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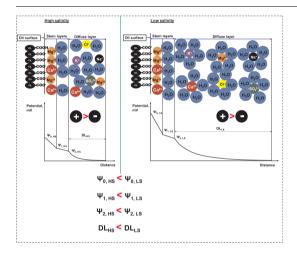
# Predicting the electrokinetic properties of the crude oil/brine interface for enhanced oil recovery in low salinity water flooding



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#### GRAPHICAL ABSTRACT



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#### ABSTRACT

The low-salinity waterflooding (LSWF) technique during enhanced oil recovery has received increasing attention over the last decade. Several studies have attempted to understand the effects of LSWF through both experiments and modelling, but their results are inconsistent due to a lack of understanding of the crude oil/brine and brine/rock interfaces. In this paper, the crude oil/brine interface was studied by developing a triple-layer surface complexation model. The carboxyl groups (–COOH) were attributed to the surface charge and electrical triple-layer development of the crude oil in LSWF. The zeta potentials of the emulsion at various pH levels and the calcium and magnesium concentrations were measured to examine the interface. These data were then directly fitted to the simulated zeta potentials to determine the surface site density of –COOH and the associated equilibrium constants for the dissociation and adsorption of calcium and magnesium. The –COOH site density was determined by fitting the pH-independent zeta potential, while the equilibrium constant values were estimated from the variations in the zeta potential with the changes in pH and the concentrations of calcium and magnesium. The determined surface complexation parameters were validated by comparing the experimental

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zeta potential data from different ionic solutions. The developed surface complexation model was used along with the estimated parameters to predict the interface of crude oil in seawater, formation water, and their dilutions. The simulated zeta potential results agreed well with the experimental data, demonstrating that the model is applicable to understand the crude oil/brine interface in LSWF. Finally, the importance of the prediction of the surface and zeta potentials in the evaluation of the interface and the estimation of electrostatic forces, and thus the wettability alteration, was discussed.

#### 1. Introduction

Over 65% of oil persists after the first and second recovery processes; therefore, a cost-effective and environment-friendly method of oil recovery is necessary to meet the increasing energy demand. Many researchers and industries have been investigating a variety of Enhanced Oil Recovery (EOR) techniques to meet the demand for oil [1–4]. Low salinity water flooding (LSWF), or smart water flooding, has recently received interest as an economical EOR method, which involves the injection of low-salinity brine, such as seawater or formation water, into a reservoir under secondary or tertiary conditions [1–12]. Several field and laboratory experiments and simulations have demonstrated improved oil recovery by LSWF after the secondary recovery [5–12], but some have not [13]. Oil recovery by LSWF is strongly dependent on the types of brines used and their salinity [7–11,14]. Therefore, a clear understanding of the crude oil/brine and rock/brine interfaces is essential for determining the effect of LSWF on FOR

Various mechanisms have been suggested that could explain the effect of LSWF such as, fines migration and permeability reduction, pH, mineral dissolution, osmotic effects, desorption of polar oil components, micro-dispersion formation, viscoelasticity, expansion of the electrical double layer (EDL), multi component ionic exchange (MIE), and wettability alteration [1-4,15-20]. Although several mechanisms have been proposed, the dominant mechanisms are still unclear. Researchers have recently agreed that wettability alteration is the most accepted mechanism regarding the effect of LSWF [1,18-21], and that EDL expansion, MIE, and electrostatic repulsion between the crude oil/ brine and brine/rock interfaces can alter the wettability. The polar components of crude oil are adsorbed to the rock's surface, through divalent cation bridging or directly to the surface. A decrease in the salinity expands the EDL between the crude oil and rock surfaces, and also removes cations adsorbed on the rock's surface, resulting in the release of adsorbed oil. In addition, lowering the salinity creates more negative oil/brine and rock/brine surfaces, which increases the repulsive forces between them. These LSWF effects alter the wettability from oil-wet to mixed-wet or mixed-wet to water-wet, increasing the release of oil from rock surfaces [18-21].

Wettability alteration strongly depends on the surface electrical charge at the crude oil/brine and rock/brine interfaces: oppositely charged surfaces attract one another, while the same surface charges generate a highly repulsive force. The surface charges of the interfaces

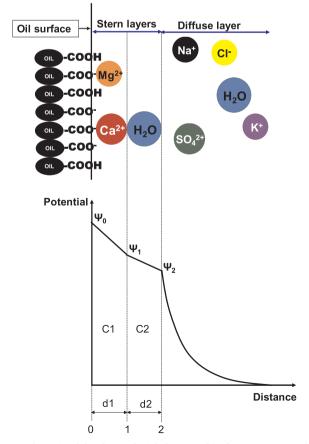
**Table 1**Crude oil properties.

Property	Value
Density (g/cm³)	0.818
Viscosity (cP)	8.398
Acid number (mgKOH/g)	0.39
Base number (mgKOH/g)	1.86
Composition	wt (%)
Saturates	46.4
	16.0
Aromatics	16.9
Aromatics Resins	12.5

are closely related to the measurable zeta potential, which is the electrical potential at the slipping plane of the EDL. The ionic strength and types of ions in the solution affect the zeta potential, and subsequently affecting the thickness of the EDL and the surface charge, which alter the wettability of the crude oil-brine-rock system. Several studies have investigated the impacts of pH, ionic strength, and cation type on the zeta potential of the crude oil and rock surface and have related the potential to the adsorption and desorption of crude oil on the rock surface [21–27]. However, the measurable zeta potential differs from

Table 2
Compositions of seawater and formation water used for zeta potential measurement.

Ion	Concentration (mg/L)	
	Formation water	Seawater
Na <sup>+</sup> Ca <sup>2+</sup> Mg <sup>2+</sup> K <sup>+</sup>	12,153	11,345
Ca <sup>2+</sup>	2133	441
Mg <sup>2+</sup>	320	1075
K <sup>+</sup>	137	439
Cl-	22,519	18,966
HCO <sub>3</sub>	141	119
SO <sub>4</sub> <sup>2-</sup>	72	2676



 $\textbf{Fig. 1.} \ \textbf{Schematic of the electrical triple-layer used in the CD-MUSIC model.}$ 

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