

HOKKAIDO UNIVERSITY

Title	Predicting the electrokinetic properties of the crude oil/brine interface for enhanced oil recovery in low salinity water flooding
Author(s)	Takeya, Miku; Shimokawara, Mai; Elakneswaran, Yogarajah; Nawa, Toyoharu; Takahashi, Satoru
Citation	Fuel, 235, 822-831 https://doi.org/10.1016/j.fuel.2018.08.079
Issue Date	2019-01-01
Doc URL	http://hdl.handle.net/2115/80085
Rights	© 2019. This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/
Rights(URL)	http://creativecommons.org/licenses/by-nc-nd/4.0/
Туре	article (author version)
File Information	Accepted-Predicting the electrokinetic properties of the crude oil.brine interface for enhanced oil recovery in low salinity water flooding.pdf



1 Predicting the electrokinetic properties of the crude oil/brine interface for

2 enhanced oil recovery in low salinity water flooding

- 3
- 4 Miku Takeya¹, Mai Shimokawara^{1, 2}, Elakneswaran Yogarajah^{1, *}, Toyoharu Nawa³, Satoru
- 5 Takahashi²
- 6
- 7 ¹ Division of Sustainable Resources Engineering
- 8 Faculty of Engineering, Hokkaido University
- 9 Kita 13, Nishi 8, Kita-ku, Sapporo, 060-8628, Japan
- 10
- ² Japan Oil, Gas and Metals National Corporation (JOGMEC)
- 12 Technology Department
- 13 Oil & Gas Upstream Technology Unit
- 14 1-2-2 Hamada, Mihama-ku Chiba-city, Chiba, 261-0025, Japan
- 15
- 16 ³ Hokkaido University
- 17 Kita 8, Nishi 5, Kita-ku, Sapporo, 060-0808, Japan
- 18
- 19 * Corresponding author
- 20 E-mail: elakneswaran@eng.hokudai.ac.jp
- 21 Tel: +81-11-706-7274
- 22
- 23
- 24
- 21
- 25
- 26

27 Highlights

- \diamond A triple-layer surface complexation model is proposed for the crude oil/brine interface.
- \diamond The electrokinetic properties are determined and verified by experimental data.
- \Rightarrow The ions' affinity toward the crude oil follows the order: Ca²⁺ <Mg²⁺ <OH⁻.
- 32 interface for EOR in LSWF.

35 Graphical abstract



39 Abstract

The low-salinity waterflooding (LSWF) technique during enhanced oil recovery has received 40 41 increasing attention over the last decade. Several studies have attempted to understand the effects of 42 LSWF through both experiments and modelling, but their results are inconsistent due to a lack of 43 understanding of the crude oil/brine and brine/rock interfaces. In this paper, the crude oil/brine 44 interface was studied by developing a triple-layer surface complexation model. The carboxyl groups 45 (-COOH) were attributed to the surface charge and electrical triple-layer development of the crude 46 oil in LSWF. The zeta potentials of the emulsion at various pH levels and the calcium and magnesium 47 concentrations were measured to examine the interface. These data were then directly fitted to the 48 simulated zeta potentials to determine the surface site density of -COOH and the associated 49 equilibrium constants for the dissociation and adsorption of calcium and magnesium. The -COOH 50 site density was determined by fitting the pH-independent zeta potential, while the equilibrium 51 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 52 53 validated by comparing the experimental zeta potential data from different ionic solutions. The 54 developed surface complexation model was used along with the estimated parameters to predict the 55 interface of crude oil in seawater, formation water, and their dilutions. The simulated zeta potential 56 results agreed well with the experimental data, demonstrating that the model is applicable to 57 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, 58 59 and thus the wettability alteration, was discussed.

60

61 Keywords: Zeta potential; Electrical triple-layer; Surface complexation model; Low salinity water;
62 IOR/EOR

- 63
- 64

65 1. Introduction

66 Over 65% of oil persists after the first and second recovery processes; therefore, a cost-effective and 67 environment-friendly method of oil recovery is necessary to meet the increasing energy demand. 68 Many researchers and industries have been investigating a variety of Enhanced Oil Recovery (EOR) 69 techniques to meet the demand for oil [1–4]. Low salinity water flooding (LSWF), or smart water 70 flooding, has recently received interest as an economical EOR method, which involves the injection 71 of low-salinity brine, such as seawater or formation water, into a reservoir under secondary or tertiary 72 conditions [1-12]. Several field and laboratory experiments and simulations have demonstrated 73 improved oil recovery by LSWF after the secondary recovery [5–12], but some have not [13]. Oil 74 recovery by LSWF is strongly dependent on the types of brines used and their salinity [7–11, 14]. 75 Therefore, a clear understanding of the crude oil/brine and rock/brine interfaces is essential for 76 determining the effect of LSWF on EOR.

77

Various mechanisms have been suggested that could explain the effect of LSWF such as, fines 78 79 migration and permeability reduction, pH, mineral dissolution, osmotic effects, desorption of polar 80 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 81 82 several mechanisms have been proposed, the dominant mechanisms are still unclear. Researchers 83 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 84 85 oil/brine and brine/rock interfaces can alter the wettability. The polar components of crude oil are 86 adsorbed to the rock's surface, through divalent cation bridging or directly to the surface. A decrease 87 in the salinity expands the EDL between the crude oil and rock surfaces, and also removes cations 88 adsorbed on the rock's surface, resulting in the release of adsorbed oil. In addition, lowering the 89 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].

92

93 Wettability alteration strongly depends on the surface electrical charge at the crude oil/brine and 94 rock/brine interfaces: oppositely charged surfaces attract one another, while the same surface charges 95 generate a highly repulsive force. The surface charges of the interfaces are closely related to the 96 measurable zeta potential, which is the electrical potential at the slipping plane of the EDL. The ionic 97 strength and types of ions in the solution affect the zeta potential, and subsequently affecting the 98 thickness of the EDL and the surface charge, which alter the wettability of the crude oil-brine-rock 99 system. Several studies have investigated the impacts of pH, ionic strength, and cation type on the 100 zeta potential of the crude oil and rock surface and have related the potential to the adsorption and 101 desorption of crude oil on the rock surface [21–27]. However, the measurable zeta potential differs 102 from the surface potential, which cannot be measured. The surface potential has been formulated in 103 various theories, such as Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, to understand the 104 interface and its interactions, but many studies have used the measured zeta potential instead of the 105 surface potential to calculate the electrostatic forces in the DLVO theory and explain the changes in 106 the disjoining pressure due to varying brine composition [27–29]. Therefore, separate computation 107 of the surface and zeta potentials is necessary to understand the electrostatic interactions between the 108 crude oil/brine and brine/rock interfaces.

109

Surface complexation models provide insight into the surface coordination reactions at the crude oil/brine and brine/rock interfaces. Diffuse double-layer surface complexation models have been used to predict the impact of the brine composition on the adsorption and desorption of crude oil and double layer expansion [12, 30–35]. Although the diffuse double layer model allows the prediction of the surface behaviour of the interfaces, it cannot directly compare the measured zeta potential of the interfaces at different solution compositions as it can only predict the surface potential. Therefore,

116 the main objective of this study is to propose an electrical triple-layer surface complexation model 117 for the crude oil/brine interface. The surface chemistry of both the crude oil/brine and rock/brine 118 interfaces affects the oil recovery in LSWF, but this study only focuses on the crude oil/brine interface. 119 A methodology is proposed to determine the surface complexation modelling parameters, such as the 120 density of surface functional groups of the crude oil and the equilibrium constants for the surface 121 species interaction with pH, calcium, and magnesium. The surface complexation modelling results 122 were compared with the measured zeta potential for the crude oil emulsion in different solutions to 123 validate the model and the determined surface complexation modelling parameters. Finally, the 124 proposed model is used to explain the behaviour of the crude oil/brine interface in terms of wettability 125 alteration in LSWF.

126

127 **2. Materials and methods**

128 **2.1 Experimental**

129 The properties of the crude oil used in the experiment are given in **Table 1**. It should be noted that 130 this crude oil has waxy characteristics, which can fluidify above 35 °C and solidify at room 131 temperature. Very recent research has investigated the effect of LSWF in waxy crude oil [36]. Sample 132 preparation and the experiments were conducted at 50 °C. The electrolyte solutions used in the 133 experiments were prepared by mixing the chemical reagents with deionised water. In this study, NaOH, NaCl, CaCl₂, and MgCl₂ solutions with different concentrations were used. Further, formation 134 135 water and seawater were prepared using NaCl, CaCl₂:2H₂O, MgCl₂:6H₂O, Na₂SO₄, and NaHCO₃, and 136 then diluted 3, 7, 20, and 30 times using deionised water. The concentrations of the prepared 137 formation water and seawater are presented in Table 2.

138

139 The zeta potential of the crude oil/brine interface was measured using Zeta-potential & Particle size 140 analyser ELSZ-1000, manufactured by Otsuka Electronics. All zeta potential measurements were 141 conducted at 50 °C. The crude oil to solution ratio was constant for each measurement: 0.1 mL (0.5%) of crude oil in 20 mL of solution. The crude oil and solution were emulsified by mixing the sample with a vortex mixer for one minute and then an ultrasonic cleaner for two minutes. The emulsion was extracted with a syringe and injected into a standard cell for measurement. The pH of each sample was measured before and after the addition of crude oil to the solution using a pH meter.

- 146 **Table 1**
- 147 Crude oil properties

Property	Value
Density (g/cm ³)	0.818
Viscosity (cP)	8.398
Acid number (mgKOH/g)	0.39
Base number (mgKOH/g)	1.86
Composition	wt. (%)
Composition Saturates	wt. (%) 46.4
Composition Saturates Aromatics	wt. (%) 46.4 16.9
CompositionSaturatesAromaticsResins	wt. (%) 46.4 16.9 12.5

148

149 **Table 2**

150 Compositions of seawater and formation water used for zeta potential measurement

Ion	Concentration (mg/L)		
	Formation water	Seawater	
Na ⁺	12153	11345	
Ca ²⁺	2133	441	
Mg^{2+}	320	1075	
K^+	137	439	
Cl-	22519	18966	

HCO ₃ -	141	119
SO4 ²⁻	72	2676

152 **2.2 Description of the surface complexation model: CD-MUSIC**

153 The charge distribution-multi site complexation model (CD-MUSIC), built-in geochemical code 154 PHREEQC, is used for the surface complexation calculations [37-39]. This model can be considered 155 as a triple-layer surface complexation model for a single site on one surface. Each ion differs in size 156 and has different interactions towards the charged surface; thus, there are various locations from the 157 surface for the ions. Many studies have highlighted the self-assemblage of oil components at the 158 oil/water interface [40-42]. The accumulation of asphaltenes and resin components or their single 159 molecule forms active surfaces at the interface. The other oil components distribute throughout the 160 oil phase and do not contribute to the formation of active surfaces even if they accumulate at the 161 interface. In this study, the emulsion prepared for zeta potential experiment was assumed to have 162 uniform characteristics, and possible accumulation may not have changed the properties of the active 163 surfaces of the oil components. Therefore, consistent with numerous studies [12, 30–35], the active 164 surfaces of oil components could be treated as a solid surface with a constant site density. The 165 carboxyl groups (-COOH) and nitrogen bases (-N) are the main polar components of the crude oil 166 from asphaltenes and resins and can contribute on the surface charge development of crude oil 167 through the dissociation and adsorption of ions [1, 12, 20, 43]. It was assumed that only the resin 168 components of the oil have -COOH surface groups that controls the surface charge and electrical 169 triple-layer formation at crude oil/brine interface during LSWF, while the nitrogen bases (-N) surface 170 groups were not considered as LSWF in slightly basic or basic conditions, based on previous studies 171 [1, 12].

172

173 On the basis of the results reported on the zeta potential experiments and the diffuse double layer 174 surface complexation model, divalent calcium and magnesium cations and hydroxyl ions are the

175 potential determining ions in the crude oil/brine interface [12, 25, 27, 30, 31]. The divalent cations 176 lose some of their water molecules and create an innersphere surface complex with the carboxyl 177 groups of crude oil forming a Stern or adsorbed layer, while other ions diffuse through the diffuse 178 layer. The sodium and chloride ions affect surface adsorption by modifying the ionic strength and 179 forming aqueous complexes [12]; thus, they do not directly adsorb on the surface. The triple layer 180 (CD-MUSIC) at the crude oil/solution interface in LSWF is illustrated in Fig. 1. The surface has three 181 planes: the 0-, 1-, and 2-planes. The surface groups are located at the 0-plane, and the diffuse layer 182 begins at the 2-plane. The potential at the 0-plane is the surface potential, and the zeta potential can 183 be directly compared to the potential at the 2-plane. The CD-MUSIC model requires the capacitance 184 of the layers and change in charge at three layers due to dissociation of surface sites and adsorption 185 of ions on the sites, in addition to surface site density and equilibrium constants which are needed for 186 double layer model as well. The capacitance of the first (0- to 1-plane) and second (1- to 2-plane) 187 Stern layers can be calculated by [38]

188

$$189 \qquad C = \frac{\varepsilon_0 \varepsilon_r}{d} \tag{1}$$

190

where ε_0 and ε_r are the absolute (8.85 × 10⁻¹² CV⁻¹m⁻¹) and relative dielectric constants, respectively. 191 192 and d is the distance between the planes. It is assumed that the dissociation reaction takes place at the 193 0-plane, whereas the innersphere complex adsorption of calcium and magnesium changes the charge at 0- and 1-planes. Therefore, the distance d1 is the size of an adsorbed ion: the size of a calcium or 194 195 magnesium ion for its adsorption or the size of a water molecule for the dissociation of -COOH. The 196 size of a water molecule is considered for the distance d2. The positions of the ions in the Stern layers 197 change the charge of three layers. The focus of this study is to determine the surface site density of -198 COOH and its associated equilibrium constants for the dissociation and adsorption of calcium and 199 magnesium. Thus, the charge distribution at three layers for -COOH dissociation and the adsorption 200 of calcium and magnesium were assumed as given in Table 3.





Fig. 1. Schematic of the electrical triple-layer used in the CD-MUSIC model

The dissociation of surface carboxyl groups and the adsorption of divalent cations on the groups canbe written as

206

207 -COOH
$$\leftrightarrow$$
 -COO⁻ + H⁺ $K_{coo^-} = \frac{\left(-COO^-\right) * \left(a_{H^+}\right)}{\left(-COOH\right)} \exp\left(-\frac{\Delta z_i F \psi_i}{RT}\right)$ (2)

208

209 -COOH + Ca²⁺
$$\leftrightarrow$$
 -COOCa⁺ + H⁺ $K_{cooCd} = \frac{\left(-COOCd\right)*\left(a_{H^+}\right)}{\left(-COOH\right)*\left(a_{Cd^{2+}}\right)}\exp\left(-\frac{\Delta z_i F\psi_i}{RT}\right)$ (3)

210

211 -COOH + Mg²⁺
$$\leftrightarrow$$
 -COOMg⁺ + H⁺ $K_{COOMg^+} = \frac{(-COOMg^+)*(a_{H^+})}{(-COOH)*(a_{Mg^{2+}})} \exp(-\frac{\Delta z_i F \psi_i}{RT})$ (4)

212

where K_{COO-} , K_{COOCa+} , and K_{COOMg+} are the intrinsic equilibrium constants for dissociation, calcium adsorption and magnesium adsorption, respectively; (-COO⁻), (-COOH), (-COOCa⁺), and (- 215 $COOMg^+$) are the concentrations (mol/m²) of the surface species of the carboxyl groups; a_j is the 216 activity of ionic species j; ψ_i is the potential at the 0-, 1-, or 2-plane (V); Δz_i is the charge distribution; 217 *R* is the universal gas constant equal to 8.31451 J/(mol.K); and *T* is the absolute temperature (K). This 218 model is implemented in PHREEQC using the SURFACE and SURFACE_SPECIES keyword data 219 blocks with the specification of charge distribution and the capacitance of the first and second Stern 220 layers [39].

- 221
- 222 Table 3

223 Charge distribution values for the dissociation and adsorption of calcium and magnesium on

224 carboxylic sites

Ions	Δz_0	$\Delta \mathbf{z_1}$	$\Delta \mathbf{z}_2$	Eq.
OH-	-1	0	0	(2)
Ca ²⁺	-1	2	0	(3)
Mg^{2+}	-1	2	0	(4)

225

226 **3. Results and discussion**

227 **3.1** Site density and deprotonation of carboxylic groups: determination and verification

228 The density of the -COOH surface groups and the equilibrium constant (K_{COO-} in Eq. (2)) value for 229 the dissociation of carboxyl groups were determined from the measured zeta potentials and the results 230 of CD-MUSIC surface complexation modelling. This model can separately predict the surface (at the 0-plane) and zeta potentials (at the 2-plane), the latter of which is directly comparable to the measured 231 232 zeta potential. This is not possible with the diffuse layer surface complexation model that can only 233 predict the surface potential, which is completely different from the zeta potential. The electrical properties of the surface and the solution composition affect the difference between these potentials, 234 235 which will be discussed in section 3.3.

237 The effects of pH and ionic strength on the zeta potential of crude oil are shown in Fig. 2. The pH of 238 the solution was adjusted using NaOH while NaCl was added appropriately to maintain the ionic 239 strength. Therefore, the concentration of Na is constant over the pH and Cl concentration decreases 240 with pH. The increase in the pH enhances the dissociation of -COOH, causing the surface to become 241 more negatively charged. The figure shows that pH does not influence the dissociation above a pH of 242 9. This is due to the complete dissociation of the -COOH surface groups. The pH required to fully 243 dissociate -COOH depends on the ionic strength: a high ionic strength requires a lower pH to fully 244 dissociate -COOH than that for a low ionic strength. This characteristic is used to determine the 245 density of -COOH. The CD-MUSIC model can predict the zeta potential of the emulsions given the 246 inputs of site density, equilibrium constant (Kcoo-), capacitance (C1 and C2), and amount and specific 247 surface area of oil. The specific surface area of oil is calculated from the measured size of the oil particles in the solution, equal to $0.5 \text{ m}^2/\text{g}$ of resins. C1 and C2 are equal to 2.253 F/m², assuming 248 249 that there is a water molecule (diameter of 2.75Å) attached to the first and second Stern layers (Eq. (1) and Fig. 1). Dissociation only changes the charge at the 0-plane (Table 3). The measured zeta 250 251 potential data at an ionic strength of 100 mM were fitted to the predicted values in two different pH 252 ranges. Initially, the simulation was performed with a log K_{COO-} of zero, and the predicted zeta 253 potentials were fitted to the measured values by only changing the -COOH site density in a pH range 254 (above 9) where the zeta potential is independent of pH. The estimated site density was used to fit 255 other zeta potential values (below a pH of 9), where the values are pH-dependent, by only adjusting the log Kcoo-. The determined -COOH site density and log Kcoo- values are 0.47 sites/nm² and -5.6, 256 respectively. The optimised equilibrium constant and site density were obtained when an R² value 257 258 close to one for the plot of experimental versus predicted zeta potential values. This methodology 259 will be used to optimise the equilibrium constants for calcium and magnesium adsorption (section 260 3.2). The estimated site density and log K_{COO} values do not differ much from those reported in the literature [12, 30, 31, 33, 34]. These values, together with C1 and C2, were used to predict the zeta 261 262 potential of the emulsions at the ionic strengths of 20 and 700 mM. The simulation results agree well

with the measured zeta potential data at low and high ionic strengths, indicating the predictive capability of the model for LSWF.

265



266

Fig. 2. Measured and predicted zeta potentials of crude oil as a function of pH at ionic strengths of
20, 100, and 700 mM. The ionic strength was adjusted with an NaCl solution.

269

3.2 Interactions between calcium and magnesium ions and crude oil: determination of equilibrium constants and prediction of zeta potentials

Divalent calcium and magnesium cations can adsorb on the surface of -COOH, and cause both the 272 273 surface and zeta potentials toward positive. The zeta potentials of crude oil emulsions in solutions with varying CaCl₂ concentrations at constant pH values of 8 and 10 and a constant ionic strength of 274 275 20 mM are shown in Fig. 3. The higher pH value was selected considering the dissociation of -COOH, which produces more than 70 % of the -COO⁻ at a pH of 8 and an ionic strength of 100 mM, and a 276 277 low ionic strength was selected to understand the adsorption in LSWF. NaOH and NaCl solutions, as 278 in section 3.1, were used to fix the pH and ionic strength, respectively. The addition of calcium to the 279 emulsion dramatically increased the zeta potential, which in turn gradually increased with the calcium 280 concentration. The calcium adsorption on -COOH surfaces was modelled by CD-MUSIC taking the

281	reactions given in Eqs. (2) and (3) and the charge distribution for calcium adsorption given in Table
282	3 . The density of -COOH and the log_K_{COO} value determined in section 3.1 were used to predict the
283	calcium interactions. The thicknesses of the first and second Stern layers were determined by the
284	respective presence of calcium ions and water molecules in the layers (Fig. 1), giving the values of
285	C1 and C2 as 3.098 F/m^2 and 2.253 F/m^2 , respectively. The only parameter required to predict the
286	zeta potential of the emulsion in the calcium-containing solution is the $log_K_{COOCa^+}$, which was
287	determined by fitting the measured zeta potential values at a pH of 8.0 with the modelling results (Fig.
288	3(A)). A value of -4.7 was obtained for the assumed positions of both calcium ions and water
289	molecules in the Stern layers. To understand the effects of the widths of the first and second Stern
290	layers on <i>log_Kcooca+</i> , the fitting was carried out for different cases. The detail of the thicknesses of
291	the Stern layers and the estimated log_K_{COOCa+} values are presented in Table 4 . The widths of the
292	Stern layers did not significantly affect $log_K cooc_{a+}$; thus, a value of -4.8±0.1 was determined to be
293	the most suitable for log_Kcooc_{a+} . The interactions between the CaOH ⁺ and -COOH surface groups
294	were not considered as there was very little CaOH ⁺ (less than 1%) in the solution, even at a high
295	CaCl ₂ concentration and a pH of 10. The calculated surface complexation modeling parameters
296	predicted the measured zeta potentials well at a pH of 10 and an ionic strength of 20 mM (Figs. 3(B)
297	and 3(C)).





Fig. 3. Measured and predicted zeta potential of crude oil as a function of Ca²⁺ concentration for (A)
a constant pH of 8.0; (B) a constant pH of 10.0; and (C) a constant ionic strength of 20 mM. The ionic
strength was adjusted with a NaCl solution.

307 Table 4

308 Thicknesses of the first and second Stern layers and the estimated log_Kcooc_{a+} values for four 309 different scenarios

	d1	d2	log_K _{COOCa+}
Case 1	Diameter of calcium	Diameter of water	-4.7
Case 2	Radius of calcium	Radius of calcium +	-4.8
		diameter of water	
Case 3	Diameter of calcium +	Diameter of water	-4.7
	diameter of water		
Case 4	Diameter of calcium +	Diameter of water * 2	-4.9
	diameter of water		

310

311 As for calcium, the influence of the magnesium ions on the zeta potential of a crude oil emulsion was 312 also studied. The zeta potential increases with the concentration of magnesium ions for the crude oil 313 in MgCl₂ solution at pH levels of 7 and 8 and an ionic strength of 20 mM (Fig. 4). A similar tendency 314 was obtained with calcium. To prevent the formation of brucite, a pH below 8 was selected. The simulation was performed in the CD-MUSIC model considering the reaction given in Eq. (4) and the 315 316 parameters estimated in section 3.1. However, the calculated value of C1 for the adsorption of 317 magnesium on the first Stern layer was 4.302 F/m², and C2 was the same as used in the calcium 318 interaction, 2.253 F/m^2 . The zeta potential measured at a pH of 8 was used to fit the modelling results 319 and the determined value of log K_{COOMg+} was -3.85 (Fig. 4(A)). As was carried out for calcium 320 (Table 4), four different scenarios for the widths of the Stern layers were assumed to estimate the log K_{COOMg+} , and the most suitable log K_{COOMg+} was -3.9±0.05. To verify the estimated parameters, 321 322 the calculation was carried out at a pH of 7 and an ionic strength of 20 mM. As explained for calcium, MgOH⁺ was not considered in the calculation as it had a negligible concentration in the solution. A 323 324 comparison between the model-predicted and measured zeta potentials is shown in Figs. 4(B) and

325 4(C). The good agreement between the model-predicted and experimental data for both calcium and 326 magnesium interactions strongly suggests that the estimated surface complexation modeling 327 parameters are applicable for LSWF. Furthermore, both the experimental and modeled zeta potential 328 results show that magnesium ions adsorb onto crude oil with a higher affinity than calcium ions.





330







Fig. 4. Measured and predicted zeta potentials of crude oil as a function of Mg²⁺ concentration for
(A) a constant pH of 8.0; (B) a constant pH of 7.0; and (C) a constant ionic strength of 20 mM. The
ionic strength was adjusted with a NaCl solution.

337 **3.3** Prediction of the zeta potential of crude oil in diluted seawater and formation water

The estimated surface complexation parameters, such as the -COOH surface site density and the 338 339 equilibrium constants for the dissociation and adsorption of calcium and magnesium ions, in sections 340 3.1 and 3.2 were used to predict the zeta potentials of the emulsions in seawater, formation water, and 341 their dilutions. Although these solutions consisted of multi-ions (Table 2), the pH and divalent cations 342 are the potential-determining ions that strongly impact the electrical triple-layer at the oil/brine 343 interface. The presence of calcium ions, whose hydration radius is higher than that of magnesium 344 ions, and water molecules in the Stern layers determines the values of C1 and C2 (Case 1 in Table 4). Figure 5 compares the experimental zeta potential with the simulation results for emulsions of 345 346 crude oil with seawater and formation water. The model predictions agreed well with the experimental 347 results. The results indicate that the zeta potential of oil in seawater or formation water is weakly negative owing to the high concentrations of calcium and magnesium. This supports the results 348 349 described in sections 3.1 and 3.2; the zeta potential does not become positive at a high concentration

because the pH has more of an impact on the zeta potential than the concentration of divalent ions.
Furthermore, a reduction in the salinity or dilution causes the zeta potential to become more negative.



Fig. 5. Comparison of the predicted and measured zeta potentials of crude oil in (A) seawater; (B)
formation water, as a function of dilution times.

The surface complexation model was applied to understand the effects of the surface charge and 358 359 potential at the crude oil/brine interface, which influence the wettability change in LSWF. Figure 360 6(A) compares the computed zeta potential with the surface potential together with the calculated 361 diffuse layer thickness for the crude oil emulsions with seawater and its dilutions. As discussed 362 previously, the measurable zeta potential differs from the surface potential. The absolute surface 363 potential was more than double the zeta potential up to a dilution of 20 times, and the potentials 364 became more negative with increasing dilution. The zeta and surface potentials could be positive and 365 negative, respectively, or vice-versa for different brine compositions, though both potentials were 366 negative in this study. The calculation of the adhesion forces in DLVO theory using the zeta potential 367 values rather than surface potential may cause incorrect prediction. Therefore, the surface potential 368 should be used instead of the zeta potential to evaluate the crude oil/brine interface and hence the 369 wettability alteration.

370

371 The concentration or amount of surface species on the -COOH surface affects the surface potential 372 and then the zeta potential. The simulation results of the surface species distribution with reducing 373 seawater salinity are shown in Fig. 6(B). The higher concentration of -COO⁻ than that of the other 374 species causes negative surface and zeta potentials. The distribution is insensitive to the salinity after 375 the seawater is diluted more than seven times; however, the absolute potential increases with dilution. As shown in Fig. 6(A), dilution strongly affects the expansion of the diffuse layer, consequently 376 causing more negative potentials. The proposed crude oil/brine interface at high and low salinities 377 378 are schematically presented in Fig. 7 along with the potential distribution, and the surface 379 complexation modelling parameters for crude oil at a low salinity are summarised in Table 5. Dilution 380 does not significantly change the concentrations of surface species (-COOH, -COO⁻, -COOCa⁺, and 381 -COOMg⁺), but it causes the potentials to become more negative at each plane due to the decreasing 382 ionic strength. The increases in the potentials and the electrical triple-layer expansion as result of the 383 lowered ionic strength affect the interaction of oil with the rock surface. It was shown that the 384 potential at the mineral/brine interface is highly negative at a low salinity [25, 27, 44]. This negative electrical potential can create a large repulsive force with crude oil and enhance the oil detachment 385 386 from the mineral surface, leading to more water-wet conditions. In addition, the ions are more 387 hydrated in the diluted solution than they are in a high-salinity solution, which may also support water-wet conditions [45-46]. Thus, the increase of surface potential at the crude oil/brine interface 388 389 and the electrical triple-layer expansion are the more pronounced mechanisms for wettability 390 alteration at a low salinity than the dissociation of -COOH and the adsorption of ions on the -COOH 391 surface.







Fig. 6. Simulated (A) surface potential, zeta potential, and diffuse layer thickness; (B) molar fraction
of surface species, as a function of dilution times at the crude oil/seawater interface



Fig. 7. Illustration of ionic and potential distributions at the crude oil/brine interface

403 **Table 5**

404 Determined surface complexation parameters of crude oil

	Value
-COOH surface site density (sites/nm ²)	0.47
Specific surface area of oil in water (m^2/g of resins)	0.50±0.1
-COOH \leftrightarrow -COO ⁻ + H ⁺	log_k at 50 °C = -5.6
$-\text{COOH} + \text{Ca}^{2+} \leftrightarrow -\text{COOCa}^{+} + \text{H}^{+}$	log_k at 50 °C = -4.8±0.1
$\text{-COOH} + Mg^{2+} \leftrightarrow \text{-COOMg}^{+} + H^{+}$	log_k at 50 °C = -3.9±0.05
C1	3.10
C2	2.25

405

406 **4.** Conclusions

407 The crude oil/brine interface was studied using a triple-layer surface complexation model. The model 408 permits the specification of the charge distribution in each plane due to the dissociation of the surface 409 functional groups of crude oil and the adsorption of calcium and magnesium ions onto them. Only 410 the carboxyl group (-COOH) contributes to the charge development of the crude oil emulsion in 411 various solutions. The density of the carboxyl group and the associated equilibrium constants for the 412 dissociation and adsorption of calcium and magnesium were determined by fitting the experimental 413 zeta potential data to those of the simulation. The independence of the zeta potential at a high pH and 414 constant ionic strength due to the complete dissociation of the carboxyl group allowed the 415 determination of its density, while the equilibrium constant for dissociation was calculated from the 416 pH-dependent zeta potential. The estimated values were verified by predicting the zeta potential of 417 the crude oil emulsion at different pH levels in two solutions with different ionic strengths. These 418 values were used to model the interactions of calcium and magnesium with the carboxyl group. Four 419 different cases for the positions of calcium and magnesium near the carboxyl group were considered to estimate the equilibrium constants of adsorption. The determined equilibrium constants were 420

421 verified for the emulsion with varying calcium or magnesium concentrations at a constant pH and 422 ionic strength. Separately determined surface complexation modelling parameters were used to 423 predict the zeta potential of crude oil in seawater and formation water as a function of the dilution 424 times. The simulation results agreed well with experimental data, which demonstrates that the model 425 is capable of predicting the interface properties. The proposed model was used to understand the 426 effects of LSWF. A decrease in the salinity causes the surface potential to become more negative and 427 expands the electrical triple-layer, thus resulting in mixed-wet or mixed-wet to water-wet conditions 428 in the reservoir for EOR.

429

444

430 References

- 431 Afekare DA, Radonjic M. From Mineral Surfaces and Coreflood Experiments to Reservoir [1] Implementations: Comprehensive Review of Low-Salinity Water Flooding (LSWF). Energy 432 and Fuels 2017;31:13043-62. 433
- Sohal MA, Thyne G, Søgaard EG. Review of Recovery Mechanisms of Ionically Modified 434 [2] 435 Waterflood in Carbonate Reservoirs. Energy and Fuels 2016;30:1904–14.
- Sheng JJ. Critical review of low-salinity waterflooding. J Pet Sci Eng 2014;120:216-24. 436 [3]
- Al-Shalabi EW, Sepehrnoori K. A comprehensive review of low salinity/engineered water 437 [4] 438 injections and their applications in sandstone and carbonate rocks. J Pet Sci Eng 2016;139:137– 61. 439
- 440 [5] Morrow N, Buckley J. Improved Oil Recovery by Low-Salinity Waterflooding. J Pet Technol 441 2011;63:106-12.
- 442 [6] Shariatpanahi SF, Strand S, Austad T. Evaluation of water-based enhanced oil recovery (EOR) 443 by wettability alteration in a low-permeable fractured limestone oil reservoir. Energy and Fuels 2010;24:5997-6008.
- 445 [7] Austad T, Shariatpanahi SF, Strand S, Black CJJ, Webb KJ. Conditions for a low-salinity 446 Enhanced Oil Recovery (EOR) effect in carbonate oil reservoirs. Energy and Fuels, vol. 26,

447 2012, p. 569–75.

- 448 [8] Alameri W, Teklu TW, Graves RM, Kazemi H, AlSumaiti AM. Wettability Alteration During
 449 Low-Salinity Waterflooding in Carbonate Reservoir Cores. SPE Asia Pacific Oil Gas Conf.
 450 Exhib., 2014.
- 451 [9] McMillan MD, Rahnema H, Romiluy J, Kitty FJ. Effect of exposure time and crude oil
 452 composition on low-salinity water flooding. Fuel 2016;185:263–72.
- [10] Yousef AA, Al-Saleh SH, Al-Kaabi A, Al-Jawfi MS. Laboratory Investigation of the Impact of
 Injection-Water Salinity and Ionic Content on Oil Recovery From Carbonate Reservoirs. SPE
 Reserv Eval Eng 2011;14:578–93.
- 456 [11] Suijkerbuijk B, Hofman J, Ligthelm DJ, Romanuka J, Brussee N, van der Linde H, et al.
- 457 Fundamental Investigations into Wettability and Low Salinity Flooding by Parameter Isolation.
- 458 SPE Improv Oil Recover Symp 2013:1–23.
- 459 [12] Qiao C, Johns R, Li L. Modeling Low-Salinity Waterflooding in Chalk and Limestone
 460 Reservoirs. Energy and Fuels 2016;30:884–95.
- 461 [13] Aladasani A, Bai B, Wu Y, Salehi S. Studying low-salinity waterflooding recovery effects in
 462 sandstone reservoirs. Journal of Petroleum Science and Engineering 2014; 120:39-51.
- 463 [14] Hua Z, Li M, Ni X, Wang H, Yang Z, Lin M. Effect of injection brine composition on
 464 wettability and oil recovery in sandstone reservoirs. Fuel 2016;182:687–95.
- 465 [15] Mahzari P and Sohrabi M. Crude oil/brine interactions and spontaneous formation of micro466 dispersions in low salinity water injection. Paper SPE-169081 presented at the SPE Improved
 467 Oil Recovery Symposium held in Tulsa, Oklahoma, USA, 12–16 April 2014.
- 468 [16] Sohrabi M, Mahzari P, Farzaneh S. A, Mills J. R, Tsolis P, and Ireland S, Novel insights into
- 469 mechanisms of oil recovery by use of low-salinity-water injection, SPE Journal, April 2017,
 470 407-416.
- 471 [17] Alvarado V, et.al. Impact of polar components on crude oil-water interfacial film formation: A
 472 mechanisms for low-salinity waterflooding, Paper SPE-170807 presentation at the SPE Annual
 - 25

- 473 Technical Conference and Exhibition held in Amsterdam, The Netherlands, 27–29 October474 2014.
- 475 [18] Jackson MD, Vinogradov J, Hamon G, Chamerois M. Evidence, mechanisms and improved
 476 understanding of controlled salinity waterflooding part 1: Sandstones. Fuel 2016;185:772–93.
- 477 [19] Mahani H, Keya AL, Berg S, Bartels WB, Nasralla R, Rossen WR. Insights into the mechanism
- 478 of wettability alteration by low-salinity flooding (LSF) in carbonates. Energy and Fuels
 479 2015;29:1352–67.
- [20] Austad T, RezaeiDoust A and Puntervold T. Chemical Mechanism of Low Salinity Water
 Flooding in Sandstone Reservoirs. paper SPE 37236 presented at the 2010 SPE Improved Oil
 Recovery Symposium held in Tulsa, Oklahoma, USA, 24–28 April 2010.
- 483 [21] Tian H, Wang M. Electrokinetic mechanism of wettability alternation at oil-water-rock
 484 interface. Surf Sci Rep 2018;72:369–91.
- [22] Chow RS, Takamura K. Electrophoretic mobilities of bitumen and conventional crude-in-water
 emulsions using the laser Doppler apparatus in the presence of multivalent cations. J Colloid
 Interface Sci 1988;125:212–25.
- 488 [23] Buckley JS, Takamura K. Influence of Electrical Surface Charges on the Wetting Properties of
 489 Crude Oils. Soc Pet Eng 1987:332–40.
- 490 [24] Myint PC, Firoozabadi A. Thin liquid films in improved oil recovery from low-salinity brine.
 491 Curr Opin Colloid Interface Sci 2015;20:105–14.
- 492 [25] Nasralla RA, Nasr-El-Din HA. Impact of cation type and concentration in injected brine on oil
 493 recovery in sandstone reservoirs. J Pet Sci Eng 2014;122:384–95.
- 494 [26] Matthew D. Jackson, Dawoud Al-Mahrouqu & Jan Vinogradov. Zetapotential in oil-water495 carbonate systems and its impact on oil recovery during controlled salinity water-flooding.
 496 Scientific Reports 2016.1-13.
- 497 [27] Xie Q, Liu Y, Wu J, Liu Q. Ions tuning water flooding experiments and interpretation by
 498 thermodynamics of wettability. J Pet Sci Eng 2014;124:350–8.

- 499 [28] Xie Q, Saeedi A, Pooryousefy E, Liu Y. Extended DLVO-based estimates of surface force in
 500 low salinity water flooding. J Mol Liq 2016;221:658–65.
- 501 [29] Hirasaki GJ. Wettability: Fundamentals and Surface Forces. SPE Form Eval 1991;6:217–26.
- 502 [30] Brady P V., Krumhansl JL. A surface complexation model of oil-brine-sandstone interfaces at
 503 100 °C: Low salinity waterflooding. J Pet Sci Eng 2012;81:171–6.
- 504 [31] Brady P V., Morrow NR, Fogden A, Deniz V, Loahardjo N, Winoto A. Electrostatics and the
 505 low salinity effect in sandstone reservoirs. Energy and Fuels 2015;29:666–77.
- 506 [32] Eftekhari AA, Thoms27-28en K, Stenby EH, Nick HM. Thermodynamic Analysis of Chalk507 Brine-Oil Interactions. Energy and Fuels 2017;31:11773–82.
- 508 [33] Xie Q, Brady P V., Pooryousefy E, Zhou D, Liu Y, Saeedi A. The low salinity effect at high
 509 temperatures. Fuel 2017;200:419–26.
- 510 [34] Chen Y, Xie Q, Sari A, Brady P V., Saeedi A. Oil/water/rock wettability: Influencing factors
 511 and implications for low salinity water flooding in carbonate reservoirs. Fuel 2018;215:171–7.
- 512 [35] Qiao C, Li L, Johns RT, Xu J. A Mechanistic Model for Wettability Alteration by Chemically
 513 Tuned Waterflooding in Carbonate Reservoirs. SPE J 2015:17.
- 514 [36] Mahzari P, Sohrabi M, Cooke A. J, Carnegie A, Direct pore-scale visualization of interactions
 515 between different crude oils and low salinity brine, J Pet Sci Eng 2018;166:73–84.
- 516 [37] Hiemstra T, Wolthers M. A Surface StructuralAapproach to Ion Adsorption: The Charge
 517 Distribution (CD) Model. J Colloid Interface Sci 1996;179:488–508.
- [38] Rahnemaie R, Hiemstra T, Riemsdijk, W. H, A new surface structural approach to ion
 adsorption: Tracing the location of electrolytes, J Colloid Interface Sci 2006;293:312-321.
- [39] Parkhurst BDL, Appelo C a J. User's Guide To PHREEQC (version 2) a Computer Program
 for Speciation, and Inverse Geochemical Calculations. Exch Organ Behav Teach J 1999;D:326.
- 522 [40] Kunieda, M et.al. Self-accumulation of aromatics at the oil-water interface through weak
 523 hydrogen bonding, J. AM. CHEM. SOC. 2010, 132, 18281–18286.
- 524 [41] Andrews A. B, et.al. Molecular orientation of asphaltenes and PAH model compounds in

- Langmuir-Blodgett films using sum frequency generation spectroscopy, Langmuir, 2011, 27,
 6049-6058.
- 527 [42] Ruiz-Morales, Y and Mullins, O. C. Coarse-grained molecular simulations to investigate
 528 asphaltenes at the oil-water interface, energy & fuel, 2015, 29, 1597-1609.
- 529 [43] Shehata, A. M.; Nasr El-Din, H. A. Spontaneous Imbibition Study: Effect of Connate Water
- Composition on Low-Salinity Waterflooding in Sandstone Reservoirs. Society of Petroleum
 Engineers: Houston, TX, 2015.
- 532 [44] Takahashi S, Kovscek AR. Wettability estimation of low-permeability, siliceous shale using
 533 surface forces. J Pet Sci Eng 2010;75:33–43.
- 534 [45] Nicolini JV, Ferraz HC, Borges CP. Effect of seawater ionic composition modified by
 535 nanofiltration on enhanced oil recovery in Berea sandstone. Fuel 2017;203:222–32.
- 536 [46] Yang G, Chen T, Zhao J, Yu D, Liu F, Wang D, et al. Desorption Mechanism of Asphaltenes
 537 in the Presence of Electrolyte and the Extended Derjaguin-Landau-Verwey-Overbeek Theory.
 538 Energy and Fuels 2015;29:4272–80.