surface groups (-COOH) and (-NH) on the oil-brine interface is dependent on the acidic and basic content of the crude oil, represented by the total acidic number (TAN) the total basic number (TBN) of the crude oil respectively. To estimate the maximum site densities of the polar groups from the oil TAN and TBN, Eftekhari et al. [45] suggested the following equations:

$$N_{S,-COOH} = 0.602 \times 10^6 \times \frac{TAN}{1000.a_{oil}.MW_{KOH}} \qquad \text{Eq. 5}$$

$$N_{S,-NH} = 0.602 \times 10^6 \times \frac{TBN}{1000.a_{oil}.MW_{KOH}} \qquad \text{Eq. 6}$$

Where $N_{S,-COOH}$ and $N_{S,-NH}$ are the carboxylic and nitrogen compounds sites densities in sites/nm^2, respectively, TAN and TBN are the total acid and base number in mg of potassium hydroxide KOH/g of oil, respectively, a_{oil} is the specific surface area of crude oil (m^2/g), and MW_{KOH} is the molecular weight of KOH which is 56.1 (g/mol). However, this approach tends to give an overestimation of the actual value coming from the calculation of maximum site densities. Bonto et al. [46] calculated the number of site density for acidic groups ranging from the maximum and minimum constraints based on experimental observations with the 0.5 (site/nm^2) minimum site density corresponding to TAN = 0.05, and the 2.5 (site/nm^2) maximum site density of corresponding to TAN = 3. The site density is then interpolated linearly with TAN between these values. A similar approach was adopted to obtain the amine group site density through the linear interpolation of TBN between upper and lower limits.

In our modelling work, both the carboxylic (-COOH) and amine (-NH) groups are modelled at the oil-brine interface to predict the zeta potential. The (-COOH) site density is linearly correlated with the acid number following the approach proposed in [42]. The site density of the (-NH) group is used as an adjustable parameter since the behaviour of the carboxylic group is more dominant than the amine group at the oil-brine interface [15, 39, 40].

The potential drop in the first and second layers is determined by the capacitance of each layer, which varied according to the thickness of each layer. The sizes of adsorbed ions determine the thicknesses of layers within the electrical interfacial layers. To calculate the capacitance, the value of the relative permittivity of water used was 80 in absolute units for all cases without including the effect of ionic strength or temperature on the water relative permittivity [47]. In the case of the adsorbed ions, the capacitance of a layer is calculated assuming half the value of water relative permittivity which decreases away from the bulk solution [48]. For the adsorbed calcium and magnesium ions and using Eq. 4 the value of the first capacitance was 3.54 and 4.92 F/m^2 respectively. The capacitance of the second layer is fixed at 2.57 F/m^2 assuming only the size of a water molecule as its size is larger than the sodium ion. More detailed discussion on the ionic radii can be found in [49]. The zeta potential in our model is assumed to be the same as the potential at the 2-plane. The model predicted zeta potential results were then compared with the experimental zeta potential values (from the published literature) to calibrate and validate the model.

The values of site densities, surface area and water thickness were extracted from the available experimental data. The surface site densities of the carboxylic group were determined from the total acid number according to the linear analogous approach suggested by Tournassat et al. [48], through the linear interpolation of the carboxylic site density with the total acid number (TAN) between an upper and lower limit. Since the basic group is considered less dominant than the carboxylic group at the oil-brine surface [15, 31, 39, 40, 46], its surface site density was treated as an adjustable parameter in this study. The specific surface area (SSA) of crude oil was adopted directly from the experimental data and assumed to be 1 m^2/g wherever not available. This assumption is based on our observation that changing the SSA value in the model within a range of 0.5 – 5 m^2/g does not have any significant impact on the calculated zeta potential values. This is attributed to the high affinity of H^+, Na^+, Ca^{2+} and Mg^{2+} to associate/dissociate to the oil surface groups. This results in the charging behaviour being more sensitive to the site density rather than the total number of sites and specific surface area, since the site saturation will occur at lower pH values [50]. The diffuse layer thickness was calculated using the approach of [51] where it equals double the screening Debye length. The Debye length is dependent on the brine salinity and given by:

$$k^{-1} = \sqrt{\frac{\varepsilon_o \varepsilon_r k_B T}{2000 N_A e^2 I}} \qquad \text{Eq. 7}$$

Where k_B is the Boltzmann constant, T is the absolute temperature, N_A is Avogadro's number, e is the electron charge, and I is the ionic strength of the solution.

The oil-brine interactions at the interface depend on several factors including the oil surface groups and the ionic composition of the brine. The oil surface groups (-NH) and (-COOH) go through association and disassociation reactions with ions in the aqueous phase. The association and disassociation reactions are controlled by the system conditions i.e. pH and temperature. The reactions used in this work are adopted from [12, 46]. The (-COOH) group undergoes deprotonation reaction to produce negatively charged (-COO⁻) and (H^+) represented by

$$-COOH \leftrightarrow -COO^- + H^+ \qquad \text{Eq. 8}$$
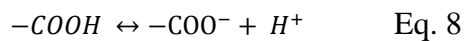
Protonation of amine group with a hydrogen ion (H^+) to produce the positively charged (-NH_2^+) group is described as

$$-NH + H^+ \leftrightarrow -NH_2^+ \qquad \text{Eq. 9}$$
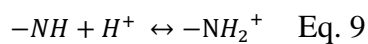
Carboxylic group (-COOH) associates with the cations present in the brine interface i.e. Na^+, Ca^{2+} and Mg^{2+}. These association reactions are expressed as

$$-COOH + Ca^{2+} \leftrightarrow -COOCa^+ + H^+ \qquad \text{Eq. 10}$$

$$-COOH + Mg^{2+} \leftrightarrow -COOMg^+ + H^+ \qquad \text{Eq. 11}$$

$$-COOH + Na^+ \leftrightarrow -COONa + H^+ \quad \text{Eq. 12}$$
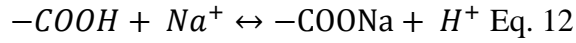
In this work, we introduce a new reaction to account for the effect of sulphate ions on the crude oil-brine interface properties, where sulphate assists in the deprotonation of the carboxylic group. The following reaction between sulphate and carboxylate group is proposed and adopted in the model

$$-COOH + SO_4{}^{2-} \leftrightarrow -COO^- + HSO_4{}^- \qquad \text{Eq. 13}$$
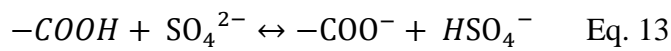
The equilibrium constants of these reactions are dependent on the temperature, pH and electro-kinetic properties of the oil-brine interface. Their values are predicted by fitting the model results to experimental results which will be discussed in the following sections.

2.1 Model Optimization

The association equilibrium constants and the amine site densities for the various crude oils were optimized so that the model results match the experimental results reported in the published literature. The model optimization process (Figure 2) starts by assigning values for the equilibrium constants of (-COOH) and (-NH) - hydrogen ion association and disassociation reactions. Then the equilibrium constant of Na^+ association to the carboxylate surface group is assigned an initial value. The next step is to use the experimental data of a study that uses NaCl as the electrolyte measuring the zeta potential at the crude oil-brine interface. The experimental data used as input for the model include; brine composition, pH, temperature, oil specific surface area, (-COOH) site density calculated from the oil total acid number and the oil and brine masses used in the zeta potential measurement. An initial value for (-NH) site density is then assumed, and the model is run. The (-NH) site density and Na^+ association equilibrium constant are then adjusted until the modelling zeta potential matches the experimental zeta potential for the first dataset. The values of the (-COOH) and (-NH) - hydrogen ion association and disassociation reactions, in addition to Na^+ association equilibrium constants that were fitted to the first dataset, are then used to validate the model against a second experimental dataset that contains the same potential determining ion Na^+ in the experiments. If the zeta potential predicted from the model matches the experimentally measured zeta potential, then a third experimental dataset, if available, was used to further

validate the model. This process is repeated for the equilibrium constants of the association reactions of Ca^{2+}, Mg^{2+} as well as sulphate reaction with the carboxylic group. A detailed description of the optimization process is given in the flowchart shown in Figure 2. The same approach is used for experimental results with temperatures higher than room temperature. The accuracy of the model was also quantified and presented for each dataset used to validate the model as follows:

$Accuracy \% = 100 - Relative\ Error \%$ Eq. 14

$Relative\ Error \% = \left| \frac{(Model\ Value - Experimental\ Value)}{(Experimental\ Value)} \right| \times 100\%$ Eq. 15

The optimized equilibrium constants for the -COOH and -NH groups disassociation were determined to be 4.7 and 6, respectively. Association constants of Na^+, Ca^{2+} and Mg^{2+} cations with (-COO-) surface groups were also evaluated in this study. The optimized equilibrium constants values for the (-COOH) cation association are found to be in close agreement with those reported by Brady and Krumhansl [13], Takeya et al. [31] and Bonto et al. [46]. These optimized association/disassociation constants are shown in Table 1. The enthalpy of the reactions were calculated assuming the van't Hoff equation and was used for further sensitivity studies as will be discussed later in the paper. These optimized values of equilibrium constants were fixed and the amine (-NH) surface group site density was allowed to be changed and optimized for each crude oil until a satisfactory match is found.

Table 1 Optimized association/disassociation constants, charge distribution and capacitance values used in the model

Surface Complexation Reaction	Log K @ 25°C	Log K @ 50°C	Enthalpy (kJ/mol)	Charge Distribution			C_1 (F/m^2)	C_2 (F/m^2)
				0-plane	1-plane	2-plane		
$-COOH \leftrightarrow -COO^- + H^+$	-4.7	-5.5 ($\pm$ 0.1)	-60	-1	0	0	2.57	2.57
$-NH + H^+ \leftrightarrow -NH_2^+$	6	7	73	+1	0	0	2.57	2.57
$-COOH + Ca^{2+} \leftrightarrow -COOCa^+ + H^+$	-3.7	-4.8	-81	-1	+2	0	3.54	2.57
$-COOH + Mg^{2+} \leftrightarrow -COOMg^+ + H^+$	-4.8	-5	-14.7	-1	+2	0	4.92	2.57
$-COOH + Na^+ \leftrightarrow -COONa + H^+$	-4	-5.5 ($\pm$ 0.1)	-110.5	-1	+0.5	+0.5	2.57	2.57
$-COOH + SO_4^{2-} \leftrightarrow -COO^- + HSO_4^-$	-3.3	-	-	-1	0	0	2.57	2.57

The developed Triple Layer Surface Complexation Model in our study was able to successfully address the limitations of the model proposed by Takeya et al. [31, 32]. Moreover, investigations of our proposed TLM model was extended further to evaluate its validity to a range of temperatures between 23 and 60°C, a wider range of pH covering the basic and acidic conditions and modelling the sodium ion adsorption on the OHP. The proposed model also includes the effect of sulphate on zeta potential at the oil-brine interface by considering its reaction with the oil carboxylate group. To highlight the novelty of the model developed in this work, a comparison between our proposed model and the existing oil-brine interface surface complexation models [12, 14, 31, 32, 46] is shown in Table 2.
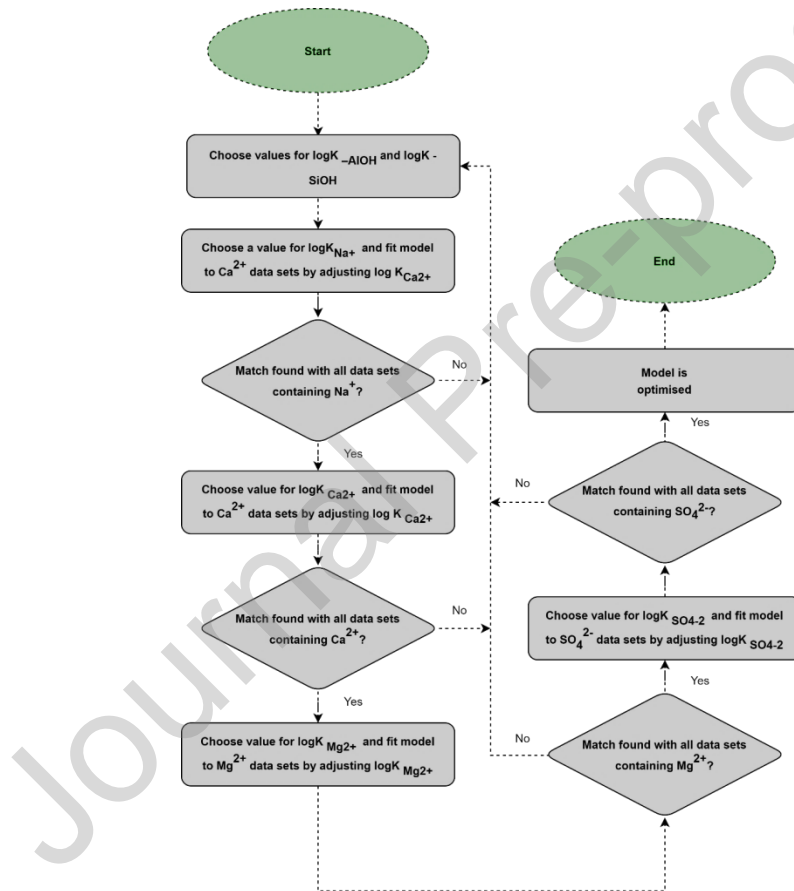

Figure 2 Crude oil-brine interface model optimization flowchart

3   Results and discussion

The published data sets of zeta potential measurements using brines and crude oils with different compositions and properties at different pH and temperature [8, 10, 31, 32, 52 - 56] were extracted and then used to calibrate and validate the constructed triple-layer model (TLM) in this study. The validated results are presented and discussed with respect to the effects of brine ionic strength, divalent cations and temperature on the zeta potential. The model validation is then followed by sensitivity analysis to understand the importance of the -

NH surface group, Na^+ adsorption to carboxylate group, SO_4^{2-} reaction with surface groups, and temperature in dictating the zeta potential of an oil-brine interface.

Table 2 Comparison between the developed model in this work and models in past published works

Model	Brady et al. [12,14]	Bonto et al. [46]	Takeya et al. [31, 32]	This Work
SCM	Double Layer	Double Layer	Triple Layer	Triple Layer
(-COOH) group	Included	Included	Included	Included
(-NH) group	Included	Included	Not included	Included
Mg^{2+} adsorption	Included	Included	Included	Included
Ca^{2+} adsorption	Included	Included	Included	Included
Na^+ adsorption	Not included	Included	Not included	Included
SO_4^{2-} reaction	Not included	Neglected	Not included	Included
Temperature effect	At 25°C and 100°C (not validated against experimental data)	Only at 25°C	Only at 50°C	At 23, 25, 50, 60°C
Correlation between -NH site density and BN	Not included	Proposed linear relationship	Not included	Correlated -NH site density with AN and BN

3.1 Model Validation

In this section, the developed model validation against some of the experimental datasets is reported. More validated experimental datasets are detailed in Appendix A. The validation of the model is carried out by comparing the model-predicted and experimentally measured zeta potential values.

3.1.1 Effect of monovalent (Na+) ions

Three types of crude oils Moutray, Leduc and ST-86-1 [10] were used in the evaluation of the effect of ionic strengths on the zeta potential using the triple-layer model (TLM) developed in this modelling study. The carboxylic site density was calculated from the acid number using the linear analogous approach discussed in section 2 while the amine group site density was optimized. The model-predicted zeta potential values at the oil-brine interface for three different ionic strengths i.e. 0.1M, 0.01M and 0.001M NaCl, at varying pH values are compared with the experimentally measured zeta potential values [10] and the results for Moutray and Leduc crude oils are shown in Figure 3a. The model's relative accuracy was

calculated and quantified in comparison with the experimental result using Eq 14. The model accuracy averaged from the results of the three crude oil types in 0.01 M NaCl brine and is shown in Figure 3b.
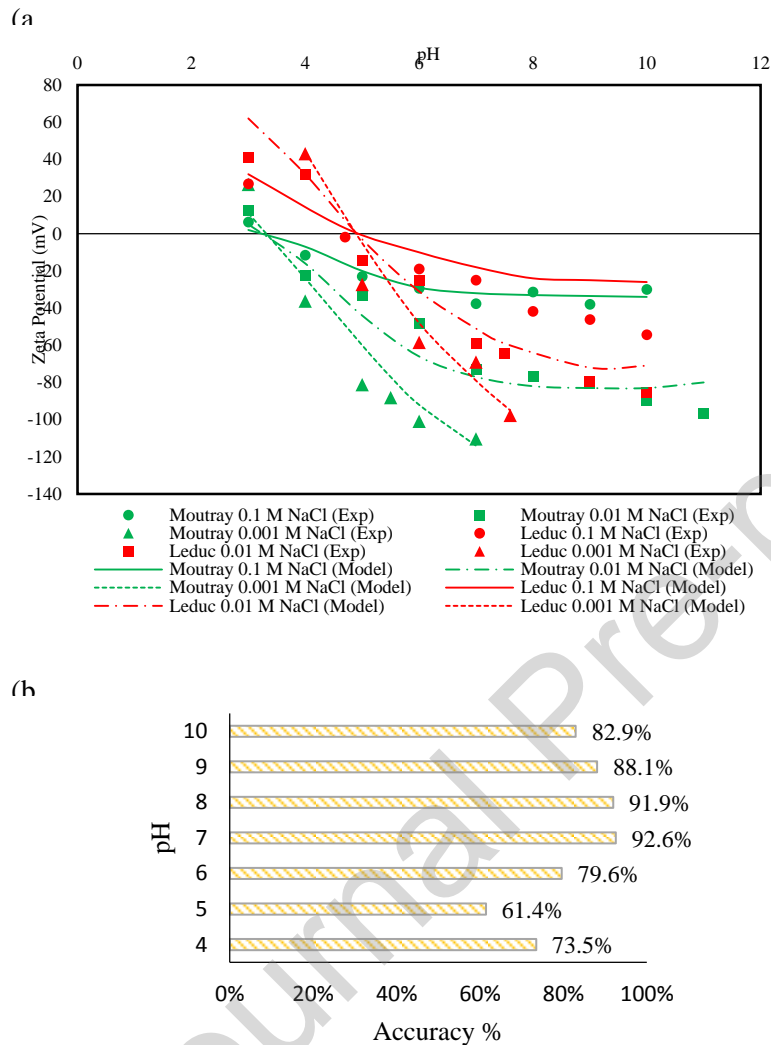
(a

(b

Figure 3 (a) Experimental and modelling zeta potential values for two Moutray and Leduc crude oils. (b) Model's average accuracy at 0.01 M NaCl (experimental results from Buckley et al [10])

3.1.2 Effect of divalent ions

The effect of divalent cations on zeta potential at the oil-brine interface is evaluated using the experimental data from [8]. The TLM was employed to predict the zeta potential values for three types of brines i.e. NaCl, $CaCl_2$ and $MgCl_2$ and two different crude oil samples: crude oil A and crude oil B, with varying acid and base numbers. The electrolyte concentrations used in the experiments and then modelled were 2000, 10,000 and 50,000 mg/L. The results of the optimized TLM model along with the experimental measurements for Crude Oil A and B are shown in Figure 4. The model accuracy was calculated for the three crude oils and

averaged over each electrolyte to understand the effect of electrolyte type and valence on the accuracy of the model (see Figure 4).
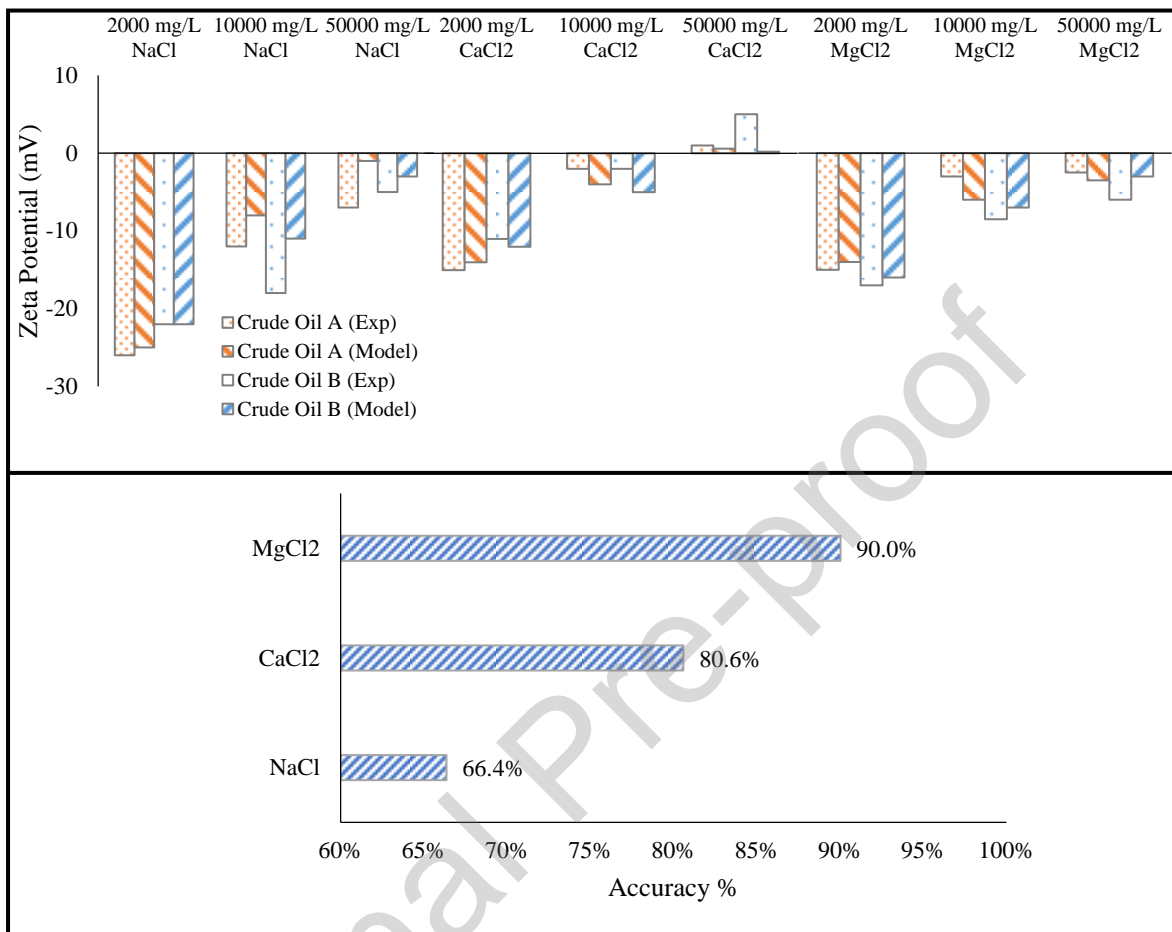

Figure 4 Above: Experimental and modelling zeta potential values for crude oils A and B using different electrolytes: NaCl, CaCl$_2$ and MgCl$_2$. Below: Model accuracy averaged for crude oils A and B (experimental results from Nasralla and Nasr-El-Din [8])

3.1.3   *Effect of temperature*

Takeya et al. [31] measured the zeta potential at the oil-brine interface at 50°C using brines with varying CaCl$_2$ and MgCl$_2$ concentrations. The experiments data were extracted and used to predict the zeta potential values. The modelling results are in very good agreement with the experimental zeta potential values (Figure 5) where the basic group site density was optimized and found to be 0.3 site/nm^2. The association equilibrium constants for cations Ca^{2+} and Mg^{2+} at 50°C were optimized as well and their values were determined to be 4.8 and 5, respectively. The average accuracy of the model-predicted zeta potential values against the experimental values ranged between 92% and 97%, as depicted in Figure 5.
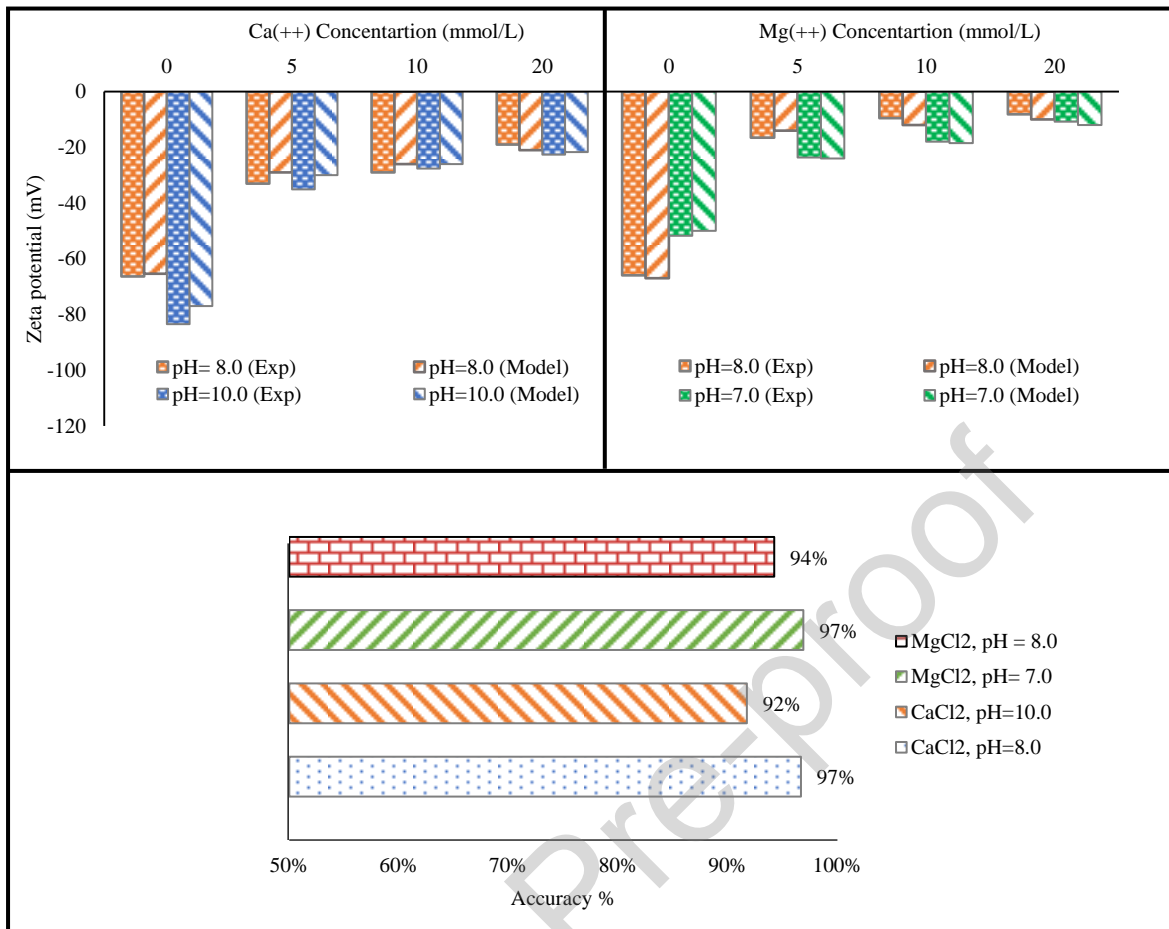
Figure 5 Above: Experimental and predicted modelling zeta potential values using CaCl$_2$ and MgCl$_2$. Below: Average model accuracy (experimental results from Takeya et al. [31]).

3.1.4 Effect of acid number (AN)

Another work that was used to demonstrate the model's ability to capture the temperature effect as well as the AN on the zeta potential is the work conducted by Takeya et al. [32]. In their work, the zeta potential was measured for two crude oil samples in various electrolytes at 50°C. They used samples from crude oil C with AN = 1.06 and crude oil D with AN = 0.07. Our proposed model was used to predict the zeta potential as presented in Figure 6a. The accuracy of the model was evaluated for the two types of crude oil and at both salinity conditions 20 mM and 100 mM NaCl. The average model accuracy for the model validation of this data set is shown in Figure 6b.
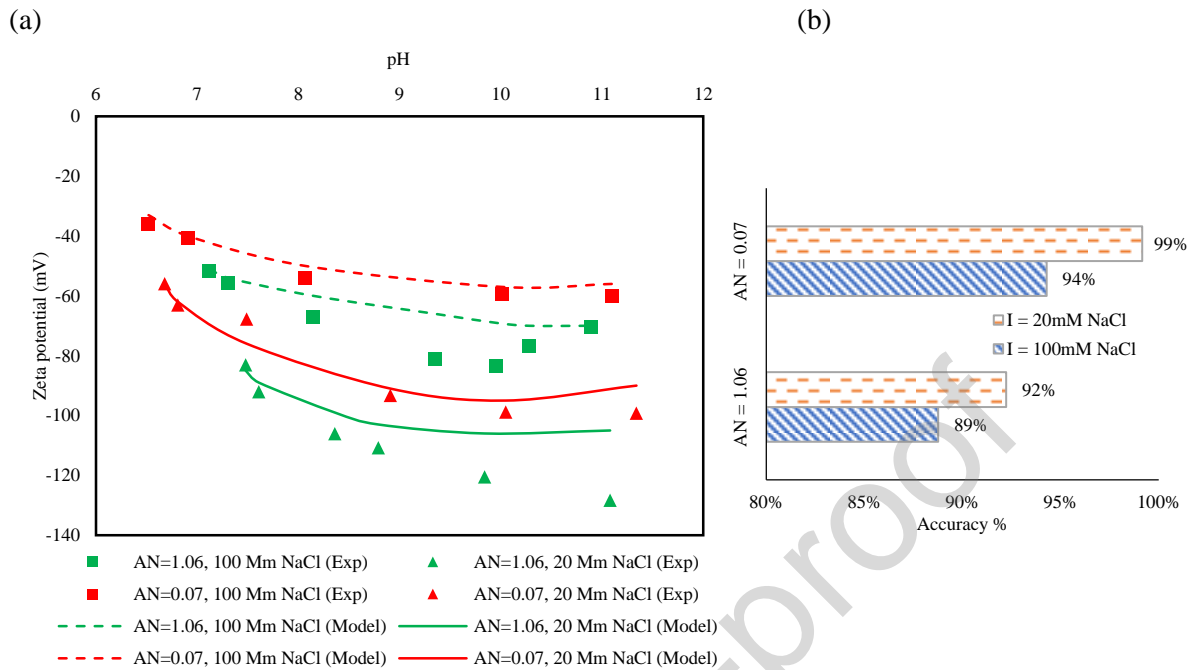
Figure 6 (a) Experimental and modelling zeta potential values for two crude oils C and D. (b) Average model accuracy (experimental results from Takeya et al. [32])

3.2 Discussion of Model Validation

The model was used to evaluate the effects of monovalent NaCl electrolyte on zeta potential by comparing the modelling results and the experimental results as shown in Figure 3. A satisfactory match between the model and experimental data with the experimental data has been obtained. The results show that an increase in pH leads to higher negative zeta potential values suggesting that the disassociation of carboxylic and basic amine sites is enhanced with the increasing pH, which in turn yielded a higher negative charge and zeta potential at the oil surface. The decrease in the ionic strength of the electrolyte resulted in a reduction in the zeta potential for the three types of crude oil. This is because the increase in ionic strength results in intensifying the presence of sodium ions in the brine, causing them to screen off the negative charge on the oil surface. This causes the zeta potential's value to move towards a less negative or more positive value, and this effect can also be quantified by altering the ionic composition concentrations in Eq. 1. Another factor that was used for matching the experimental results is the pH value at which the zeta potential is always zero i.e. isoelectric point. It can be noticed from Figure 3 that for crude oil Moutray and Leduc, the isoelectric point (IEP) predicted from the optimized model is close to the IEP observed from the experimental results. The trend of the model results matches the trend of other reported experimental results by Nasralla and Nasr-El-Din [8] and Kolltveit [52].

As discussed previously, more negative zeta potential values are desirable in a sandstone reservoir to result in a more water-wet reservoir. An electrolyte with less NaCl concentration or less salinity, in general, is desirable. This highlights the target of low salinity waterflooding in sandstone reservoirs. Further analysis in combination with sandstone rock-brine interface and DLVO theory would reveal more insights into the quantitative side of designing a low salinity waterflood. These analyses are the target of forthcoming publications by the authors. Figure 3a presents the accuracy of the model-averaged for the three crude oil types at electrolyte concentration 0.01 M NaCl. The accuracy of the model was plotted against the pH values as shown in Figure 3b. The results show that the model gives higher accuracy and better prediction at intermediate pH values around pH = 7 and 8 with an average accuracy of 92.6% and 91.9%, respectively. For pH values below 7, the model has a lower accuracy with an average of 71% between pH = 4 and pH = 6. For pH values between 9 and 10, the model has an accuracy of 88.1% and 82.9%, respectively. The same observation can be made for the other experimental studies used in this study involving varying pH values. This can be attributed to the fact that lower pH values are not well represented in the experimental datasets used for model optimization, hence the model suffers at this lower pH range. The generalised framework presented for model optimization has a scope of improving the model accuracy at lower pH values using an expanded and more comprehensive experimental datasets whenever available.

The modelling results of the divalent ions (Mg^{2+} and Ca^{2+}) effects imply that the TLM model developed in this study predicts the zeta potential values to a reasonably close agreement for both the crude oil A and B for different brines shown in Figure 4. These results demonstrate that, for the same concentration, divalent cations bearing electrolytes ($CaCl_2$ and $MgCl_2$) show higher zeta potential values than the monovalent NaCl electrolyte. This highlights the importance of divalent cations in the formation and injected water on the oil-brine interface and thus wettability alteration. It is a result of the increased ionic strength of brine in the presence of Ca^{2+} and Mg^{2+} ions because of their di-valency. It is also believed that the affinity of calcium and magnesium ions to the negatively charged surfaces is higher than that of Na^+ due to their smaller sizes in comparison to Na^+ [57]. Moreover, they result in a higher potential drop due to their smaller sizes leading to the higher ability to screen surface charge [29]. The accuracy of the zeta potential prediction using the model in the different electrolytes was evaluated and presented in Figure 4. It can be seen that the model gave better predictions when divalent cations electrolytes were used i.e. $CaCl_2$ and $MgCl_2$, with average accuracies of 80.6% and 90.0%, respectively. While the replicated zeta potential for the NaCl

experiments had a lower average accuracy of 66.4%. The higher accuracy in predicting $CaCl_2$ and $MgCl_2$ cases in comparison with the NaCl cases might be explained by the fact that the divalent cations, Mg^{2+} and Ca^{2+}, tend to screen the surface charge more than the monovalent Na^+ ions. This leads to further suppression of zeta potential values especially around intermediate pH values, in the experimental and model predictions resulting in higher prediction accuracy. However, in the cases where Na+ was present, this suppression of zeta potential values is lower which magnifies the discrepancies between the experimental and modelling values, thus leading to the lower model accuracy.

The model was also able to replicate experimental results performed at a higher temperature of 50 °C from the work of Takeya et al. [31] as shown in Figure 5. The results show that an increase in the concentration of calcium and magnesium ions increases the zeta potential value. It is worth noting that the original model proposed in [31] successfully matched their experimental work. However, the effects of amine groups on the oil surface and the adsorption of sodium ions on the OHP were not considered in their experimental and modelling work.

The combined effect of temperature and acid number (AN) was evaluated by the proposed TLM as evident in Figure 6 by replicating the results of the work conducted by Takeya et al. [32]. It is observed from Figure 6 that the increase in AN leads to increasingly negative values of zeta potential. This is attributed to the increased (-COOH) groups that disassociate to give (-COO-) at the oil surface when the AN increases, leading to a higher negative oil surface charge. The model accuracy for this data set was evaluated and presented in Figure 6b. The results show that the model gave high average accuracies for predicting the zeta potential values which were ranging between 89% and 99% in comparison with the experimental data. Figure 6b also indicates that the model gives higher accuracies for higher AN values and lower salinities. This is also observed in modelling other data sets studied in this work such as Nasralla and Nasr-El-Din [8] and Kolltveit [52]. Temperature affects the zeta potential by changing the chemical equilibrium constants and changing the charge density-potential relationship through the Poisson Boltzmann equation (see Eq. 1 - Eq. 3). The validated results discussed above, demonstrate the model's ability to capture the various effects of ionic strengths, divalent cations and temperature on the zeta potential at the oil-brine interface. The model's performance was significantly better than the model presented in [46] in replicating the measured zeta potential from published literature. This is a result of utilising TLM, rather than DLM, where the adsorption of ionic species was modelled at

different electrostatic planes within the electrical interfacial layer. In addition to using TLM, the model was able to include the effects of (-NH) oil group, Na^+ adsorption, sulphate reaction with oil carboxylic group and temperature on the zeta potential on the oil-brine interface, overcoming the limitations of previously developed oil-brine the triple-layer model [31, 32].

The relationship between the (-NH) site density and crude oil TAN and TBN was investigated by statistically analysing the modelling optimized site density and correlating it to both TAN and TBN using nonlinear regression. The following correlation was obtained as a result of the analysis

$$N_{s(-NH)} = 0.01 + 0.031TBN + 0.07TAN \quad \text{Eq. 16}$$

A comparison between the optimized (-NH) site density values for each crude oil and correlation-calculated (-NH) site density shows that the correlation was able to predict the optimized (-NH) site density to a good extent with an acceptable R-square value of 0.78. The correlation (Eq. 16) shows that the site density of the amine group site density is dependent not only on the total base number but also on the acid number. This can be explained by the fact that the base and acid numbers are believed to be related as the acid-base chemical equilibria depends on the system's pH as well as considering it in the sense that an acid is a protonated base and a base is a deprotonated acid [58, 59]. Hence the basic group (-NH) site density can also be related to both the base and acid number.

The correlation (Eq. 16) developed in this work provides accurate predictions of the (-NH) site density in comparison to the model optimised values. However other correlations and approaches suggested previously to calculate the (-NH) site density, namely the ones suggested by Eftikhari et al. [60] and Bonto et al. [46], tend to greatly overestimate the (-NH) site density. Figure 7 compares the (-NH) site density values predicted by the correlation developed in this work and the correlations/approaches suggested by Eftikhari et al. [60] and Bonto et al. [46] in contrast to the optimized (-NH) site density values. The comparison shows that Eftikhari et al. [60] correlation greatly overestimates the (-NH) site density in comparison to the optimized values used for model validation. This overestimation in some cases is greater than 100-fold. Bonto et al. [46] approach provides a more conservative estimation of the (-NH) site density in comparison to the approach of Eftikhari et al. [60]. However, from Figure 7 it can be observed Bonto et al. [46] correlation still overestimates the value of site density in contrast to both the optimized and correlation estimated (-NH) site density values. Combining this conclusion with the studied effect of (-NH) site density on the

zeta potential (see Figure 8), we can conclude that the approaches suggested by Eftikhari et al. [60] and Bonto et al. [46] in most of the cases would provide zeta potential values that have very high positive values to the extent that it might never be negative regardless of the pH or ionic strength of the electrolyte. Hence, the use of correlation would be most appropriate for providing a more accurate value of (-NH) site density on crude oil surfaces.
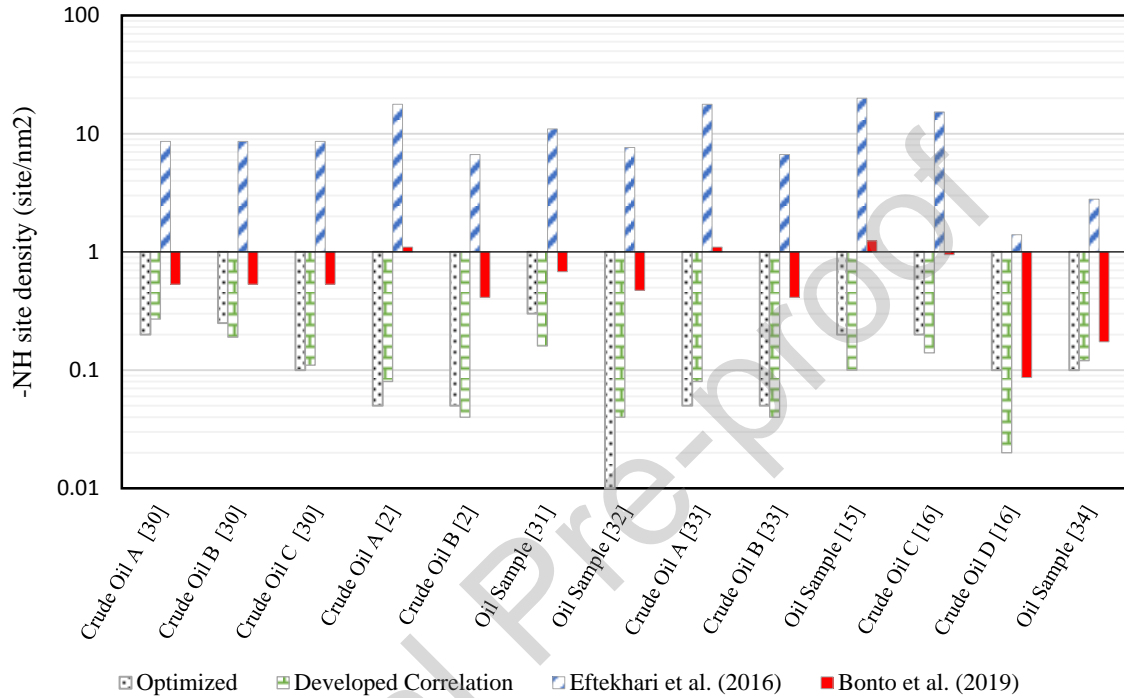

Figure 7 Comparison between the estimation of (-NH) site density for different crude oil samples [8, 10, 31, 32, 52 - 56] using the developed correlation in this work and the correlations/approaches suggested by Eftekhari et al. [60] and Bonto et al. [46] in contrast to the model-optimized values

3.3 Sensitivity Analysis

After validation, the model was then used to understand the significance of -NH surface group, SO_4^{2-} reaction with surface groups, and temperature in dictating the zeta potential of an oil-brine interface. This is investigated by altering the input parameter values of the -NH site density, SO_4^{2-} and system's temperature in the model from a base case's values (see Table 3).

Table 3 Base case values for sensitivity analysis

Parameter	Value
(-COOH) site density (site/nm^2)	1
(-NH) site density (site/nm^2)	0.1
Temperature (°C)	25
pH	3 - 12

Electrolyte	0.05 M NaCl

3.3.1 Effect of -NH group on zeta potential

The presence of basic compounds at the oil surface affects the oil surface charge. The effect of basic compounds is more pronounced at a pH of less than 5. This is because the (-NH) group hydrogen ion association is dependent on the hydrogen ion concentration in the brine i.e. pH. When there is an excess of hydrogen ions at low pH, the association between the (-NH) group and H^+ increases significantly which increases the concentration of ($-NH_2^+$). This leads to the increase of amine groups on the oil surface resulting in the higher zeta potential values at the oil-brine interface as seen in Figure 8. The validated triple-layer model was further evaluated using different values of (-NH) surface site density: 0, 0.1, and 0.2 site/nm^2. To study the combined effect of basic site density and ionic strength, two NaCl molarities were used i.e. 0.05 M and 0.2 M. It is apparent from Figure 8, that raising the ionic strength from 0.05 to 0.2 M, results in a less pronounced effect of basic compounds on the zeta potential value. Hence, as the ionic strength increases, the cations in the solution will have a greater impact on the zeta potential and the effect of the (-NH) group becomes less pronounced.
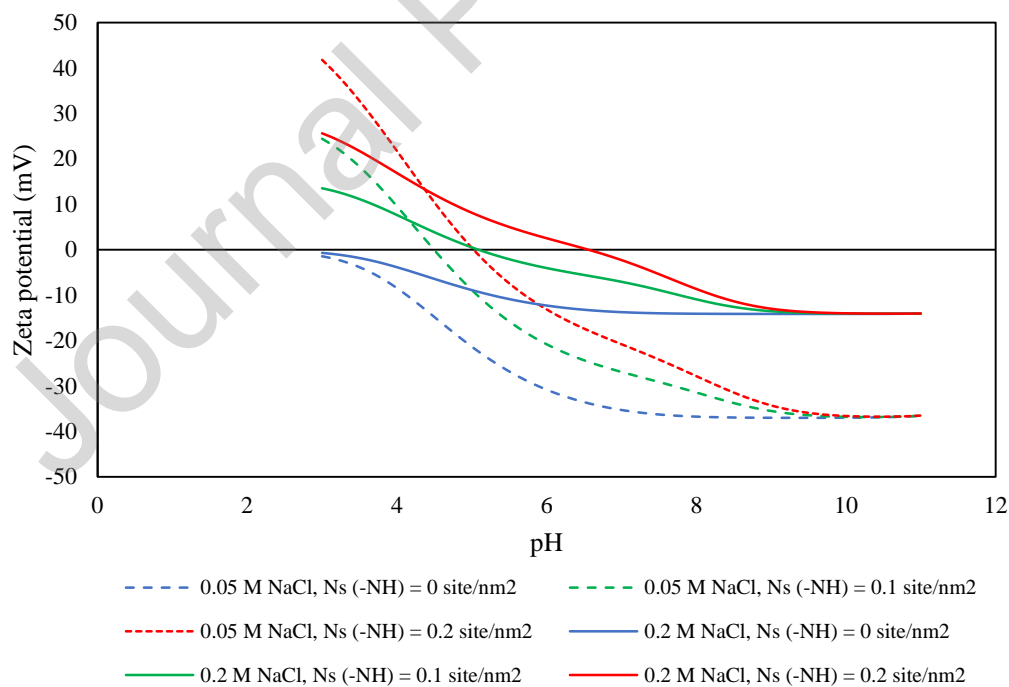

Figure 8 Effect of (-NH) surface site density on zeta potential at 0.05 M NaCl and 0.2M NaCl

The results of this sensitivity analysis indicate that crude oils with higher TBN would result in more positive zeta potential values. This directly results in a decrease in the electrostatic double-layer forces component in the disjoining pressure, the component that is responsible

for repulsing the oil-brine and rock-brine interfaces from each other and hence creating a more stable water wet COBR system. In other words, crude oils with higher basic polar compounds are expected to result in the wettability of a sandstone reservoir to be less water-wet or more oil-wet.

3.3.2 Effect of SO_4^{2-} reaction with the carboxylic group on zeta potential

The model was used to investigate the effect of the presence of sulphates in the brine ionic composition on the zeta potential at the oil-brine interface. Three concentrations of sodium sulphates were used in the model including 0, 0.001, and 0.002 M Na_2SO_4. Although only small concentrations were used in this sensitivity study, the effect of brine sulphates on the zeta potential is evident in Figure 9. The modelling results show that increasing the concentration of the sodium sulphates in the brine causes the zeta potential at the oil-brine interface to become more negative within the studied range and specifically as the system's pH increases. The sulphate presence in the brine affects the zeta potential by reacting with the carboxylate group on the oil surface according to the proposed reaction (Eq. 13). This reaction results in the hydrogen ions disassociating from the (-COOH) group and associates with SO_4^{2-} to form mono-hydrogen sulphate (HSO_4^-). This also promotes the presence of the negatively charged (-COO⁻) group at the oil surface and consequently makes the overall oil surface charge and zeta potential at the oil-brine interface more negative. It is expected that the effect of the negatively charged sulphate ion (SO_4^{2-}) in the brine on the zeta potential will be more pronounced when modelling its presence as an ion rather than as a salt i.e. Na_2SO_4 because in this model the sodium ion adsorption on the negatively charged (-COO⁻) is also accounted for, thus, increasing the concentration of Na_2SO_4 in the brine will increase both the concentrations of the sodium ions and sulphate which will have opposite effects on the zeta potential value. Similar observations of the effect of sulphate on the zeta potential were reported in the published experimental studies of Zhang and Austad [61], Zhang et al. [62] and Austad et al. [63].
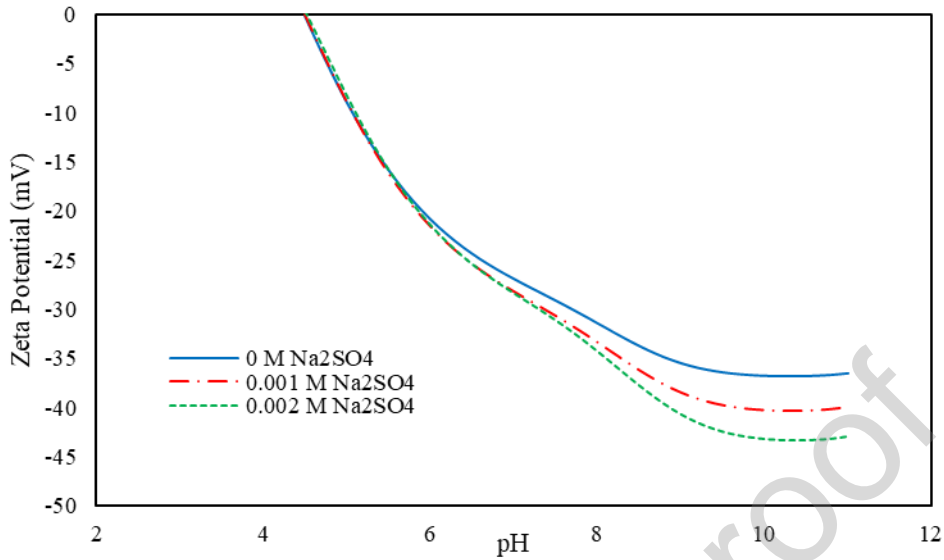
Figure 9 Effect of Na$_2$SO$_4$ concentration in brine on zeta potential

3.3.3 *Effect of temperature on zeta potential*

Temperature affects the zeta potential property by changing the chemical equilibrium constants and affecting the charge density-potential relationship. Changing the chemical reactions equilibrium constants changes the affinity of the different potential determining ions (PDIs) to associate with oil surface groups and consequently affecting the abundance of charged surface groups and oil surface charge. In the developed TLM, the change of the chemical equilibrium constants is accounted for by including the reaction enthalpy (see Table 1) which allows for the calculation of the equilibrium constant at different temperatures based on the equilibrium constant at 25°C.

This effect was investigated in this work through the constructed TLM using five different temperature values: 25, 50, 70, and 100°C. With the successively higher temperatures, the zeta potential values become more negative at a given pH, especially at pH higher than 4.6 (refer to Figure 10). Increases in pH and temperature promote the formation of negatively charged (-COO$^-$) groups at the oil surface leading to more negative zeta potentials at the oil-brine interface. Furthermore, the zeta potential becomes more sensitive to pH with the increasing temperatures as depicted in Figure 10. These results suggest that the temperature effect should always be accounted for when estimating the zeta potential at the oil-brine interface and ignoring this effect would result in highly inaccurate values, especially at pH values higher than 4.5. Results obtained in this study are in line with the observations were reported by Ishido et al. [64], Jayaweera et al. [65], Dai and Chung [66], Revil et al. [67]

where the zeta potential measured at interfaces between different brines and materials becomes more negative as the temperature increases. Hence, sandstone reservoirs at higher temperatures are expected to have more water-wet conditions which are more favourable for oil production. This would also indicate that the injection of low salinity water into reservoirs should be done using pre-heated water to prevent reversing the wettability inside the reservoir into more oil-wet conditions. This finding implies that the use of hot low salinity waterflooding should always be considered rather than just using low salinity waterflooding. This is in addition to the role that the pre-heated injected water can do in reducing the oil viscosity which would result in an improved sweep efficiency. The developed TLM in this work coupled and a rock-brine TLM, heat and mass transfer analysis would give more insight into the advantages and mechanistic side of hot low salinity waterflooding in sandstone reservoirs.
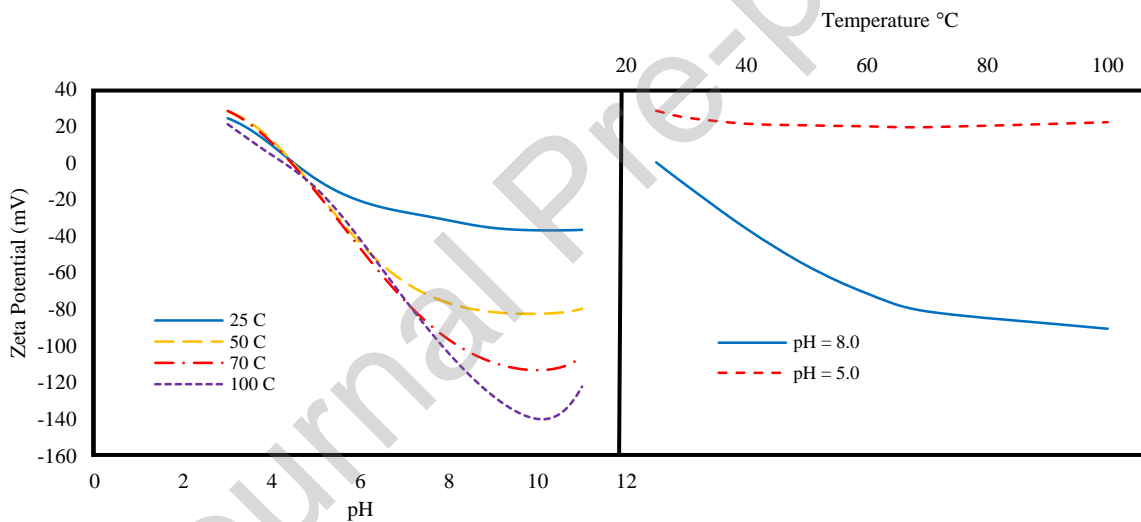

Figure 10 Zeta potential change with (Left) pH at different temperatures and (Right) temperature at pH = 5.0 and pH = 8.0

4   Conclusion

A triple-layer surface complexation model was developed and validated against 9 published studies with 16 different types of crude oils. This is the first work to utilise triple-layer surface complexation modelling for predicting the zeta potential at the oil-brine interface at varying temperatures while accounting for the basic (-NH) oil surface group interactions, the adsorption of sodium ions on the both outer Helmholtz plane (OHP) and inner Helmholtz plane (IHP) as well as including the effect of sulphate present in the brine's ionic composition on the zeta potential at the oil-brine interface. Keeping in mind the assumptions made, the main findings of this work are:

- The model was successful in replicating the experimental results reported in different previous studies. The model showed average accuracies between 66% and 99% for the studied data sets. Higher accuracies were observed when predicting the zeta potential against experimentally measured zeta potential at lower salinities, intermediate pH and higher TAN. The model was successfully applied to predict zeta potential values at temperatures between 23 and 60°C, salinities between 60 and 40,000 ppm and pH conditions in the range 2 – 11.

- Upon analysing the optimized (-NH) values, a correlation between the (-NH) site density, TBN and TAN is reported. This indicates that knowledge of both the TAN and TBN of the studied crude oil would be important in modelling the crude-oil brine interactions. Sensitivity analysis conducted, concluded that higher amounts of polar oil compounds, is less favourable as it may result in less water-wet conditions inside the reservoir.

- Model sensitivity analysis showed that increasing the temperature increases the negativity of the zeta potential at the oil-brine interface, especially when the system's pH value is above 4.5. Significantly, this indicates that injecting low salinity water at elevated temperatures is more favourable than injecting low salinity water with ambient temperature to avoid reversing sandstone's wettability into less favourable oil-wet conditions and to reap the benefit of better sweep efficiency through reducing oil viscosity by the pre-heated injected water.

- Finally, the results from the sensitivity analysis showed that increasing the concentration of the sodium sulphates in the brine causes the zeta potential at the oil-brine interface to become more negative within the studied range and specifically as the system's pH increases. The sulphate presence in the brine affects the zeta potential by reacting with the carboxylate group on the oil surface which results in an increased number of the negative (-COO$^-$) promoting a more negative charge at the oil surface.

CRediT authorship contribution statement

Motaz Saeed: Writing - original draft, Visualization, Investigation, Methodology, Software, Data curation, Formal Analysis. **Prashant Jadhawar**: Conceptualization, Visualization, Supervision, Writing - review & editing. **Yingfang Zhou**: co-supervision, review**. Rocky Abhishek**: Validation, Formal Analysis, review.

Declaration of Competing Interest

☒ The authors declare that they have no known competing financial interests or personal

relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Appendix (A)

In this appendix, we report the validation of the proposed model against various experimental data sets that were used in this work.

Modelling Kolltveit (2016)[52] Experiments:

Three types of crude oils A, B and C [52] were used in the evaluation of the effect of ionic strengths on the zeta potential using the triple-layer model (TLM) developed in this modelling study. The carboxylic site density was calculated from the acid number using the linear analogous approach discussed in section 2.3. The model-predicted zeta potential values at the oil-brine interface for three different ionic strengths i.e. 0.12M, 0.03M and 0.006M NaCl, at varying pH values are compared with the experimentally measured zeta potential values [52]. The basic site density was used as a fitting parameter. Figure 11 depicts a satisfactory match between the model and experimental data with the experimental data has been obtained.
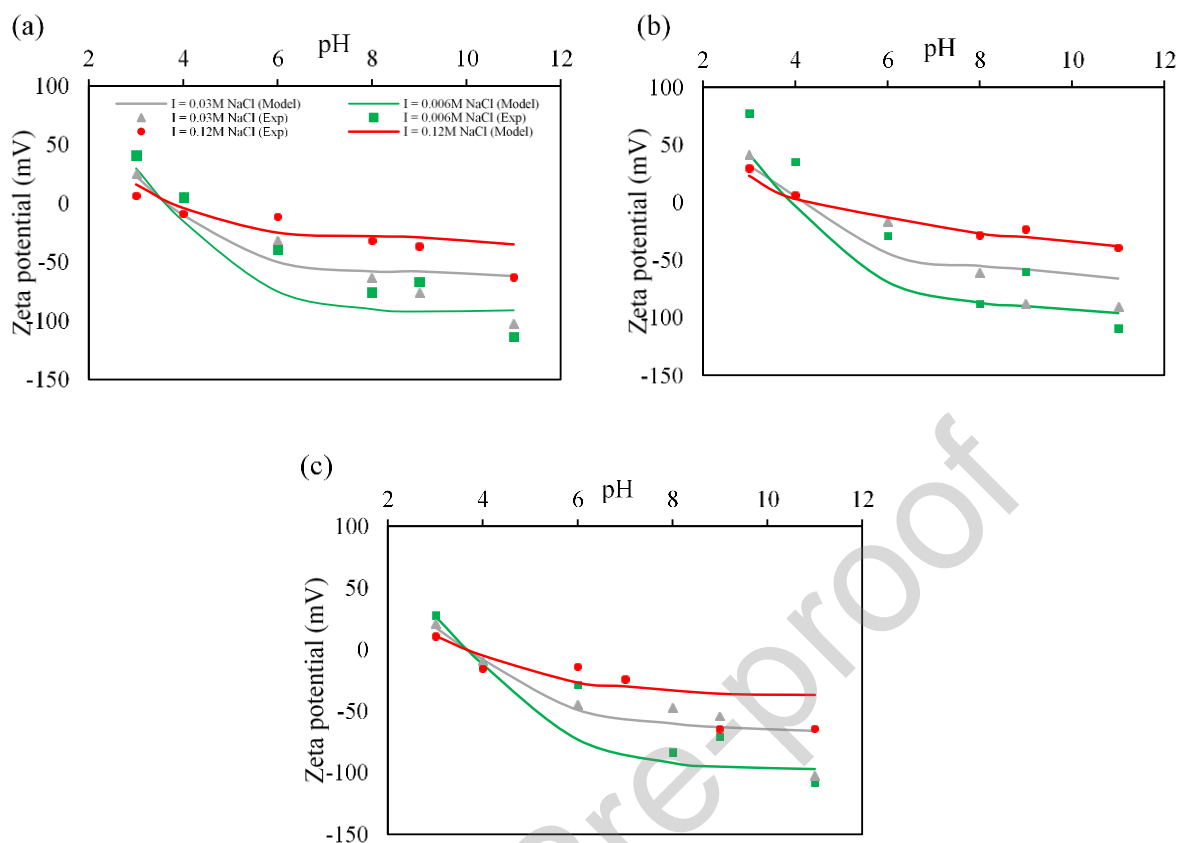
Figure 11 Experimental and modelling zeta potential values for three different crude oils: (a) Crude oil A, (b) Crude oil B and (c) Crude oil C (experimental results from Kolltveit [52])

The results show that an increase in pH leads to higher negative zeta potential values suggesting that the disassociation of carboxylic and basic amine sites is enhanced with the increasing pH, which in turn yielded a higher negative charge at the oil surface. All of three types of crude oil used in the experiments and modelling has a relatively high TAN i.e. 3, 2 and 1 mg/g KOH, which resulted in an overall high negative values of zeta potential at high pH conditions because of the increased concentration of (-COOH) surface groups at the oil surface that progressively disassociates as the system's pH increases. Another factor that was used for matching the experimental results is the pH value at which the zeta potential is always zero i.e. isoelectric point. It can be noticed from Figure 11 that for crude oil A, B and C, the isoelectric point (IEP) predicted from the optimized model is close to the IEP observed from the experimental results.

Modelling Pooryousefy et al. [53] Experiments:

The effect of divalent cations on the predicted zeta potential is also investigated by modelling the experimental results of Pooryousefy et al. [53]. The triple-layer model simulated the zeta

potential values at low and high concentrations of $CaCl_2$ brine. The carboxylic site density was calculated from the TAN and was found to be 1.54 site/nm^2. The results of the model fitted to the experimental results are depicted in Figure 12a. An increase in the concentration of $CaCl_2$ gives rise to the zeta potential values owing to increased calcium ion abundance in the electrolyte. The model was successful in predicting the zeta potential sign while giving a good approximation for its value. In the case of 2000 mg/L $CaCl_2$ brine, the difference between the measured and predicted zeta potential values was approximately 1.0 mV. When modelling the higher concentration experiment of 50000 mg/L, the model predicted the zeta potential to be 0.6 mV which compares well to the 1 mV experimentally value. It is also worth noting that a high concentration of calcium chloride electrolyte resulted in changing the sign of the zeta potential which indicates that the negative surface charge of the surface was highly electrically screened by the adsorbed calcium ions.

Modelling Ayirala et al. [54] Experiments:

The developed triple-layer model was also able to capture the effect of divalent cations on the zeta potential reported in [54]. Four different brines comprising NaCl, $MgCl_2$, $CaCl_2$, Na_2SO_4 were evaluated at the pH of 6.32, 6.32, 6.05, 6.27, respectively, and at 5761 ppm concentration in their laboratory work and were simulated through the modelling in this study (see Table 4). The experimental and modelling results are shown in Figure 12b. The model was able to replicate the measured zeta potential to an appropriate extent. However, the difference between the model-predicted and experimental results can be attributed to the carboxylic site density approach adopted in this work, which estimates the number of sites available according to an analogous approach.

Table 4 Brine composition used in experiments Ayirala et al. [54]

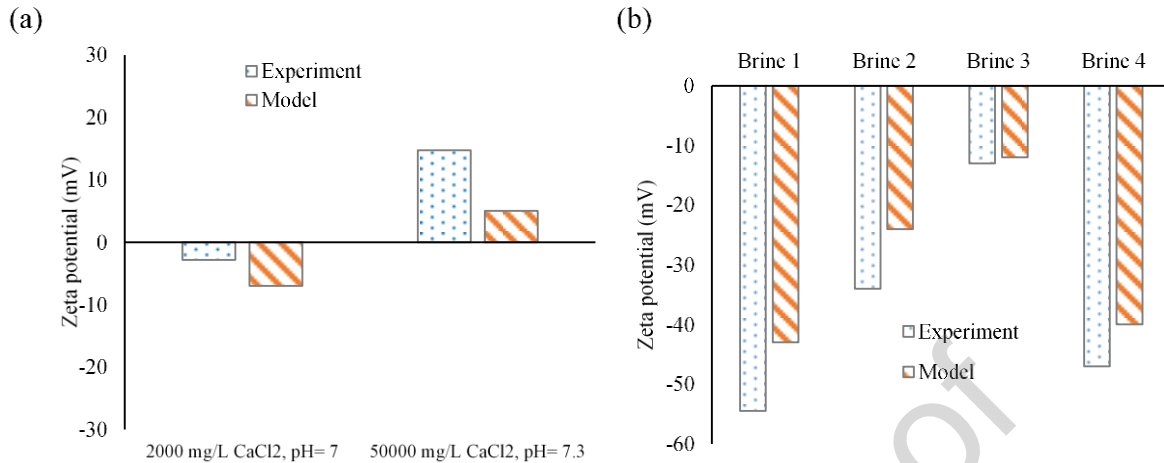| Brine		ppm	pH
Brine 1	NaCl	5761	6.32
Brine 2	$MgCl_2$	5761	6.32
Brine 3	$CaCl_2$	5761	6.05
Brine 4	Na_2SO_4	5761	6.27

(a)

(b)

Figure 12 Predicted zeta potential values compared to the experimental results of (a) Pooryousefy et al. [53] and (b) Ayirala et al. [54]

Modelling Yang et al. [56] Experiments:

The model was also run using the experimental data from [56] where the zeta potential measurements were conducted at 60°C. The results from the model along the experimental results are presented in Figure 13. The association equilibrium constants used at 60°C were assumed to be the same at 50°C assuming no significant deviation will occur. From Figure 13, it evident that the model replicates the zeta potential values measured at experiments where $CaCl_2$ was used to an excellent extent. However, the modelling results of the zeta potential at the interface between the crude oil and the NaCl brine did not match the experimental results, specifically, at lower concentrations. This miss-match between the experimental and modelling work can be attributed to uncontrolled experimental conditions. To justify this result, we look at the results of [32] where similar conditions were used when testing the zeta potential of an oil-brine interface and using a crude oil sample with properties close to the one used in [56]. However, the experimental results of [32] showed much higher absolute zeta potential values compared to those measured by Yang et al. [56].
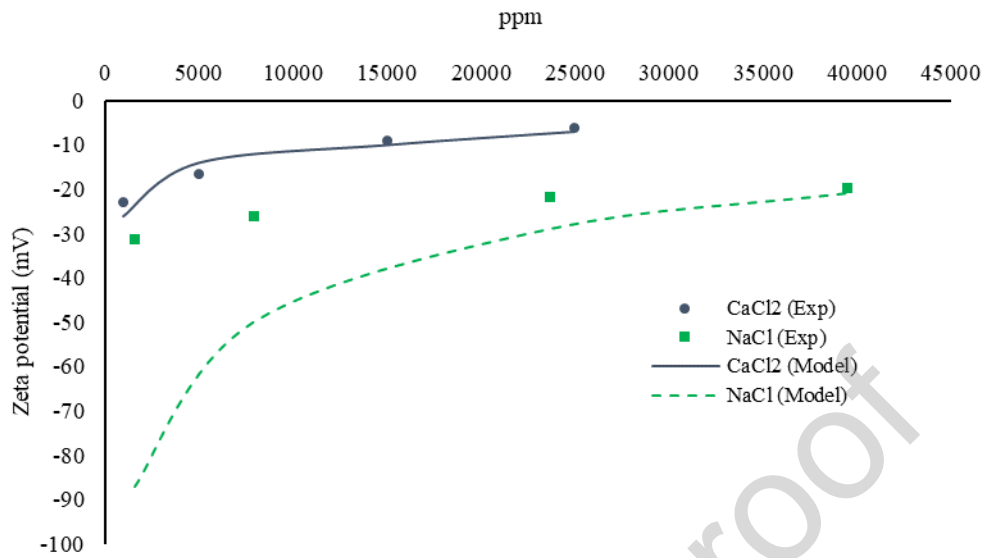
Figure 13 Experimental and predicted modelling zeta potential values at 60°C (experimental results from Yang et al. [56])

Modelling Nasralla et al. (2013) Experiments:

Nasralla et al. [55] studied the wettability alteration effect during low salinity waterflooding LSWF through the experimental measurement of zeta potential values for two types of crude oils at room temperature and pH range of 3 and 12. They used different brines in their work including seawater, aquifer and diluted aquifer water. The zeta potential at the oil-brine interface was modelled using the developed TLM and the results fitted to the measured values are presented in Figure 14.
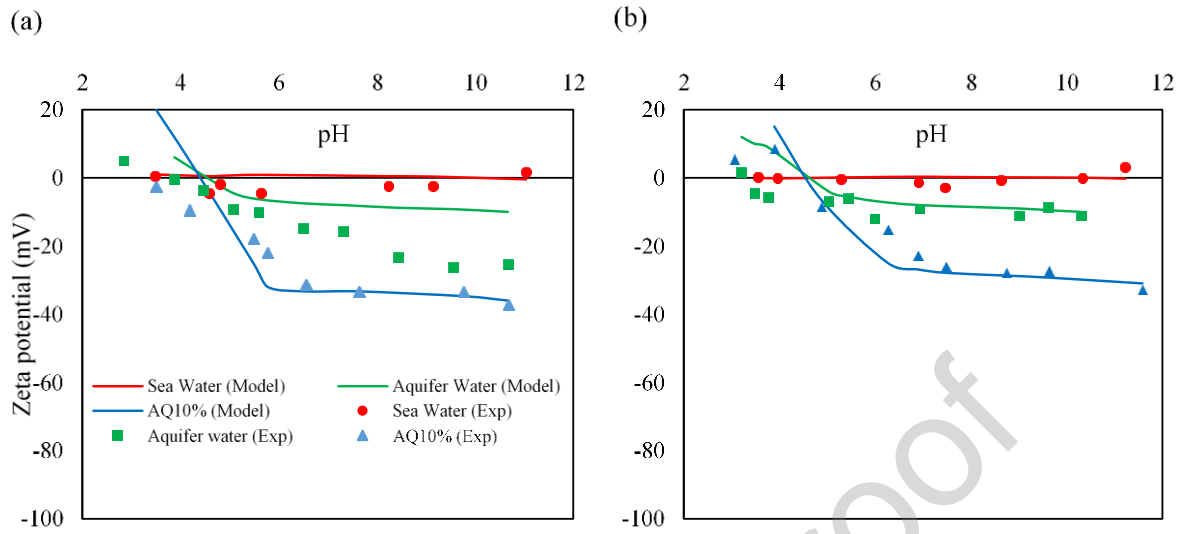
(a)   (b)

Figure 14 Experimental and modelling zeta potential values for two different crude oils: (a) Crude oil A and (b) Crude oil B (experimental results from Nasralla et al. [55])

The model also managed to simulate the effects of multi-component electrolyte on the zeta potential as demonstrated in Figure 14 by replicating the results of Nasralla et al. [55]. The results of the model show a good match to the experimentally measured zeta potential. The results indicate that seawater yielded the highest zeta potential values due to the high concentration of salts. The trend of zeta potential for both crude oil samples shows an expected increase with the increase in brine pH for all types of brines used. The optimized (-NH) site density for crude oil A and crude oil B was found to be 0.05 and 0.05 site/nm^2, respectively. The model succeeded in predicting the zeta potential for both types of crude oil to a satisfactory extent above pH value of 4. However, below pH = 4, the model fails to predict the zeta potential value for the reported experimental measurements. This can be explained by the fact that brines used in the experimental work [55] contained several ions i.e. Na^+, Ca^{2+}, Mg^{2+}, Sr^{2+}, HCO_3^- and SO_4^{2-}, however, in our model only Na^+, Ca^{2+}, Mg^{2+}, and SO_4^{2-} were adopted in the evaluation of the adsorption in the developed TLM.

Highlights:

- Developed a triple-layer surface complexation model (TLM) to describe oil-brine interactions.

- Addressed the limitations of the existing models by capturing the effect of varying temperatures on the oil-brine interface interplay, addition of amine base surface groups at the oil surface to describe both acidic and basic system conditions, and the inclusion of sodium ion adsorption on the outer Helmholtz plane.

- Triple-layer model Validation using data of 16 different types of crude oil from 9 published experimental studies with accuracy between 66% and 99%.

- A correlation between (-NH) site density and total acid/base numbers is proposed.

- The sensitivity study indicates that a higher concentration of basic polar oil compounds is less favourable as it may result in less water-wet conditions in the reservoir.