Research Article

A Synergy between Controlled Salinity Brine and Biosurfactant Flooding for Improved Oil Recovery: An Experimental Investigation Based on Zeta Potential and Interfacial Tension Measurements

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In this study, we have investigated the effects of brine and biosurfactant compositions on crude-oil-rock-brine interactions, interfacial tension, zeta potential, and oil recovery. The results of this study show that reduced brine salinity does not cause significant change in IFT. However, addition of biosurfactants to both high and low salinity brines resulted in IFT reduction. Also, experimental results suggest that the zeta potential of high salinity formation brine-rock interface is positive, but oil-brine interface was found to be negatively charged for all solutions used in the study. When controlled salinity brine (CSB) with low salinity and CSB with biosurfactants were injected, both the oil-brine and rock-brine interfaces become negatively charged resulting in increased water-wetness and, hence, improved oil recovery. Addition of biosurfactants to CSB further increased electric double layer expansion which invariably resulted in increased electrostatic repulsion between rock-brine and oil-brine interfaces, but the corresponding incremental oil recovery was small compared with injection of low salinity brine alone. Moreover, we found that the effective zeta potential of crude oil-brine-rock systems is correlated with IFT. The results of this study are relevant to enhanced oil recovery in which controlled salinity waterflooding can be combined with injection of biosurfactants to improve oil recovery.

1. Introduction

The crude-oil-rock-brine (CORB) system is a complex system that involves fluid-fluid and rock-fluid interactions and the properties of each component are fundamental to the mechanisms involved in the system. Rock-fluid interactions related to reservoirs have been studied through different methods such as adsorption, electrophoretic mobility, zeta potential measurements, adhesion, and contact angle measurements for better understanding of this complex system [1]. The interfacial phenomenon at the rock-fluid interface is controlled by electric double layer (EDL) effects and understanding of interactions between ions and rock surface is fundamental [2]. Reservoir fluids such as crude oil, formation brine, injection brine, and enhanced oil recovery (EOR) fluids such

as surfactants are comprised of ions or polar components in one form or another. These components can have chemical interactions with the bulk solution or the rock surface. The ions commonly found in formation and injection brine are H^+, Ca^{2+}, Mg^{2+}, Na^+, HCO_3^-, Cl^-, and SO_4^{2-} and they have the tendency to form complexes in bulk aqueous phase or at the rock surface [3]. Also, the polar components of crude oil exhibit surface activity that enable them to adsorb directly on the rock surface, thereby altering the rock surface wettability [4]. These polar components and the rock surface have no charges of their own, but the presence of water in the system makes both rock and oil interfaces charged [1, 5]. The net charge at the oil-brine and rock-brine interfaces influences the stability of water film between oil and rock surfaces based on Deryaguin-Landua-Verwey-Overbeek (DLVO) theory [6,

7] that describes the net force between two surfaces due to combined effects of van der Waals and electrostatic forces. Depending on the brine composition, electrical potential of the same polarity at both oil-brine and rock-brine interfaces promotes electrostatic repulsion and stability of water film which increases surface water-wetness. On the contrary, electrostatic attraction will result in destabilised water film from rock surface and adsorption of oil component [5, 8].

The electrical potential distribution within the EDL can be characterised by zeta potential which can also be used to describe the electrostatic forces between the rock-brine and oil-brine interfaces [9, 10]. Several studies have used zeta potential measurements to interpret wettability alteration in EOR processes of which [2, 3, 11–13] are examples. Furthermore, a recent study by Jackson et al. [14] has shown that optimum brine composition for an effective controlled salinity brine (CSB) flooding in carbonate rocks can be designed based on the zeta potential and wettability measurements. The zeta potential at the brine-rock interface is usually determined from rock-water in single-phase zeta potential measurements while the system containing both water and crude oil yields the effective zeta potential at oil-brine and rock-brine interfaces [15]. The zeta potential is however said to be affected not only by the ionic strength of brine but also by pH, composition, and surfactant concentration [2]. Previous studies have associated successive CSB flooding with rock-fluid interaction that is related to modification of electric double layer [14, 16], while others have related it to fluid-fluid interaction that is related to interfacial tension (IFT) reduction [17] and formation of microdispersions micelles [18].

Other studies have explored the EOR potential via combining low salinity brine with chemical surfactant injection in the bid to increase oil production and their results show better recovery with combined process than applying either of the techniques alone [19–21]. Addition of surfactants has also been shown to be efficient in decreasing oil-brine interfacial tension and altering of rock surface wetness [22–24]. The rock surface wettability can be altered by surfactant adsorption depending on the orientation of surfactant molecules during the adsorption process, which is related to the nature of the charged surface and the polar end of surfactants [25]. When surfactant adsorbs onto rock surface with its hydrophobic groups oriented away from the rock surface, the surface hydrophobicity will increase, thereby making the rock surface less water-wet. Conversely, surfactant adsorption with its hydrophilic groups oriented from the rock surface increases the surface water-wetness. The cumulative effects of continuous chemical surfactants flooding however constitute environmental threat due to their toxicity and nondegradability nature [26]. Hence, there has been increased research on biologically generated surfactants (biosurfactants) as substitute for chemical surfactants and studies have reported the biosurfactants to be as efficient as chemical surfactants in different applications [27]. Also, past studies have reported EOR potential of biosurfactants (e.g., [22, 28–34]) but effect of biosurfactants on zeta potential of CORB system has not been

TABLE 1: Composition of brines electrolytes used in this work. Formation brine (FMB) represents a typical composition and ionic strength of formation brines; seawater (SW) has typical composition and ionic strength; controlled salinity brine (CSW) is 90 times diluted SW.

Ions	FMB (M)	SW (M)	CSB (mM)
Na	1.463	0.550	6.100
Ca	0.420	0.014	0.200
Mg	0.091	0.045	0.500
Cl	2.485	0.620	6.900
SO	0.002	0.024	0.300
Ionic strength	3.000	0.750	8.300

explored. The main objective of this study, therefore, is to investigate the potential of synergy between CSB and biosurfactants for further improvement of oil recovery and to investigate their effect on rock-fluid interactions. To achieve this aim, experiments on fluid-fluid and rock-fluid interactions based on IFT, wettability, and zeta potential measurements using crude oil and brine compositions were carried out. For the first time, the experimental results of this study show a correlation between changes in effective zeta potential, wettability, IFT, and ultimately oil recovery from carbonate rock samples saturated with brines and biosurfactants.

2. Material and Method

2.1. Materials and Sample Preparation. All the brines were prepared with reagent grade of sodium chloride (NaCl), calcium chloride dihydrate ($CaCl_2.2H_2O$), magnesium chloride hexahydrate ($MgCl_2.6H_2O$), and sodium sulphate (Na_2SO_4) salts from Sigma Aldrich, UK, in deionized water from Thermo Scientific Barnstead Smart2pure system with 18.2 MΩcm conductivity and purity >95%. Three main brines: formation brine (FMB), sea water (SW), and controlled salinity brine (CSB), were used in this study. The compositional breakdown of these brines is presented in Table 1. The FMB is an example of brine composition and salinity that is typical of hydrocarbon reservoirs, while SW has the composition and salinity of synthetic sea water often used as injection fluid in hydrocarbon reservoirs and CSB is the composition and salinity of injection brine used for EOR application. In this study, the CSB was designed based on 90 times diluted SW. The choice of using 90 times diluted SW as a CSB is consistent with previous experimental studies in sandstone and carbonate rocks (e.g., [35–37]). Also, our choice of dilution factor was based on the stability of biosurfactants in injected brines. Biosurfactant precipitation was observed in brines of salinity higher than 0.0083 M in previously published study carried out with the same materials [38]. The rock sample used in this study is Estaillades limestone from France. The X-ray diffraction analysis shows the main composition of the core samples as calcite (95% $CaCO_3$) with trace composition of 4% $MgCO_3$ and 1% $CaSO_4$. Four core samples were used for core flooding; the basic properties of all the cores are presented in Table 2. The two biosurfactants used in this study

TABLE 2: Basic properties of core plugs.

Core plug	L (cm)	D(cm)	ϕ (%)	k (mD)
Wettability samples				
C04	7.61	3.72	30	131
C07	7.63	3.75	31	129
C08	7.60	3.78	27	127
C23	7.62	3.74	33	130
C24	7.63	3.79	30	127
C25	7.64	3.74	25	130
C28	7.64	3.79	25	127
Core flooding samples				
C13	7.64	3.76	0.30	130
C16	7.61	3.79	0.31	127
C27	7.61	3.78	0.28	127
C30	7.66	3.72	0.26	132

TABLE 3: Crude oil properties.

Properties	Quantity
Viscosity @ 25°C (Pa.s)	0.0506
Density @ 25°C (kg/m^3)	908
API @ 25°C (°)	24.75
TAN (mg KOH/g)	3.91
TBN (mg KOH/g)	1.40
Asphaltene (wt.%)	0.85

are rhamnolipid of Agae Technology USA and greenzyme from Biotech Processing Supply, Dallas, Texas. Rhamnolipid is an example of whole cell biotransformation synthesis of carbohydrate sources while greenzyme is an example of enzymatic synthesis source. The crude oil used in this study is a dead oil from the North Sea and its properties measured at 25°C are presented in Table 3.

2.2. Methods

2.2.1. Interfacial Tension (IFT) Test. The IFT test was carried out in two steps with brines (FMB, SW, and CSB) described in Table 1. In the first step, the oil-brine IFT was investigated without biosurfactants. This was carried out in order to investigate the effect of salinity variation of oil-brine IFT. In the second step, the effect of biosurfactants on brine of varied salinity was investigated, with the addition of fixed concentration (1 wt%) of biosurfactants to the brines investigated in the first step. All the IFT measurements were taken at least three times and the presented results are the average of these measurements and the tests were carried out at 23±1°C with the Du Nouy ring method with the aid of Sigma703D tensiometer. The biosurfactant concentration and the system temperature used in this IFT test were adopted in the core flooding experiments.

2.2.2. Measurements of Wettability Indices. Seven intact carbonate core samples were used in spontaneous imbibition tests, with four of these seven samples being subjected to

subsequent forced imbibition (waterflooding) experiments. Prior to carrying out the measurements, the core samples were cleaned in a Soxhlet extractor following the procedure described by Alroudhan et al. [39]. The samples were cleaned with methanol for 24 h followed by drying the samples in oven at 80°C for minimum of 24 h. After the samples cooled down, they were saturated with the FMBEq brine thereafter, flooded with crude oil down to irreducible water saturation, and aged for six weeks at 75°C. After ageing, each core sample was placed in an Amott cell containing the aqueous solution of interest, and the volume of produced oil was recorded until no oil production was observed. The forced imbibition experiments were carried out with injection of brine identical to the one used in the preceding stage and at the rate of 0.02 cc/s until no further oil production was observed. The volume of oil produced from spontaneous and forced imbibition was used to calculate the Amott wettability index of water using (1) [14, 40].

$$I_w = \frac{\Delta S_{ws}}{\Delta S_{ws} + \Delta S_{wf}}, \tag{1}$$

where S_{ws} is the change in water saturation during spontaneous imbibition and S_{wf} is the change in water saturation during forced imbibition. For the spontaneous imbibition investigations, three of the core samples (C04, C07, and C08) were subjected to brine changes after no further oil production was observed with the first brine. In the first core sample (C04), the aged sample was first imbibed with FMB until no recovery was observed thereafter; the imbibition

fluid was changed to CSB. In the second sample (C07), the aged rock sample was first imbibed with CSB until no recovery was observed; then the imbibing fluid was changed to CSB with addition of greenzyme (CSBS-G). Finally, in the third rock sample (C08), the aged sample was first imbibed with CSB and, thereafter, the imbibition fluid was changed to CSB with addition of rhamnolipid (CSBS-R). Also, for the rock and fluids samples used for the wettability index tests, only the oil recovery made from the spontaneous imbibition was used for rate of spontaneous imbibition calculations.

2.2.3. Zeta Potential Measurements. The zeta potential measurements were carried out on intact core samples at 100% water saturation and residual oil saturation (S_{or}) based on streaming potential method with the set-up and procedures described in [15, 41]. The single-phase zeta potential measurement of the core sample was carried out when the core sample was fully saturated ($S_w = 1$) with FMB that was equilibrated with rock offcuts for more than 100 h. The value and polarity of the single-phase zeta potential, i.e., zeta potential at rock-brine interface of +7.13 mV, was adopted from Jackson et al. [14] who used the same core sample and FMB in their experiments. The two-phase effective zeta potential was measured on rock samples saturated with different brines (FBM, CSB, and CSB combined with rhamnolipid (CSBS-R) and CSB combined with greenzyme (CSBS-G)) and crude oil at residual oil saturation ($S_w = 1 - S_{or}$). This was compared with the single-phase zeta potential and used to interpret the polarity of the zeta potential at oil-brine interface. The crude oil used in this study has different properties from those used by Jackson et al. [14]. However, the comparison between the effective two-phase zeta potential measured with FMB by Jackson et al. [14] (approximately +4 mV at $I_w = 0.18$) and the value obtained in this study (+4.27 mV at $I_w = 0.18$) suggests that crude oil used in this study is similar to that used by Jackson et al., 2016, and the zeta potential at oil-brine interface is negative.

2.2.4. Core Flooding Experiment. The brines (FMB) used for connate water saturation in all the core samples were initially equilibrated with rock offcuts in order to establish equilibrium condition between carbonate rock, electrolyte, and CO_2 using the method described by Alroudhan et al. [39]. This brine is referenced equilibrated formation brine (FMBEq). This basically involves placing of carbonate offcuts into formation brines in a closed system with air gap in order to allow CO_2 dissolution into the solution as obtainable in carbonate deposition. The pH of the solution was monitored until a stable pH was attained. This procedure was carried out because previous study [42] has shown that nonequilibrium or inadequate equilibrium of the carbonate rock samples will affect the zeta potential measurements. Prior to the flooding experiments, all the cores were first cleaned in Soxhlet apparatus with toluene for 24 h after which they were cleaned with methanol for another 24 h and then dried in the oven at 70°C for 48 h. The cores were allowed to cool off and their dimensions were taken before they were saturated with FMBEq under vacuum for minimum of 24 h.

The saturated cores were placed in the core holder and further saturated under pressure after which the cores were drained with oil to establish irreducible water saturation. Thereafter, the cores were aged in oven at 75°C for six weeks in order to alter the wettability. The aged cores were then flooded with different brines (FMB, CSB, CSBS-R, and CSBS-G). All the flooding experiments were carried out based on similar procedures; the investigating brine was injected from the bottom using a constant injection rate of 0.02 cc/s until no significant oil production (i.e., oil to brine volume ratio of 1:45) was observed. Then injection rate was increased to 0.05 cc/s in order to ensure displacement of all the mobile oil. The effluents from each flooding experiment were analysed based on pH and specific conductivity measurements using a Thermo Scientific pH meter and a Mettler Toledo conductivity meter. Increased pH is one of the mechanisms associated with successful CSB flooding whose effect is attributed to IFT reduction and ion exchange; hence, pH of all flooding was monitored. Also, pH measurements can give an indication of the effects of rock-fluid interactions that could be helpful with understanding of CORB interactions. The specific conductivity measurement was used to monitor the overall ionic activity and to validate the activity of potential determining ions (PDIs), since ionic activity resulting from dynamic CORB interactions is fundamental to most proposed mechanisms such as multi-ion exchange (MIE), electric double layer (EDL) expansion, and rock dissolution. Finally, the concentrations of divalent cations (Ca^{2+} and Mg^{2+}) in all the effluents were analysed with microwave plasma atomic emission spectroscopy (MP-AES) for all the effluents. Dilution of varied ranges was used based on the concentration of ions in a given set of flooding effluents.

3. Results and Discussion

3.1. Oil-Brine Interfacial Tension. Figure 1 shows the results of IFT measurements of crude oil and brine of varied salinity with and without biosurfactant addition. For the brines without biosurfactant addition (black), slight increase in IFT with increase in salinity was observed with the lowest IFT of 15.56±0.5 mN/m being obtained with CSB that has lowest salinity. It is worth noting that precipitation of rhamnolipid was observed in FMB and SW solutions, signifying its sensitivity to high salinity medium while greenzyme was soluble in all brines. The results of IFT investigations involving the use of biosurfactants are also presented in Figure 1. It is obvious that addition of rhamnolipid and greenzyme to each brine generated a general reduction in their respective IFT. Different trends of IFT reduction with change in brines were however observed with the use of rhamnolipid and greenzyme. The IFT is reduced to less than 0.5 mN/m and progressively decreasing with decreasing salinity using rhamnolipid. However, the IFT of less than 5 mN/m and progressively decreasing with increasing salinity was observed with greenzyme. These results show that both rhamnolipid and greenzyme can reduce oil-brine IFT in both high and low salinity system with rhamnolipid being more efficient in IFT reduction especially at lower salinity, while
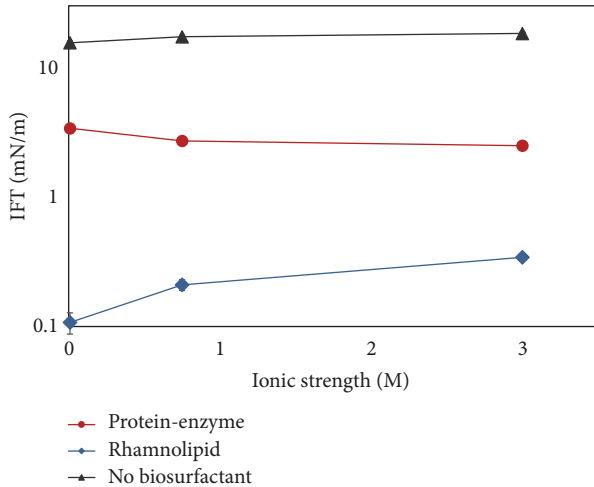
FIGURE 1: Crude oil-brine IFT as a function of the ionic strength. The symbols correspond to the three brines tested in this work: CSB (ionic strength 0.083 M); SW (ionic strength 0.75 M); FMB (ionic strength 3 M). The black line and triangles correspond to IFT measurements without any biosurfactant; the red line and symbols are the results of IFT measured in the system with 1 wt.% of greenzyme; the blue line shows the results obtained with 1 wt.% of rhamnolipid. The error bars in these experiments are based on the instrument accuracy and repeatability and do not exceed the size of the symbols in the figure.

the efficiency of greenzyme IFT reduction is enhanced in high salinity brine.

IFT reduction is one of the mechanisms postulated to be responsible for low salinity brine increased oil recovery by McGuire et al. [17] and Sohrabi et al. [18] also attributed effective low salinity flooding to fluid-fluid interactions. However, from the oil-brine IFT measurements based on varied brine salinity, only slight IFT reduction from 18.36 to 15.56 mN/m was observed with decrease in salinity from 3 M to 0.0083 M. This is equivalent to IFT reduction factor of 15.25, which is not significant enough because lower IFT is required to increase capillary number that will enhance mobility of the residual oil saturation in reservoir rock pores. Hence, this result shows that IFT reduction may not be a possible mechanism for CSB enhanced oil recovery in this system. Addition of rhamnolipid and greenzyme to these brines will however result in IFT reduction. This is a good requirement for EOR process since IFT reduction will promote oil-brine mixing and emulsification that will result in increased capillary number and mobilisation of trapped oil from the rock pores.

3.2. Wettability Alteration: Spontaneous Imbibition. The results of the four Amott wettability index tests carried out on initially oil-wet carbonate core samples are presented in Figure 2. Each of the data points in Figure 2 corresponds to the experiment in Figure 4(a), in which different brine solutions were allowed to imbibe into the carbonate samples aged with crude oil. The larger values of reported Amott wettability index to water correspond to more water-wet
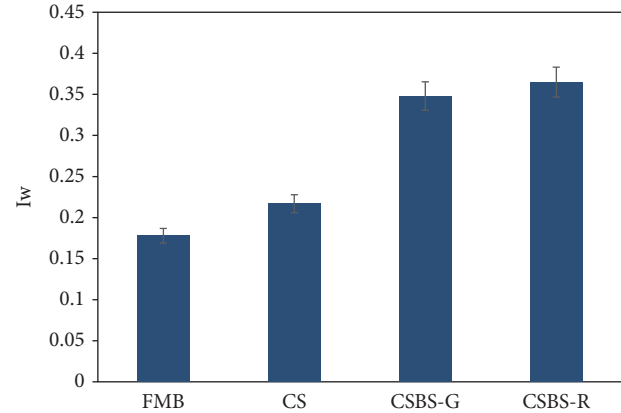

FIGURE 2: Amott water wettability index using formation brine (FMB), controlled salinity brine (CSB), controlled salinity water with greenzyme (CSBS-G), and controlled salinity water with rhamnolipids (CSBS-R).

conditions. However, the reported values of up to 0.35 with CSBS-R are still considered to correspond to weakly oil-wet conditions [14, 43]. Although CSB, CSBS-G, and CSBS-R all altered the rock surfaces wetness toward increasing water-wetness, CSB and CSBS-G however produced some side effects on CORB systems as illustrated in Figure 3. While crude oil in its original appearance was displaced from the core samples by spontaneously imbibing FMB and CSBS-R (Figures 3(f) and 3(i)), the oil produced by spontaneous imbibition of CSB and CSBS-G (Figures 3(g) and 3(h)) had an appearance of emulsion with more pronounced emulsification observed with CSB. Furthermore, spontaneous imbibition of CSBS-R was accompanied by a gradual change in colour of the aqueous solution with time until a milky colour, as illustrated in Figure 3(e), was observed and oil production ceased. The physical appearance of the crude oil produced by spontaneous imbibition of CSBS-R was not affected as shown in Figure 3(i).

The effect of aqueous solutions on the rate of spontaneous imbibition is shown in Figure 4. The rate of spontaneous imbibition in this study is defined as the total amount of oil produced related to the time that corresponds to the cessation of oil production; for example, the rate of spontaneous imbibition observed with single CSB (Figure 4(a), red squares) is estimated as 13.03% OIIP over 60 days, i.e., 0.22% OIIP per day. The imbibition rate of all the solutions was generally slow and most of the oil was produced during forced imbibition. This is an indication of initially strongly oil-wet condition of the system, since water-wet system is usually characterised by fast and high volume of water imbibition [44]. From Figure 4(a), the imbibition rates of each fluid are correlated to the water wettability index (Figure 2) with the exception of CSBS-G and CSBS-R. The total oil recoveries of 8.97%, 13.03%, 18.18%, and 17.42% were observed with FMB, CSB, CSBS-G, and CSBS-R imbibition, respectively. Our results show that oil production is related to the wetting condition of the system, with the maximum recovery corresponding to weakly oil-wet rocks. A slightly higher recovery was observed
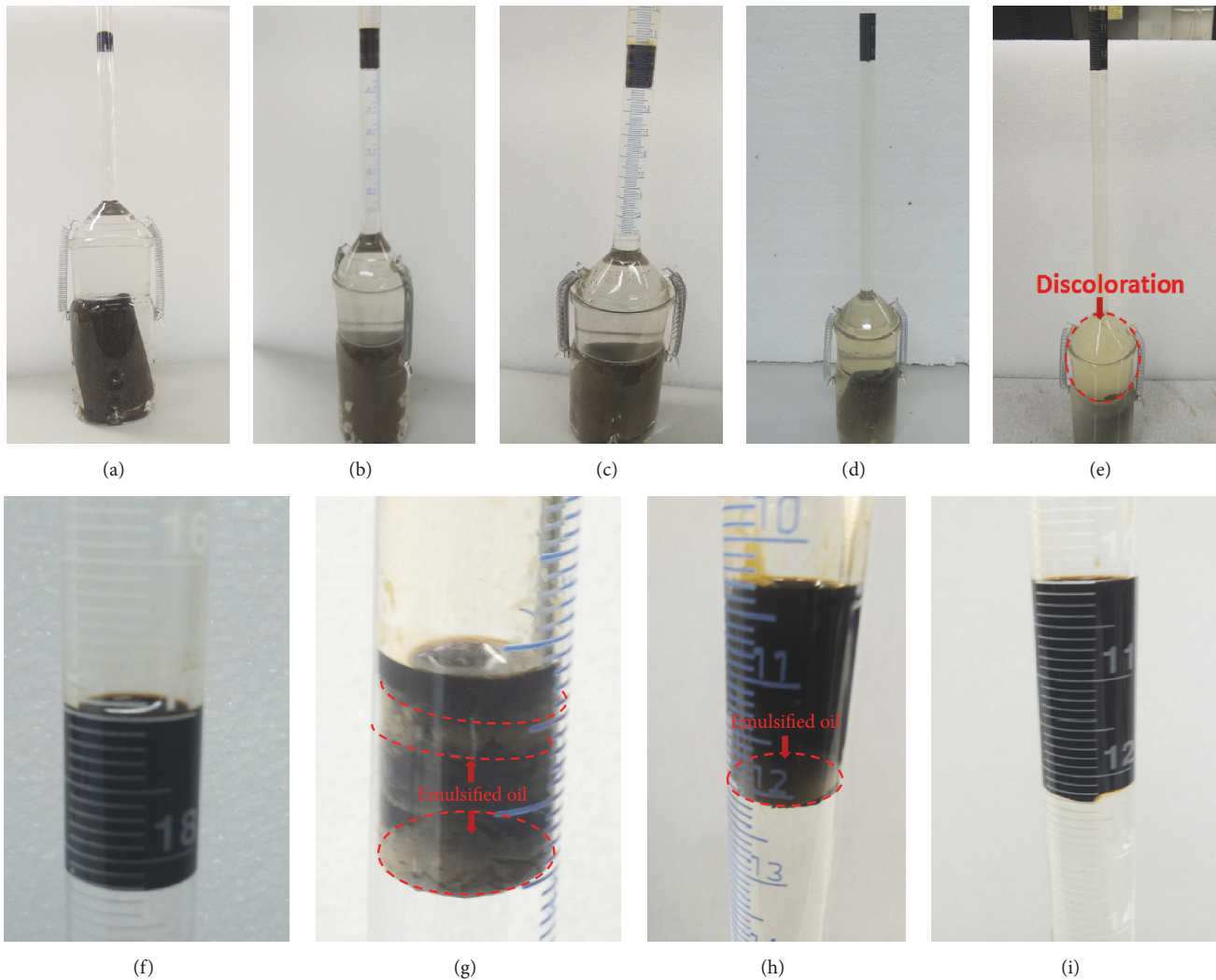
FIGURE 3: Spontaneous imbibition investigations: (a) core sample C23 in formation brine [FMB]; (b) core sample C24 in controlled salinity brine [CSB]; (c) core sample C25 in controlled salinity biosurfactant with greenzyme [CSBSB-G]; (d) core sample C28 in controlled salinity biosurfactant brine with rhamnolipids [CSBSB-R]; (e) observed changes in CSBSB-R system after about 25 days of imbibition; (f) sample of oil produced during FMB imbibition; (g) sample of oil produced during CSB imbibition; (h) sample of oil produced during CSBSB-G imbibition; (i) sample of oil produced during CSBSB-R imbibition.

with greenzyme (0.76%) while higher wettability alteration was observed with rhamnolipid (compare 0.37 with 0.35 in Figure 2). Furthermore, the imbibition rate of CSBS-G (18.18% OIIP over 75 days) into the core was characterised by continuous imbibition process with elongated oil production, while the rate of CSBS-R imbibition (17.42% OIIP over 30 days) into the core was very fast with oil production cessation after the observed changes in the solution. This shows that the greenzyme activity in this CORB system can be sustained for a longer period of time than rhamnolipid. This can be associated with the observed changes in the rhamnolipid solution (Figure 3(e)) that impeded further imbibition process. Rhamnolipid tends to precipitate in high salinity medium due to its composition [38] and this was evident in the observed change in brine solution during CSBS-R imbibition. This suggests that application of rhamnolipid

in oil reservoirs to improve oil recovery may be associated with its precipitation; hence adequate compatibility test is recommended before reservoir application.

Figure 4(b) shows the results of the spontaneous imbibition experiments, in which the effect of change in imbibing fluids was investigated. The rates of spontaneous imbibition of the fluids into the cores were comparable with the results shown in Figure 4(a), in which continuous imbibition of a single fluid was used in each core sample. In this suite of experiments, the volume of oil produced during spontaneous imbibition of CSB as the first imbibing fluid was 2.9 ml to 3.5 higher than that observed with the FMB as the first imbibing fluid. The change in the imbibing fluids from FMB to CSB, from CSB to CSBS-G, and from CSB to CSBS-R resulted in additional oil production of 7.69%, 6.72%, and 6.06%, respectively (these values represent the incremental
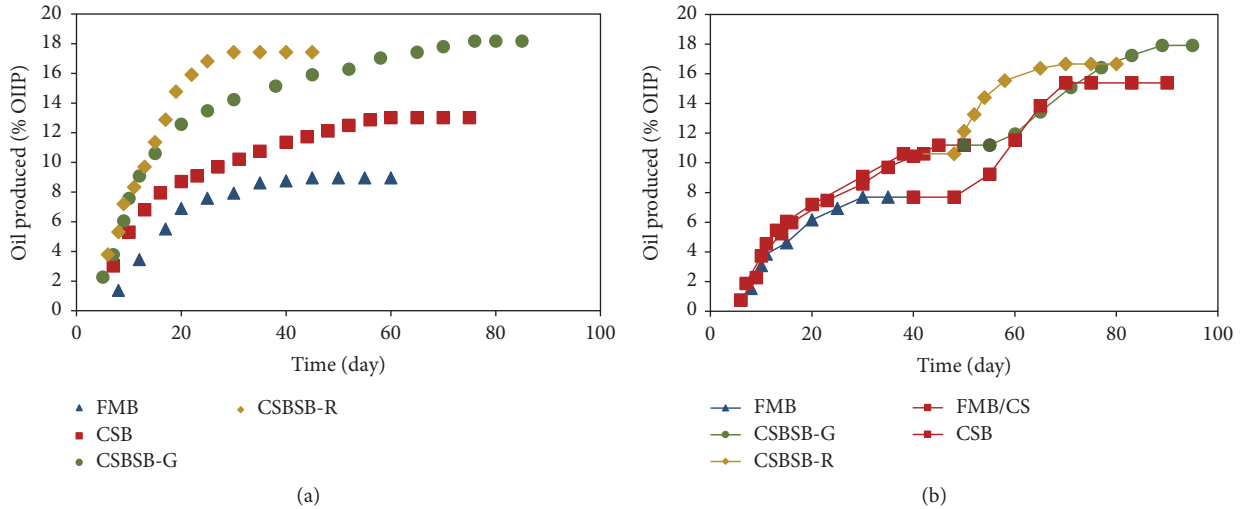
FIGURE 4: Rate of spontaneous imbibition of FMB (blue circle), CSB (dark red square), CSBSB-G (green rhombus), and CSBSB-R (golden triangle). Plot (a) shows rate of imbibition using single brine solution while (b) shows rate of imbibition with change in brine solutions.

oil recovery following the transition from FBM to CSBS-R and CSBS-G, i.e., the difference between the final oil recovery during the first and the second phases of the experiment). This implies that application of these solutions in EOR process will result in increased oil recovery relative to continuous flooding with high salinity FMB.

All the investigated rock samples were characterised by low imbibition rates (<17.42% OIIP over 30 days, i.e., <0.58% OIIP per day) suggesting that rock samples were strongly oil-wet after the ageing. The wettability of the rock surfaces was however found to be increasingly less oil-wet with the use of FMB, CSB, CSBS-G, and CSBS-R as imbibing fluids. The results are consistent with the spontaneous imbibition at similar conditions and indicate the ability of CSB and bio-surfactants to shift the wetting state of rock sample towards being more neutral (i.e., initially oil-wet rock samples became less oil-wet when using these solutions). Furthermore, the results of this study show that CSB imbibition increases oil recovery relative to FMB but the process was accompanied by apparently emulsified oil production, which is consistent with the core flooding experiments carried out by Udoh et al. [34]. This suggests the possibility of formation of microdispersion of micelles [18] or rock dissolution [45, 46] during CSB displacement process. Also, the use of CSBS-G and CSBS-R increases oil recovery relative to FMB and CSB applications with CSBS-R process being characterised by fastest imbibition rate. This effect is attributable to its high surface activity that enhances oil-brine IFT reduction and increase in capillary effect [34, 38].

3.3. Zeta Potential and Interfacial Charge Measurement.

The zeta potential of single-phase strongly water-wet core that defined the charge at rock-brine charge interface was found to be 7.13 mV (taken from [14]), which shows that the rock-brine interface is positively charged when saturated with high salinity FMB. The two-phase zeta potential measurements of all the brines were taken at S_{or} and the results are presented
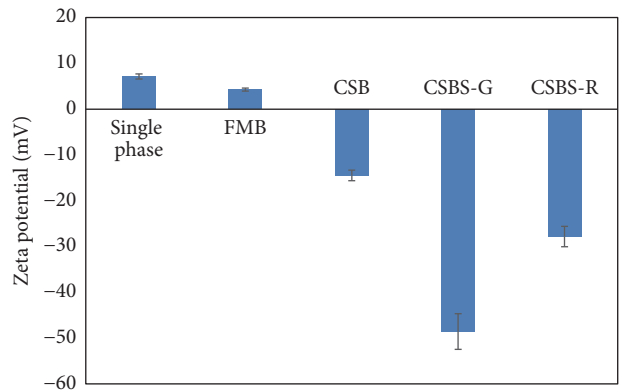

FIGURE 5: Zeta potential of single- and multiphase systems measured in this work. Single-phase value corresponds to the zeta potential measured in the rock samples saturated with FMB (Sw=1); FMB corresponds to the zeta potential measured at the end of the secondary FMB waterflooding when the rock sample was saturated with formation brine and residual oil (Sor=0.32); CSB corresponds to the zeta potential measured at the end of CSB flooding when the rock sample was saturated with CSB and residual oil (Sor=0.23); CSBS-R corresponds to the zeta potential measured at the end of CSB combined with 1 wt.% rhamnolipid waterflooding when the rock sample was saturated with CSBS-R and residual oil (Sor=0.19); CSBS-G corresponds to the zeta potential measured at the end of CSB combined with 1 wt.% greenzyme waterflooding when the rock sample was saturated with CSB-R and residual oil (Sor=0.17). The error bars reflect the accuracy of the instrument, noise level in measured voltage, and repeatability of results.

in Figure 5. Since the same rock and crude oil compositions were used in the investigations, the effect of change in brine composition on CORB interactions is reflected by the corresponding changes in the effective zeta potential. The measured zeta potential at S_{or} with FMB flooding was found to be 4.27 mV, which is less positive than the single-phase

zeta potential; this suggests that the effective charge at oil-brine interface is negative. These opposite charges at rock-brine and oil-brine interfaces favour electrostatic attraction and stabilisation of oil film on the rock surface.

However, the injection of CSB, CSBS-R, and CSBS-G solutions resulted in negative zeta potential, signifying that the rock-brine and oil-brine interfaces are both negatively charged. This shows that injection of these solutions into the rock changed the charge at the rock-brine interface from positive to negative, thereby making the oil-brine and rock-brine interfaces negatively charged although at varied degrees. This will result in electrostatic repulsion between the two interfaces and ultimately in wettability alteration and improved oil recovery. This observation is consistent with previous studies on natural carbonates, although these studies were carried out with single- phase system [2, 12, 39, 47]. Jackson et al. [14] however investigated this in both single and two-phase systems, and they observed that conventional flooding yielded a more negative zeta potential with reduction in brine salinity. Furthermore, zeta potential is said to be affected not only by ionic strength of brine but also by pH and surfactant concentration [2]. This is evident in the results of this study as seen by different levels of negative zeta potential observed with CSB, CSBS-R, and CSBS-G solutions. Increased negative zeta potential was observed with the use of CSBS-R and CSBS-G solutions relative to CSB injection; this shows that addition of rhamnolipid and greenzyme to CSB increased electrostatic repulsion between rock-brine and oil-brine interfaces. This resulted in increased oil recovery as shown in Section 3.4.

3.4. Core Flooding. The results of the various core flooding experiments carried out are presented in this section.

3.4.1. Formation Brine (FMB) Flooding. Figure 6 shows the result of the high salinity FMB flooding. Initial recovery of about 66% OIIP was made with injection of more than 5 PV with high water production and no significant oil production being observed but with increased injection rate, recovery was increased to 66.67% with about 11 PV injection and continuous flooding brought the total recovery to 67.93%. From the differential pressure curve, an initial high pressure drop was observed with the oil production which later started declining before the flow rate was increased and the associated differential pressure also increased slightly before stabilising at 20 psi that corresponds to 68% OIIP recovery. This system was confirmed to be oil-wet (Amott) and high salinity injected FMB had higher viscosity relative to low salinity brines used in this study. Figures 6(b) and 6(c) show the effluent analyses of this flooding. The pH, conductivity, and ion concentrations were relatively steady with no significant changes being observed. The Ca^{2+} concentration in the produced brine was similar to the injected concentration but a slight reduction in Mg^{2+} concentration relative to injected concentration was observed. This suggests the possibility of adsorption of Mg^{2+} on the rock surface. Relating this result to the zeta potential measurement of the system, it is evident that the opposite charges at rock-brine and oil-brine interfaces

favour oil adsorption. Also, the adsorption of Mg^{2+} on the rock surface may reduce the permeability of the system. Generally, no obvious changes in effluents analyses can be related to the produced oil. The recovery made from this flooding is used as base case for the subsequent flooding with controlled salinity brine and biosurfactant applications.

3.4.2. Controlled Salinity Brine (CSB) Flooding. Figure 7 shows the results of CSB flooding process. It is worth noting that an apparently emulsified oil production was observed during this flooding at residual oil saturation after most of the continuous oil had been produced. An initial recovery of about 71.57% OIIP was made with injection of about 5.27 PV of CSB flooding with very high water-cut and an increase in rate increased recovery to 73.66% with 10.25 PV injection and an ultimate recovery of 77.08% was made with injection of about 40 PV. This is about 9.15% higher than recovery made with FMB, signifying better recovery capacity of CSB. The differential pressure during this flooding shows similar profile to that of FMB flooding but with higher differential pressure that stabilised at 25 psi which corresponds to 77% OIIP recovery. The increase in differential pressure recorded with CSB suggests that the wettability shifted to more water-wet, which normally corresponds to flow of water within wetting layers, which is consistent with the results of the wettability test. The results of effluents analysis of this flooding show increased pH (7.40-8.18) relative to the secondary FMB flooding with a pH range of 6.52-6.45 but the pH was relatively stable throughout the flooding with a slight drop with increase in injected PV. The conductivity measurements show initial high values that progressively reduce with increase in injected volume. The results of ions analysis of this flooding are presented in Figure 7(c). Higher concentration of Ca^{2+} and Mg^{2+} ions relative to their respective injected values was observed. The initial high concentration can be attributed to connate water saturation effects due to high concentration of these ions in the FMB, and with injection of about 40 pore volumes of CSB, higher Ca^{2+} ion was still observed while Mg^{2+} ion almost reduced to injected value.

Oil-brine emulsion formation during low salinity water-flooding has been associated with saponification of oil and formation of in situ surfactant due to increase in pH [17]. The observed effluent pH in this study did not show remarkable change that is adequate to trigger any formation of in situ surfactant. Furthermore, the results of the IFT test (Section 3.1) show no significant IFT reduction with the use of this brine. Also, the mixture of this brine with crude oil in fluid-fluid interaction was not characterised by apparently emulsified oil formation. Hence, the observed change in oil may be associated with rock-fluid interaction and the improved oil recovery observed with CSB cannot be attributed to IFT reduction. Relating the result of this flooding to the zeta potential measurements (Section 3.3), it was evident that CSB injection inverted rock-brine interfacial charge from positive to negative. This invariably leads to electrostatic repulsion between the rock-brine and oil-brine interfaces. When the repulsive force is much greater than the bonding force, oil desorption from the rock surface occurred, thereby leading
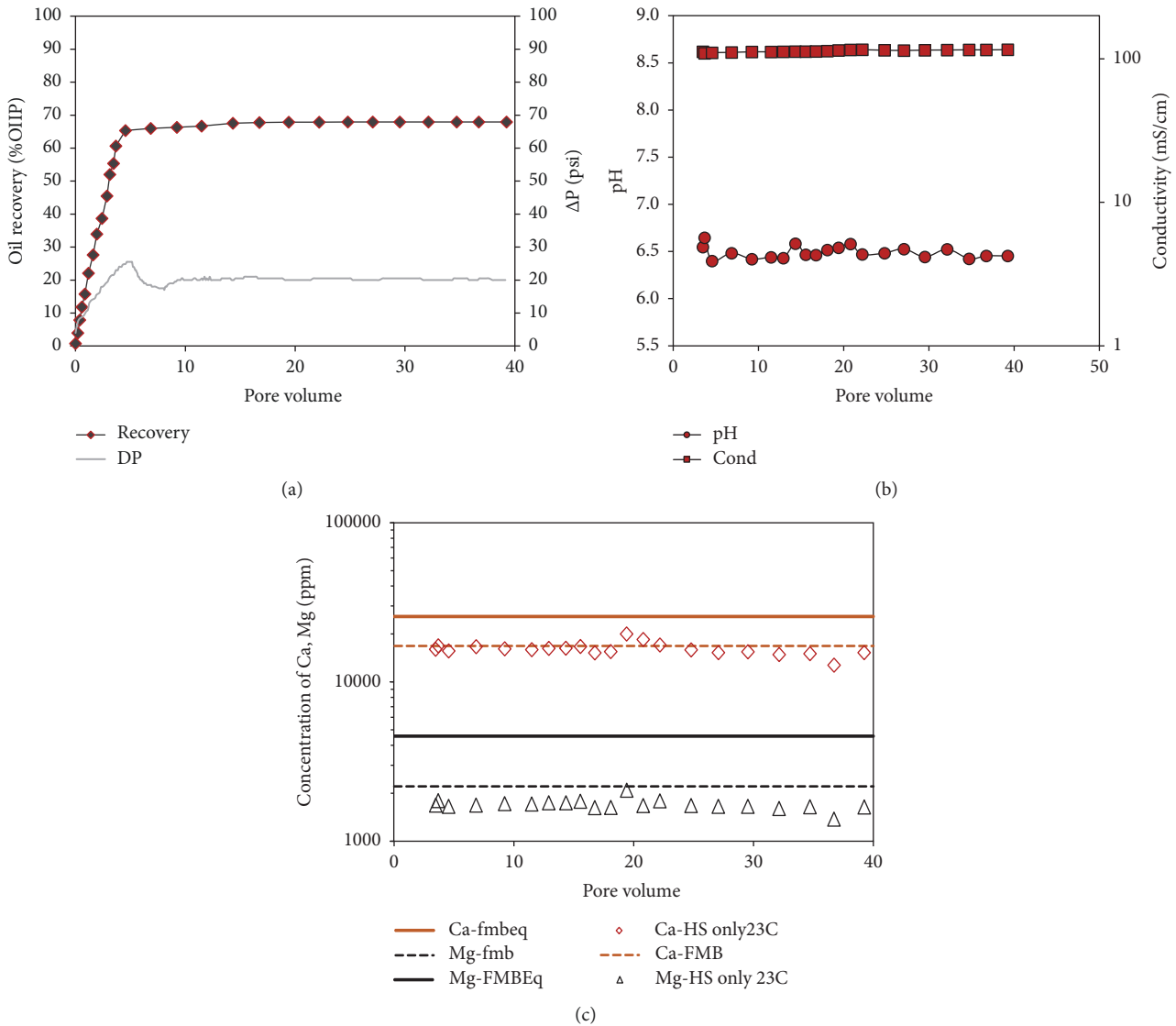
FIGURE 6: Secondary FMB flooding on core C30, (a) cumulative oil recovery and differential pressure; (b) pH (circles) and conductivity (squares) of effluents; (c) Ca^{2+} (rhombi) and Mg^{2+} (triangles) ions of effluents. The straight lines indicate concentration of Ca^{2+} (coloured) and Mg^{2+} (black) in connate water saturation (—) and injected brine (---).

to increased oil recovery. Hence, this study has further established EDL expansion as a mechanism for effective CSB flooding. The excess Ca^{2+} production and the observed emulsified oil production during CSB flooding process suggest the possibility of complimentary effect of rock dissolution as a mechanism for effective CSB flooding observed in this study. Previous studies by Hiorth et al. [45, 46] proposed rock dissolution resulting from thermodynamic equilibrium destabilisation in the CORB system by CSB injection as mechanism for effective CSB flooding. The rock dissolution is said to be enhanced by higher acid number crude oil and it is interesting to know that the crude oil used in this study is highly acidic with total acid number (TAN) of 3.9050 mgKOH/g which is much higher than TAN of all the crude oil (0.05, 0.15, 0.2) used by Jackson et al. [14] in the previous study on this carbonate. Hence, effective CSB flooding observed in

this study is attributable to combined effect of surface charge inversion that leads to EDL expansion and rock dissolution.

3.4.3. Controlled Salinity Biosurfactant Brine Flooding.
Figure 8 shows results of flooding with controlled salinity biosurfactant brine (CSBS) injection using greenzyme and rhamnolipid with core C13 and core C16, respectively. In both flooding experiments, most of the oil was produced before water breakthrough after which continuous intermittent oil production was observed with lots of water production. In the first flooding (CSBS-G) in which greenzyme was added to CSB (Figure 8(a)), oil recovery of about 78.24% was made with 10 PV injection, but with continuous injection, a total recovery of 82.76% was made with injection of about 38 pore volumes. During the second flooding (CSBS-R)
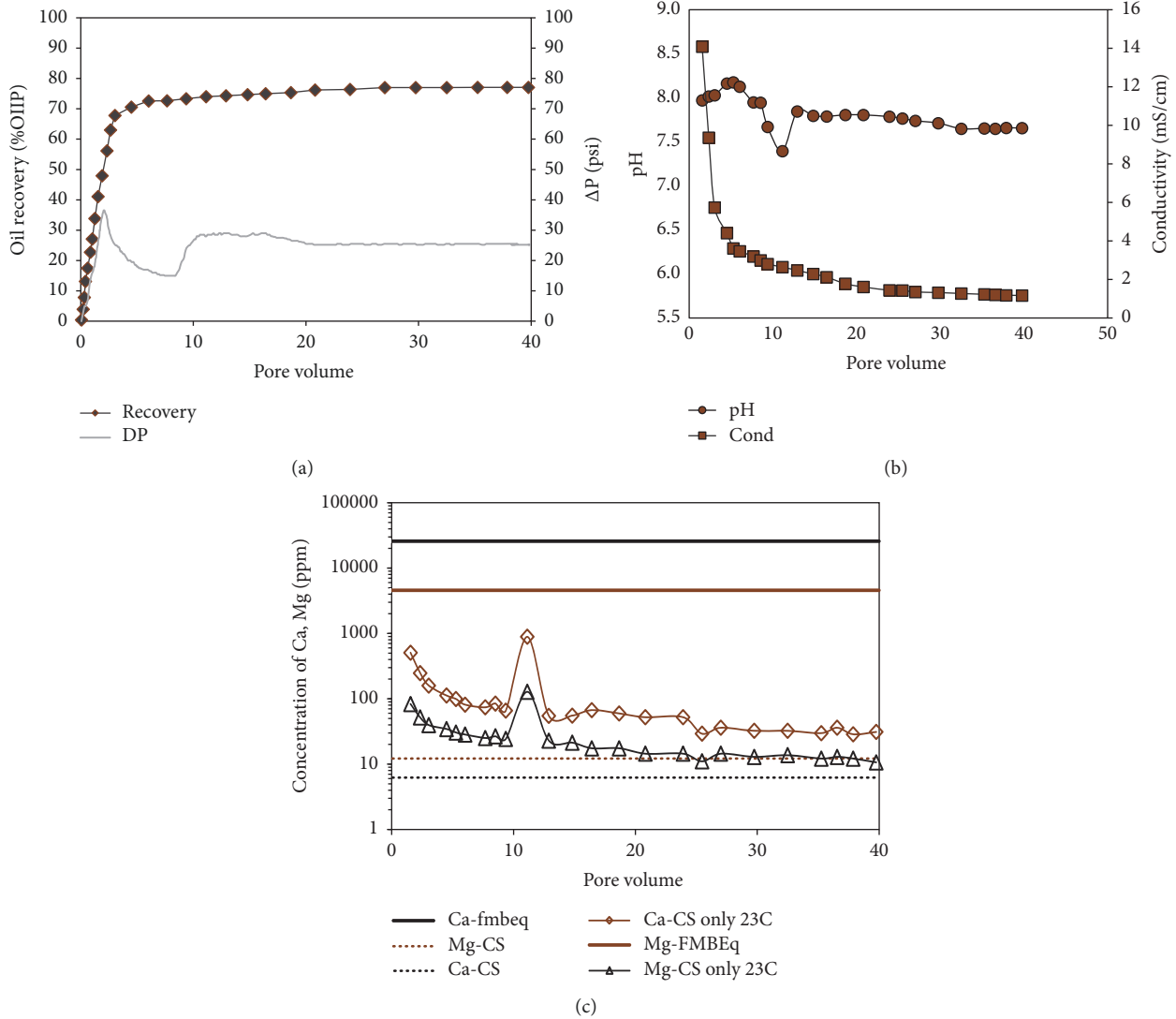
(a)

(b)

(c)

FIGURE 7: Secondary CSB flooding on core C27, (a) cumulative oil recovery and differential pressure; (b) pH and conductivity of effluents; (c) Ca^{2+} and Mg^{2+} analyses of effluents. The straight lines indicate concentration of Ca^{2+} (coloured) and Mg^{2+} (black) in connate water saturation (—) and CSB injected (…).

in which rhamnolipid was used (Figure 8(b)), an initial recovery of 74.24% was made with injection of about 10 PV and a total recovery of 80.56% was made with injection of about 38 PV. These are equivalent to incremental recoveries of 14.83% and 12.65% over FMB flooding and 5.68% and 3.50% over CSB flooding with addition of greenzyme and rhamnolipid, respectively. Similar differential pressure profile was observed from the two flooding experiments with CSBS-G having higher stabilising differential pressure than CSBS-R but close to CSB flooding. The differential pressure of the CSBS-G (Figure 8(a)) stabilised at 25 psi with oil recovery of 83% which is similar to the CSB flooding. Higher pressure difference in CSB and CSBS-G compared to FMB is the result of shift toward water-wet conditions, therefore decrease in relative permeability. However for CSBS-R flooding (Figure 8(b)), the differential pressure stabilised at 15 psi with oil recovery of 81%. This differential pressure is

much lower than that of CSB and CSBS-G although their recoveries were not too dissimilar. We hypothesise that is related to rock interacting with CSBS-R as suggested by "discolouration" and that could change brine viscosity and/or rock permeability.

Fundamentally, biosurfactants are surface active agents that effect changes at interfaces. Relating the results of these flooding experiments to IFT investigation using these biosurfactants, it is obvious that their IFT reduction capacity contributed to the observed better recovery in their flooding process. Since both of them have IFT reduction capacity, this helps them generate good displacement front as evident by early oil production with most of the oil being produced before water breakthrough in their respective flooding. Although these biosurfactants did not generate ultralow IFT (0.001 mN/m) that will enhance mobility of trapped oil, Ehrlich et al. [48] however noted that crude oil with high acid
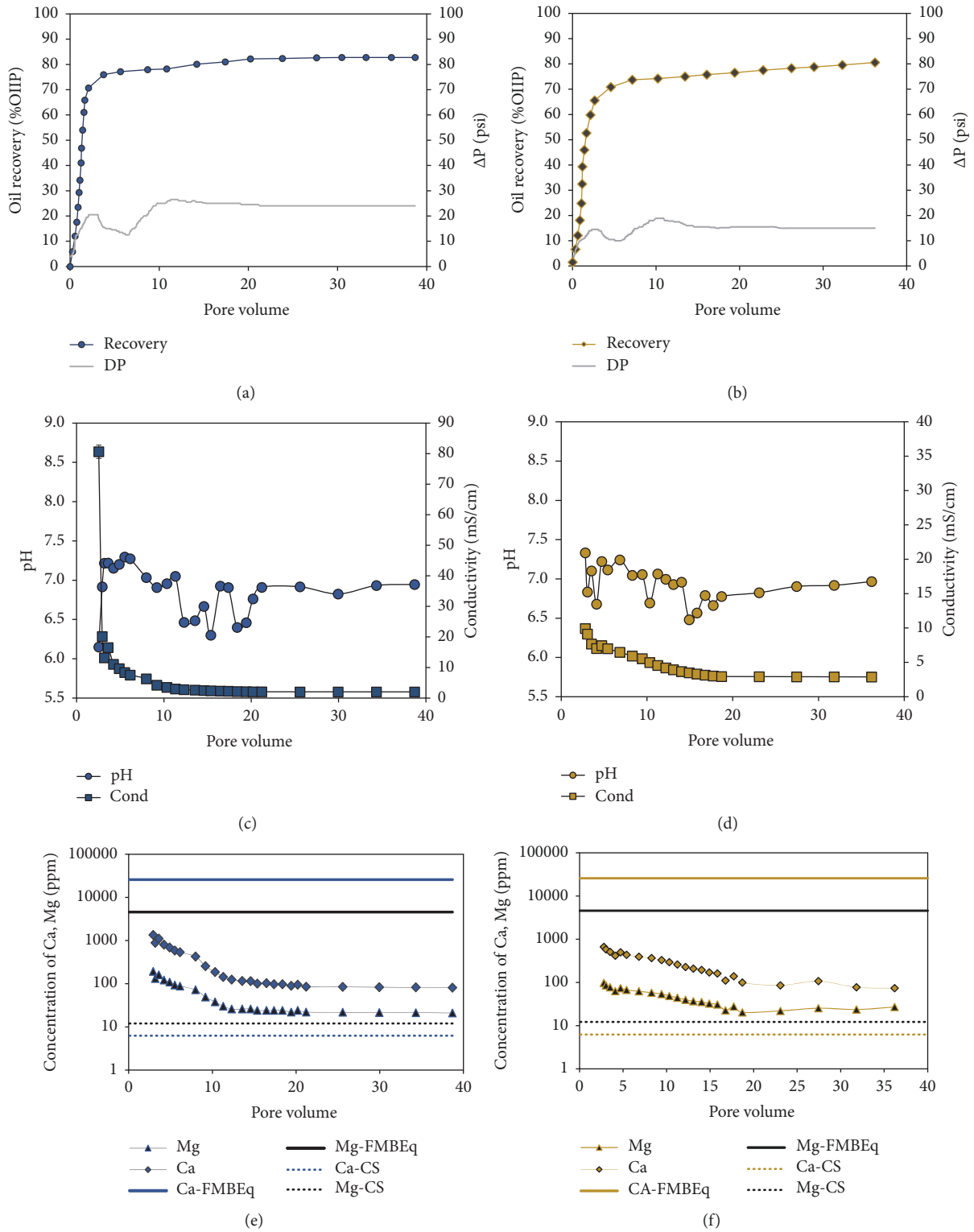
(a)

(b)

(c)

(d)

(e)

(f)

FIGURE 8: Secondary CSBSB flooding application greenzyme (a, c, e) and rhamnolipids (b, d, f): (a-b) cumulative oil recovery and differential pressure; (c-d) pH and conductivity of the effluent; (e-f) Ca^{2+} and Mg^{2+} analyses of the effluent. The straight lines indicate concentration of Ca^{2+} (coloured) and Mg^{2+} (black) in connate water saturation (—) and CSB injected (...).
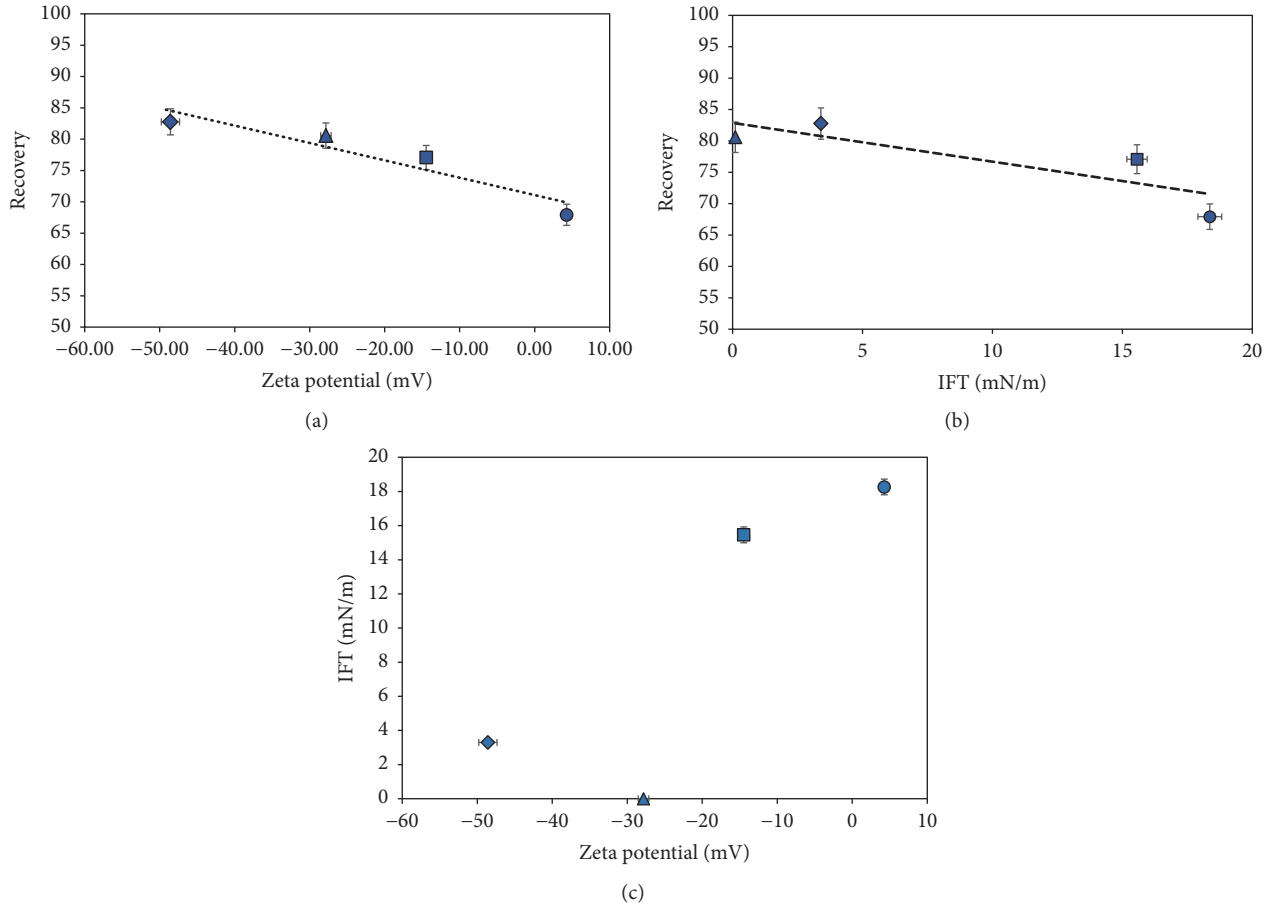
(a)

(b)

(c)

FIGURE 9: Correlation between continuous secondary recovery and (a) zeta potential; (b) correlation between recovery and IFT during FMB (circle), CSB (square), CSBS-G (rhombus), and CSBS-R (triangle) flooding. (c) Relationship between interfacial tension and zeta potential during FMB (circle), CSB (square), CSB-R (triangle), and CSB-G (rhombus) applications.

number (>0.2) that is flooded with brine that has capacity to generate IFT less than 0.5 dynes/cm will result in increased oil production. There was however a variance in the IFT results and oil recovery. Expectantly, application of rhamnolipid with capacity to generate lower IFT ought to result in higher recovery, but contrary was the case. This variance can be attributed to high sensitivity of rhamnolipid to high salinity as evident by its precipitation in such medium (more details are available in [38]). Core flooding is a dynamic process characterised by continuous mixing and diffusion of injected fluid with connate water saturation in the core. The mixing of CSB-rhamnolipid solution with high salinity connate water in the core may have impacted its performance. Contrariwise, greenzyme has demonstrated high tolerance for high salinity and its IFT capacity is also enhanced with increase in salinity.

The recovery made from these flooding experiments was however consistent with the results of zeta potential measurements that reflect the effect of dynamic rock-fluid interactions. The greenzyme application generated higher electrostatic repulsion at rock-brine and oil-brine interfaces than rhamnolipid. This expectantly should enhance more oil desorption from the rock surface than rhamnolipid, which is consistent with the results of the recovery from the

two flooding experiments. However, the difference in their zeta potential (20.74) seems to outweigh recovery difference (2.18%); the factor responsible for this is not very clear, and further investigations will be required for full understanding of the processes involved. The results of effluent analysis of the two flooding experiments also show similar trends with a relatively stable neutral pH (7±0.5) and initial high conductivity that levels off at low range. The pH of these flooding experiments however lies between FMB (6.52-6.45) and CSB (7.40-8.18). Finally, the results of ion analysis of these flooding experiments presented in Figures 8(e) and 8(f) show similar trends with higher concentrations of Ca and Mg ions relative to their respective injected values. This is consistent with the results obtained from CSB flooding. This can be related to change in thermodynamic equilibrium in the CORB system induced by change in injection brine salinity [45, 49] that promotes rock dissolution.

Furthermore, the results of zeta potential and IFT measurements were correlated with oil recovery from all the flooding using the same brines. Figure 9 shows the results of this correlation. A negative linear correlation was observed with increase in zeta potential as well as IFT with change in brines from CSBS⟶CSB⟶FMB. This implies that more

recovery is expected with increased electrostatic repulsion at rock-brine and oil-brine interfaces and increase in reduced oil-brine IFT. High salinity FMB that recovered the least oil production was associated with the highest IFT and positive zeta potential, while CSB combined with biosurfactants generated the highest oil recovery with lowest IFT and zeta potential, although to a varied degree based on their composition. Relating the IFT measurement directly with zeta potential as demonstrated in Figure 9(c), it is obvious that a direct correlation exists between IFT and zeta potential measurements of different brines. The brine with lower IFT is associated with lower or increasing negative zeta potential and vice versa. Zeta potential measurements however reveal the effect of biosurfactant composition of CORB interactions which may be related to their adsorption capacity.

4. Conclusion

The effects of brine composition on CORB system have been investigated in this study and obtained results are relevant to oil production from hydrocarbon reservoirs. The obtained results show the following.

(1) Rock-brine interface is found to be positively charged when saturated with high salinity FMB. However, when crude oil is also present in the system alongside the formation brine the effective zeta potential becomes less positive, suggesting that crude oil-FMB interface is negatively charged.

(2) Injection of CSB and CSB with biosurfactants resulted in the negative effective zeta potential suggesting that rock-brine interface also becomes negatively charged. This implies that initially oil-wet rock becomes more water-wet after injection of CSB and CSB with biosurfactants, thus resulting in improved oil recovery.

(3) Addition of biosurfactants to CSB results in increasing magnitude of the negative zeta potential; therefore further increase in electrostatic repulsion between oil-brine and rock-brine interfaces takes place. The enhanced electrostatic repulsion results in slightly improved oil recovery.

(4) Salinity reduction does not have significant effect on oil-brine IFT; hence, improved oil recovery observed with CSB cannot be attributed to IFT reduction associated with reduced salinity. Addition of biosurfactants to brines can however reduce IFT and increase oil mobility. However, the incremental oil recovery observed with biosurfactants added to CSB was minute and attributed to a combined effect of reduced IFT and increased wetness towards water obtained with the addition of biosurfactants.

(5) Wettability measurements carried out using Amott wettability method show that rock samples saturated with FMB are oil-wet and become progressively more water-wet when FMB is displaced with CSB, CSBS-G, and CSBS-R. These results are consistent with core flooding tests and changes in the zeta potential.

(6) Inversion of initially positive rock-FMB zeta potential during CSB and CSB with biosurfactant injection is identified as the main mechanism for wettability alteration and improved oil recovery has been further established in this study. The results of this study suggest possible rock dissolution as a contributing factor to improved oil recovery via multi-ion exchange.

(7) The effective zeta potential in crude oil-brine-rock systems is found to correlate with the measured IFT, suggesting that oil-brine interfacial electrical charge is affected by biosurfactants.

Data Availability

The conclusions of this study were based on the results presented in the result section of the article and the data are included in the supplementary file.

Conflicts of Interest

The authors declare no conflicts of interest.

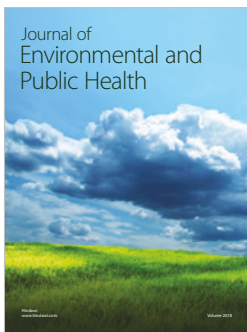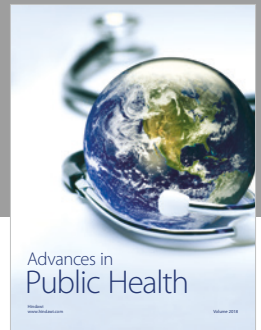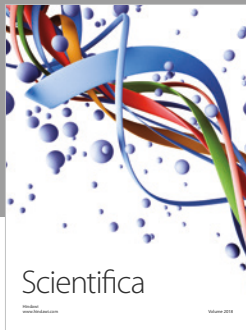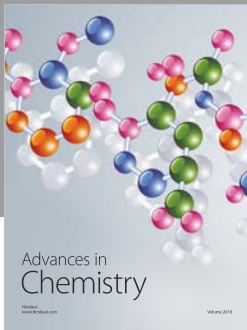## Acknowledgments

Supplementary Materials

Table 1 presents the results of the zeta potential measurements. The single phase is the measured zeta potential when the core pores were saturated with 100% formation brine (FMB) without any oil. The FMB measurement is two-phase zeta potential measurement at residual oil saturation after flooding the core with formation brine. The measured zeta potential at residual oil saturation during flooding with controlled salinity brine (CSB) is represented by "CSB" in the table, while the measured zeta potentials with the use of combined controlled salinity biosurfactant flooding using rhamnolipid (CSBS-R) and greenzyme (CSBS-G) are presented as "CSBS-R" and "CSBS-G," respectively. Both measurements were carried out as residual oil saturation. The measured values of oil-brine interfacial tension are presented in Table 2. The same crude oil was used for all the measurements and the same concentration of biosurfactants (1%) was added to all brine solutions. Three brine solutions with different ionic strength were used and the measured IFT using these brine solutions are presented as "no biosurfactant." The measured IFT when greenzyme and rhamnolipid were added to these brine solutions are referenced "greenzyme" and "rhamnolipid," respectively. Finally, Table 3 presents supplementary data from core flooding experiments. The quantity of the oil initially in place (OIIP), initial water saturation (Swi), and oil initial oil (Soi) were determined and calculated from volume of water produced during oil injection into the core plugs, while the residual oil saturation (Soi) was calculated from the volume of oil produced from

each of the flooding experiments. All of these properties were measured and calculated for each of the core samples as summarised in the table. The identity of the brine solution used for each flooding experiment is described by the brine sample. *(Supplementary Materials)*

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