Controlled Salinity-Biosurfactant Enhanced Oil Recovery at Ambient and Reservoir Temperatures—An Experimental Study

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Abstract: In this paper, a thorough experimental investigation of enhanced oil recovery via controlled salinity-biosurfactant injection under typical reservoir temperature conditions is reported for the first time. Sixteen core flooding experiments were carried out with four displacing fluids in carbonate rock samples and the improved oil recovery was investigated in secondary, tertiary and quaternary injection modes. The temperature effect on oil recovery during floodings was compared at two temperatures (23 °C and 70 °C) on similar rock samples and fluids using two types of biosurfactants: GreenZyme® and rhamnolipids. The results of this study show that injection of controlled salinity brine (CSB) and controlled salinity biosurfactant brine (CSBSB) improve oil recovery relative to injection of high salinity formation brine (FMB) at both high and low temperatures. At 23 °C, CSBSB improved oil recovery by 15–17% OIIP compared with conventional FMB injection, and by 4–8% OIIP compared with CSB injection. At 70 °C, the injection of CSBSB increased oil recovery by 10–13% OIIP compared with injection of FMB, and by 2–6% OIIP compared with CSB injection. Furthermore, increase in the system temperature generally resulted in increased oil recovery, irrespective of the type of the injection brine. The results of this study have demonstrated for the first time the enhanced oil recovery potential of combined controlled salinity brine and biosurfactant applications at temperature relevant to hydrocarbon reservoirs. The results of this study are significant for the design of controlled salinity and biosurfactant flooding in carbonate reservoirs.

Keywords: controlled salinity waterflooding; controlled salinity-biosurfactant EOR; EOR; reservoir conditions

1. Introduction

Hydrocarbon reservoirs are complex systems that comprise two or three immiscible fluid phases (water, oil and/or gas), in which rock-fluid and fluid-fluid interactions play an important role in controlling the efficiency of hydrocarbon recovery. Enhanced oil recovery (EOR) techniques aim at improving oil reservoir recovery factor and are dependent on the methods’ ability to influence fluid-fluid and rock-fluid interactions under a specific reservoir temperature regime. Previous studies have demonstrated the significance of injection brine composition in oil recovery processes under different descriptions such as low salinity water, smart water and controlled salinity brine (CSB). Increased recovery has been reported from most applications in both sandstone and carbonate rocks, but the underlying mechanism is still debatable [1]. The observed increased recovery from CSB injection has been attributed to different mechanisms such as wettability alteration, multi ion exchange, rock dissolution, double layer expansion, etc. [2–5]. Positive effects of CSB injection are not always observed [6], even though additional recovery as high as 25% OIIP compared with high salinity water injection is reported in a previous study [7]. It seems however that the CSB-increased recovery is observed when the initial wetting state is mixed-wet or oil-wet and wettability alteration towards water-wetness is attained after
injection of modified water [e.g., 8–10]. From all indications, there is the possibility of a combination of mechanisms rather than a single mechanism being responsible for the observed increased recovery.

Moreover, previous studies [11–13] have explored the potential of combining low salinity brine with chemical surfactant flooding and the results showed that the combined technique recovers more oil than either of the methods applied alone. The continuous use of chemical surfactants however constitutes an environmental threat due to their toxicity and non-degradable nature [14]. Other studies have also shown that biologically generated surfactants (biosurfactants) can serve as a substitute for their chemical counterparts [14–16]. Although the high cost of massive production of biosurfactants had previously limited their wide applications, recent studies have however shown that they can be generated from waste products and cheap renewable natural substrates [17]. Some biosurfactant production process have reached an advanced stage and are being commercialised, but despite this fact, biosurfactants are still underutilised for EOR relative to chemical surfactants [18]. Furthermore, the use of biosurfactants has not been thoroughly investigated before, especially at relevant reservoir conditions and they are still poorly understood.

Although some previous studies have investigated the EOR potential of different types of biosurfactants but most of those studies were carried out on sandstone and some of them were not carried out with fluids relevant to oil reservoirs. For instance, Wang et al. [19] investigated EOR potential of rhamnolipid in sand pack flooding with buffer-brine solution (citrate NaHPO4 buffer, with 2 wt% NaCl added) adjusted to pH 5.0 and n-octane at room temperature. Pornsunthorntawee et al. [16] reported positive effect of two biosurfactants produced by *Bacillus subtilis* and *Pseudomonas aeruginosa* in comparison to three chemical surfactants (Tween 80, SDBS, and Alforterra 145-5PO) in their applications in sand pack flooding. Nasiri et al. [20] also reported positive EOR effect of GreenZyme® in Berea sandstone core flooding and spontaneous imbibition experiments using seawater. Furthermore, Al-Sulaimani et al. [21] reported 13% oil recovery in tertiary application of a bio-surfactant generated from *Bacillus subtilis* on sandstone core flooding at reservoir temperature of 60 °C, while Al-Bahry et al. [22] reported an 9.7% additional recovery of residual oil saturation during Omani sandstone flooding with formation brine and a biosurfactant produced by *Bacillus subtilis* B20 at 60 °C. Souayeh et al. [23] also reported the EOR potential of lipopeptide bio-surfactant in Berea sandstone core flooding experiments carried out at 60 °C using aqueous biosurfactant solutions of varied dilutions.

Furthermore, in a previous study by Udoh et al., [24] the effect of brine composition and biosurfactants on oil recovery process in carbonate rock core flooding was investigated. In that study, injection of high salinity formation brine (FMB), controlled salinity brine (CSB) and controlled salinity brine combined with biosurfactant (CSBSB) were used in different injection modes. The results of the study showed positive effects of CSB and CSBSB flooding but the effluent analysis from each flooding showed the effect of the injected fluid on the crude oil-brine-rock (CORB) system. Also in that study, the authors did not report results from separate waterflooding experiments conducted with FMB and CSB solutions which could be compared with the results obtained with CSBSB for a better understanding of the effect. The aim of this study is to investigate the EOR potential of CSB and CSBSB injection by carrying out thorough core flooding experiments using fluids comprising major salts at concentrations typical for formation brine injected at various sequences consistent with oil recovery scenarios, and also to investigate the effect of temperature on oil recovery and the performance of CSB and CSBSB injection schemes.
2. Materials and Methods

2.1. Rock Samples

We used sixteen Estaillades carbonate rock samples in this study. The main composition of the samples was determined by X-ray diffraction (see the Supplementary Materials for details) and scanning electron microscopy analyses and the identified mineralogy of the samples is: 95% calcite, 4% dolomite and 1% anhydrite. The mineralogy of all rock samples was found to be nearly identical as they were all cut from a single quarry block. The dimensions, porosity, absolute (liquid) permeability and initial water saturation of the core plugs are presented in Table 1.

Table 1. Properties of rock samples used in this study. Here: L is length, D is diameter, ϕ is porosity, K is absolute permeability, and Swi is initial water saturation in core flooding experiments. Typical experimental error inclusive of instrument accuracy and repeatability is ±3 mD and ±2% for permeability and porosity, respectively.

<table>
<thead>
<tr>
<th>Core plug ID</th>
<th>L (cm)</th>
<th>D (cm)</th>
<th>ϕ (%)</th>
<th>K (mD)</th>
<th>Swi</th>
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<tr>
<td>C03</td>
<td>7.60</td>
<td>3.79</td>
<td>30</td>
<td>127</td>
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</tr>
<tr>
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<td>3.74</td>
<td>28</td>
<td>131</td>
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<tr>
<td>C09</td>
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<td>3.77</td>
<td>27</td>
<td>129</td>
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<td>3.79</td>
<td>31</td>
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<tr>
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<td>3.76</td>
<td>30</td>
<td>130</td>
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<tr>
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<td>127</td>
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<td>32</td>
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<td>32</td>
<td>127</td>
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<tr>
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<td>31</td>
<td>128</td>
<td>0.44</td>
</tr>
<tr>
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<td>28</td>
<td>132</td>
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</tr>
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<td>28</td>
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<tr>
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<td>134</td>
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<tr>
<td>C30</td>
<td>7.66</td>
<td>3.72</td>
<td>26</td>
<td>132</td>
<td>0.31</td>
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</tbody>
</table>

2.2. Crude Oil

North Sea crude oil was used in this study. The density, viscosity, API gravity, total acid number (TAN), total base number (TBN) and asphaltene property of the crude oil measured based on the standard test method (ASTMD) by Intertek (Aberdeen, Scotland) are presented in Table 2.

Table 2. Crude oil properties. Here: API is the American Petroleum Institute gravity.

<table>
<thead>
<tr>
<th>Oil properties</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 23 °C (kg/m³)</td>
<td>906</td>
</tr>
<tr>
<td>Density at 70 °C (kg/m³)</td>
<td>874</td>
</tr>
<tr>
<td>Viscosity at 23 °C (Pa·s)</td>
<td>0.060</td>
</tr>
<tr>
<td>Viscosity at 70 °C (Pa·s)</td>
<td>0.009</td>
</tr>
<tr>
<td>API at 23 °C (°)</td>
<td>24.750</td>
</tr>
<tr>
<td>API at 70 °C (°)</td>
<td>30.492</td>
</tr>
<tr>
<td>TAN (mgKOH/g)</td>
<td>3.905</td>
</tr>
<tr>
<td>TBN (mgKOH/g)</td>
<td>1.400</td>
</tr>
<tr>
<td>Asphaltene (wt. %)</td>
<td>0.850</td>
</tr>
</tbody>
</table>
2.3. Bio-Surfactants

Two bio-surfactants were used in this study: Rhamnolipids (R) and GreenZyme® (G). Rhamnolipids of 90% purity (R90) were supplied by Agae Technology LLC (Corvallis, OR, USA) and they are member of the glycolipid biosurfactant family. The liquid chromatography mass spectrometry (LCMS) analysis of the sample shows that the rhamnolipids sample consists of mixture of monorrhamnolipids and dirhamnolipids of the form R-C_{10}C_{10} and RR-C_{10}C_{10} with a molecular mass of 505 and 651 g/mol, respectively. Pure GreenZyme® (100%) was supplied by Biotech Processing Supply (Dallas, TX, USA) and it is a water soluble protein-enzyme produced from DNA of selected oil-eating cultured microbes. GreenZyme® has active H+ and OH- sites that make it highly diffusive in water and its molecular weight is between 80,000 and 90,000 g/mol.

2.4. Brines

Compositional properties of all brines used in core flooding experiments are provided in Table 3. All brines used in the laboratory experiments were prepared with reagent grade NaCl, CaCl_2·2H_2O, MgCl_2·6H_2O and Na_2SO_4 salts (Merck Life Science, Gillingham, UK) dissolved in deionized water produced by a Barnstead Smart2pure system (Thermo Scientific, Waltham, MA, USA). The formation brine (FMB) is an artificial solution of a composition and salinity typical for connate water of hydrocarbon reservoirs, while the controlled salinity brine (CSB) is 90 times diluted seawater designed for EOR process and is similar to the CSB used in [25]. The composition of the CSB was designed based on the zeta potential measurements reported in [26] using the streaming potential method that has been previously reported to be useful for a wide range of rock mineralogy and technological applications (e.g., [27–29]). A high salinity brine (FMB) was allowed to equilibrate with off-cuts of Estiallades rock for more than 50 days, so that the electrolyte pH stabilized at the value of 6.4 within 2% measurement inaccuracy, at which point the chemical equilibrium between the mineral and brine was assumed to have been established and the brine was used to saturate rock samples. In core flooding experiments, the initial brine (connate FMB) was first displaced by crude oil to establish the initial water saturation of \( S_{wi} \), and then either the same FMB, CSB, CSB with 1 wt.% rhamnolipid (CSBSB-R) or CSB with 1 wt.% GreenZyme® (CSBSB-G) were injected during the imbibition phase of the experiment. Injection sequence of brines was designed to mimic secondary, tertiary or quaternary waterflooding with either FMB, CSB, CSBSB-R, CSBSB-G or their combination. Interfacial tension between the crude oil and all brines at 23 °C is reported in [26]. The design of the core flooding experiments will be discussed in more detail in subsequent section.

Table 3. Electrolytes and their properties. Concentration of individual ions is given in M (mol/L) and ppm units. Brine concentration expressed as total dissolved solids (TDS) is provided in parts per million (ppm). pH values correspond to 23 °C and (70 °C).

<table>
<thead>
<tr>
<th>Ions</th>
<th>FMB</th>
<th>CSB</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M</td>
<td>ppm</td>
</tr>
<tr>
<td>Na⁺</td>
<td>1.463</td>
<td>33,619.74</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.420</td>
<td>88,100.71</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.091</td>
<td>2211.76</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>2.485</td>
<td>16,832.76</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.002</td>
<td>384.24</td>
</tr>
<tr>
<td>Ionic strength</td>
<td>3,000</td>
<td>-</td>
</tr>
<tr>
<td>TDS</td>
<td>-</td>
<td>141,149</td>
</tr>
<tr>
<td>pH</td>
<td>6.7 (6.5)</td>
<td>7.8 (7.4)</td>
</tr>
</tbody>
</table>
2.5. Rock Sample Preparation

Prior to carrying out core flooding experiments, the samples were cleaned with methanol for minimum of 24 hours in a Soxhlet apparatus to remove all dirt or salt residues from previous experiments and then dried in the oven at 80 °C for 48 hours. However, for core samples that were previously contacted with brine and oil, the procedure described by Alroudhan et al. [30] was adopted. The cleaned and dried rock samples were used to measure the core properties presented in Table 1. The pore volume, and hence porosity, was determined using the imbibition method by direct comparison of dry and fully saturated with FMB rock samples. For the absolute (liquid) permeability measurement, the core samples were initially saturated with FMB under vacuum for at least 12 hours and then placed in a Hassler type core flooding cell where the same FMB was pumped through the sample at different flow rates and the steady state pressure difference across the sample was measured. The permeability was determined from the slope of the plot of flow rate against the pressure difference. The saturated samples were then subjected to unsteady state drainage with crude oil injection at constant rate of 1 mL/min in order to avoid fingering of the displacing phase until no water was produced and connate (initial) water saturation, $S_{wi}$ was established. Thereafter, the cores were aged in oven at 75 °C for six weeks in order to alter their wettability. A detailed study on the wettability alteration of these cores is presented in the work done by Udoh and Vinogradov [26].

2.6. Core Flooding Experiments

Core flooding experiments were carried out with a bespoke design setup assembled in-house, which consists of a stainless steel Vinci Hassler core holder (Vinci Technologies, Nanterre, Paris, France; a Vindum dual cylinder high precision high pressure syringe pump (Vindum Engineering Inc., Sandpoint, ID, USA; ± 0.1% accuracy and ± 10⁻⁵ mL/min resolution); two hydraulic piston accumulators; a confining pressure pump; back pressure regulator; differential pressure transducer (± 0.006 V of the full scale non-linearity) and data acquisition system. For core flooding experiments conducted at elevated temperature, a heating jacket by Vinci (±0.5 °C accuracy) was used around the Hassler core holder. The schematic of the core flooding setup with the component parts is shown in Figure 1.
In order to be consistent with oil production from a real reservoir, we designed our core flooding experiments to be carried out in different injection stages termed secondary, tertiary and quaternary injection. The secondary injection and the associated secondary brine correspond to injection of brine into rock samples saturated with crude oil and initial FMB at $S_{wi}$. The secondary injection was investigated using FMB to simulate conventional waterflooding, CSB to mimic secondary injection of controlled salinity water (low salinity waterflooding) and CSBSB-R or CSBSB-G to simulate the chemical enhanced oil recovery (EOR) flooding in the secondary mode. The tertiary injection experiments correspond to injection of CSB in the secondary mode, with subsequent injection of either CSBSB-R or CSBSB-G to simulate secondary low salinity waterflooding followed by chemical EOR flooding in the tertiary mode. The investigated flooding sequences are therefore denoted by: CSB$\rightarrow$CSBSB-R and CSB$\rightarrow$CSBSB-G. The quaternary injection experiments correspond to injection of FMB in the secondary mode (first brine to displace oil), followed up by injection of CSB to mimic the low salinity waterflooding in the tertiary mode and subsequent injection of CSBSB-R or CSBSB-G as an equivalent of the final stage of oil recovery when chemical EOR methods are used. Thus, the flooding sequences used in these experiments are denoted by: FMB$\rightarrow$CSB$\rightarrow$CSBSB-R and FMB$\rightarrow$CSB$\rightarrow$CSBSB-G.

The secondary, tertiary and quaternary injection protocols were used to simulate oil production from a real reservoir and to cross-compare oil recovery obtained with different injected brines at different injection stages and two temperatures. The switch between the
secondary, tertiary and quaternary injections took place after oil production in the preceding injection ceased. Regardless of the injection sequence, the initial injection rate was kept at 1 mL/min during the secondary injection until no further oil production was observed. Then the rate was increased to 3 mL/min and kept at this value until the end of the core flooding experiment. In the experiments, which required change of injected brine, the pumping was stopped for the brine change but then injection resumed at the same 3 mL/min rate. All core flooding experiments were carried out at two temperatures: 23 °C and 70 °C.

3. Results

3.1. Secondary Injection of FMB and CSB

Figure 2 shows the results obtained from secondary core flooding experiments when single brine was injected into rock samples saturated with oil and connate FMB (Table 3). Figures 2a–c show the results of the secondary injection of the formation brine (FMB). Figures 2d–f show the results of secondary injection of the controlled salinity brine (CSB). Higher oil recovery was observed with higher temperature in both types of secondary waterflooding experiments (Figures 2a and d). Moreover, higher oil recovery was observed with CSB compared with FMB in the secondary mode for both tested temperatures. The ultimate oil recovery of 68% OOIP was obtained in the experiment carried out at 23 °C with FMB, while the ultimate oil recovery of 83% OOIP was obtained at 70 °C. This is consistent with previously published results (e.g. [25,31,32]). For the 23 °C core flooding experiment, oil recovery with FMB ceases at approximately 67% OOIP after injecting at the rate of 1 mL/min and additional 1% OOIP was recovered by increasing the injection flow rate to 3 mL/min (Figure 2c). For the 70 °C core flooding experiment, oil recovery with FMB ceases at approximately 78% OOIP after injecting at the rate of 1 mL/min and additional 4% OOIP was recovered by increasing injection flow rate to 3 mL/min (Figure 2b).
Figure 2. Oil recovery during secondary injection of FMB (a–c) and CSB (d–f). Red diamonds (a, b) correspond to waterflooding experiments carried out at 70 °C on rock sample C29 with initial water saturation of $S_{wi} = 0.32$, while blue diamonds (a, c) correspond to the experiments at 23 °C on rock sample C30 with $S_{wi} = 0.31$. Red squares (d, e) correspond to waterflooding carried out at 70 °C on sample C27 at $S_{wi} = 0.37$, while blue squares (d, f) represent the results obtained with C26 at 23 °C and with $S_{wi} = 0.39$. Grey curves show the measured pressure difference across the samples and vertical dashed lines indicate a transition from the injection rate of 1 mL/min to 3 mL/min.

The ultimate oil recovery of 77.08% OIIP was obtained in the experiment carried out at 23 °C with CSB, while the ultimate oil recovery of 90.96% OIIP was obtained at 70 °C. For the 23 °C CSB core flooding experiment, oil recovery ceases at approximately 72.66%
OIIP after injecting at the rate of 1 mL/min and additional 4.42% OIIP was recovered by increasing injection flow rate to 3 mL/min (Figure 2f). While for the 70 °C CSB core flooding experiment, oil recovery ceases at approximately 86.48% OIIP after injecting at the rate of 1 mL/min and additional 4.48% OIIP was recovered by increasing injection flow rate to 3 mL/min (Figure 2e).

3.2. Secondary Injection of CSBSB-R and CSBSB-G

Figure 3 shows the results obtained from core flooding experiments conducted in secondary mode when single brines of controlled salinity brine combined with bio-surfactants (rhamnolipid (R) and GreenZyme® (G)) were injected into rock samples saturated with oil and connate FMB. Figures 3a–c show the results of injection of CSBSB-G, while Figures 3d–f show the results of CSBSB-R injection. Higher oil recovery was observed with higher temperature in both types of secondary flooding experiments (Figures 3a and 3d). Higher oil recovery was observed with CSBSB-G compared with CSBSB-R in the secondary mode at 23 °C but CSBSB-R injection resulted in higher oil recovery at 70 °C. The ultimate oil recovery of 82.76% OIIP was obtained in the CSBSB-G flooding carried out at 23 °C, while the ultimate oil recovery of 93.10% OIIP was obtained at 70 °C. For the 23 °C flooding, oil recovery with CSBSB-G ceases at approximately 77.14% OIIP after injecting at the rate of 1 mL/min and additional 5.62% OIIP was recovered by increasing injection flow rate to 3 mL/min. For the 70 °C flooding, oil recovery ceases at approximately 87% OIIP after injecting at the rate of 1 mL/min and additional 5.88% OIIP was recovered by increasing injection flow rate to 3 mL/min.
Figure 3. Oil recovery during secondary injection of CSBSB-G (a-c) and CSBSB-R (d-f). Red circles (a, b) correspond to biosurfactant flooding carried out at 70 °C on rock sample C14 with initial water saturation of $S_{wi} = 0.38$, while blue circles (a, c) correspond to the experiments at 23 °C on rock sample C13 with $S_{wi} = 0.43$. Red triangles (d, e) correspond to biosurfactant flooding carried out at 70 °C on sample C18 at $S_{wi} = 0.45$, while blue triangles (d, f) represent the results obtained with C16 at 23 °C and with $S_{wi} = 0.42$. Grey curves show the measured pressure difference across the samples and vertical dashed lines indicate a transition from the injection rate of 1 mL/min to 3 mL/min.

During the CSBSB-R flooding, the ultimate oil recovery of 80.56% OOIP was obtained in the experiment carried out at 23 °C, while the ultimate oil recovery of 95.87% OOIP was
obtained at 70 °C. For the 23 °C flooding, oil recovery ceases at approximately 73.73% OIIP after injecting at the rate of 1 mL/min and additional 6.85% OIIP was recovered by increasing injection flow rate to 3 mL/min. While for the 70 °C CSBSB-R flooding, oil recovery ceases at approximately 85.67% OIIP after injecting at the rate of 1 mL/min and additional 10.20% OIIP was recovered by increasing injection flow rate to 3 mL/min.

3.3. Tertiary Injection Sequences CSB→CSBSB-G and CSB→CSBSB-R

The results of the core flooding experiments in which secondary brine injection was followed up by tertiary injection into rock samples saturated with oil and connate FMB are presented in Figure 4. In these floodings, CSB was injected in the secondary mode while the CSBSB brines were injected in the tertiary mode. Figures 4a–c and 4d–e show the results of injection of the CSBSB-G and CSBSB-R, respectively. From these experiments, higher oil recovery was observed with higher temperature in both injection sequences (Figures 4a and 4d). In the experiments in which CSBSB-G injection was implemented in the tertiary mode at 23 °C (Figure 4c), oil recovery of 77.73% OIIP was obtained in the secondary CSB injection. The tertiary flooding with CSBSB-G however resulted in an ultimate recovery of 81.60% OIIP which is equivalent to 3.87% OIIP incremental oil recovery. For the 70 °C flooding (Figure 4d), an initial oil recovery of 90.76% OIIP was made with secondary CSB injection and additional 3.23% OIIP was recovered with tertiary injection of CSBSB-G. This brought the total oil recovery from this injection sequence to 93.79% OIIP.

When CSBSB-R brine was injected in the tertiary mode after the secondary injection of CSB at 23 °C (Figure 4f), oil recovery of 76.69% OIIP was obtained in the secondary CSB injection. Additional recovery of 5.22% OIIP was made with the tertiary injection of CSBSB-R, which yielded an ultimate recovery of 81.91% OIIP. The secondary CSB injection at 70 °C (Figure 4e) resulted in 76.69% OIIP oil recovery while implementation of the CSBSB-R injection in the tertiary mode resulted in the ultimate recovery of 94.31% OIIP and corresponding incremental recovery of 7.57% OIIP.
Figure 4. Oil recovery during secondary injection of CSB and tertiary injection of CSBSB. Red hollow and filled circles (a, b) correspond to the applications of CSB and GreenZyme ® (CSBSB-G) in secondary and tertiary flooding respectively carried out at 70 °C on rock sample C11 with initial water saturation of $S_{wi} = 0.45$, while blue circles (a, c) correspond to the experiments at 23 °C on rock sample C09 with $S_{wi} = 0.42$. Red hollow and filled triangles (d, e) correspond to the applications of CSB and rhamnolipid (CSBSB-R) in secondary and tertiary flooding respectively carried out at 70 °C on sample C20 at $S_{wi} = 0.45$, while blue triangles (d, f) represent the results obtained with C17 at 23 °C and with $S_{wi} = 0.45$. Grey curves show the measured pressure difference across the samples and vertical dashed lines indicate a transition from the injection rate of 1 mL/min to 3 mL/min.
3.4. Quaternary Injection Sequences FMB→CSB→CSBSB-G and FMB→CSB→CSBSB-R

Figure 5 shows the results obtained from the quaternary core flooding experiments conducted with three brines subsequently injected into rock samples. The FMB was injected in the secondary mode, while CSB was injected in the tertiary mode and CSBSB-G and CSBSB-R brines injected in the quaternary mode. Figures 5a–c and 5d–e show the results of injection of the CSBSB-G and CSBSB-R, respectively. For both types of quaternary core flooding experiments, higher oil recovery was observed with higher temperature (Figures 5a and 5d). In the experiments in which CSBSB-G injection was implemented in the quaternary mode at 23 °C (Figure 5c), oil recovery of 71.45% OIIP was obtained after secondary FMB injection but this was increased to 83.52% OIIP during CSB tertiary injection and the ultimate oil recovery of 85.38% OIIP was obtained at the end of quaternary CSBSB-G injection. For the 70 °C experiments (Figure 5b), the initial oil recovery of 82.79% OIIP was made with secondary FMB injection, and tertiary CSB injection increased the recovery to 87.14% OIIP and the quaternary CSBSB-G injection resulted in the ultimate oil recovery of 90.02 OIIP.

Furthermore, when CSBSB-R was injected in the tertiary mode after the secondary CSB flooding at 23 °C (Figure 5f), oil recovery of 66.99% OIIP was obtained after the secondary FMB injection but tertiary CSB injection increased the recovery to 80.01% OIIP and the quaternary CSBSB-R injection resulted in the ultimate recovery of 82.78% OIIP. For the 70 °C experiment (Figure 5e), 82.04% OIIP oil recovery was made at the end of secondary FMB injection and the tertiary CSB injection increased the recovery to 90.59% OIIP, while the quaternary CSBSB-R injection resulted in the ultimate recovery of 92.45% OIIP.
Figure 5. Oil recovery during secondary injection of FMB, tertiary injection of CSB and quaternary injection of CSBSB. Red patterned, hollow and filled circles (a, b) correspond to the applications of FMB, CSB and GreenZyme (CSBSB-G) in secondary, tertiary and quaternary flooding respectively carried out at 70 °C on rock sample C06 with initial water saturation of $S_w = 0.41$, while blue circles (a, c) correspond to the experiments at 23 °C on rock sample C03 with $S_w = 0.44$. Red patterned, hollow and filled triangles (d, e) correspond to the applications of FMB, CSB and rhamnolipid (CSBSB-R) in secondary, tertiary and quaternary flooding respectively carried out at 70 °C on sample C22 at $S_w = 0.44$, while blue triangles (d, f) represent the results obtained with C15 at 23 °C and with $S_w = 0.44$. Grey curves show the measured pressure difference across the samples and vertical dashed lines indicate a transition from the injection rate of 1 mL/min to 3 mL/min.
4. Discussion

We report results from thorough experimental investigation of synergy between the use of controlled salinity waterflooding and biosurfactants injection for EOR conducted for the first time at relevant reservoir conditions of temperature. Figure 6 shows oil recovery obtained from secondary injection of FMB, CSB, CSBSB-G and CSBSB-R. The conventional injection of FMB yields the lowest oil recovery at both 23 °C and 70 °C. Compared with oil recovery obtained with FMB, the highest incremental oil recovery of 15% OIIP at 23 °C is observed with CSBSB-G thus making secondary injection of CSBSB-G most beneficial for low temperature reservoirs. However, injection of CSB yields additional 9% OIIP of incremental oil recovery and injection of CSBSB-R results in 13% OIIP incremental recovery making the former the most economically viable and the latter nearly as efficient as CSBSB-G. On the other hand, at elevated temperature of 70 °C, the highest oil recovery in the secondary mode was obtained with CSBSB-R so that additional 13% OIIP is produced compared with conventional FMB injection, while CSB injection yields additional 8% OIIP and CSBSB-G produces additional 10% OIIP compared with FMB injection. Therefore, for typical reservoir conditions of temperature, additional 5% OIIP can potentially be produced using CSBSB-R relative to the controlled salinity waterflooding alone. However, injection of CSBSB-G into reservoirs at 70 °C does not improve oil production significantly compared with CSB injection and the ultimate recovery from both types of EOR methods is found to be the same within the experimental uncertainty.

Figure 6. The ultimate oil recovery obtained with secondary injection of FMB, CSB and CSBSB-G and CSBSB-R. The red columns in the figure correspond to experiments conducted at 70 °C while the blue columns correspond to 23 °C experiments. The error bars represent the inaccuracy of measured produced volumes.

Figure 7 presents the summary of ultimate oil recovery obtained with all tested injection sequences at 23 °C and 70 °C. It is found that the higher oil recovery at 70 °C is obtained with injection of CSBSB-G or CSBSB-R in either the secondary or tertiary modes compared with FMB or CSB injection. More specifically, in comparison with the secondary injection of CSB at 70 °C, an incremental oil recovery of 2.2% OIIP and 5% OIIP was obtained with CSBSB-G and CSBSB-R, respectively. In contrast, at 23 °C in the secondary injection mode,
4.8% OIIP and 4.6% OIIP of extra oil relative to CSB injection was recovered with CSBSB-G and CSBSB-R respectively. On the other hand, oil recovery obtained with CBBSB-G or CSBSB-R in the quaternary mode is similar (within the experimental uncertainty) to that observed with CSB injected in the secondary mode, which implies that the synergy between the controlled salinity waterflooding and biosurfactant injection is beneficial only at early stages of field development. Although, the incremental oil recovery using biosurfactants injected in the quaternary mode is indistinguishable from the secondary injection of CSB, this study has achieved its aim at thoroughly investigating all possible injection scenarios and our results demonstrate for the first time that a synergy of controlled salinity water injection with the use of bio-surfactants is beneficial at early stages of field development. This study also advises against implementing injection of CSBSB-R or CSBSB-G in quaternary mode, but further work might be required to probe new bio-surfactants to improve oil recovery by this synergetic EOR method at later stages of field development. Oil recovery observed at 23 °C is the highest for all modes of injection of CSBSB-G and CSBSB-R compared with either FMB or CSB injection, thus making this synergetic EOR method beneficial for shallower reservoirs at low temperature. For secondary and quaternary injection sequences a higher oil recovery is obtained with CSBSB-G at 23 °C, while injection of CSBSB-R results in higher recovery at 70 °C. However, during tertiary injection of CSBSB-G or CSBSB-R similar oil recovery is observed for both tested temperatures. Note, that even though the results presented in Figure 6 and Figure 7 were obtained from different coreflooding experiments, the conditions of these experiments including temperature and injection rate were well controlled and kept identical across all experiments. Moreover, the petrophysical properties of all rock samples (porosity and permeability) were also the same within the experimental error (Table 1), and the same crude oil was used in all the experiments thus making the comparison presented in Figure 6 and Figure 7 valid.

Figure 7. The ultimate oil recovery obtained with various injection sequences of FMB, CSB, CSBSB-G and CSBSB-R. In this figure, ‘II’ corresponds to the secondary injection, ‘III’ – to the tertiary injection, and ‘IV’ – to the quaternary injection of the corresponding solutions. The red columns in the figure correspond to experiments conducted at 70 °C while the blue columns correspond to 23 °C experiments. The error bars represent the inaccuracy of measured produced volumes and not the experimental repeatability although select experiments were repeated to confirm >97% reproducibility of the results.
5. Conclusions

- We report results of core flooding experiments conducted for the first time in carbonate rock sample flooded with controlled salinity brine containing biosurfactants at typical reservoir temperature of 70 °C. The injection of CSBSB-R and CSBSB-R was carried out in secondary, tertiary and quaternary modes to replicate waterflooding of real oil reservoirs.

- Our results obtained at 23 °C show that use of CSBSB-G or CSBSB-R improves oil recovery by 15-17% OIIP compared with conventional FMB injection, and by 4-8% OIIP compared with CSB injection.

- At 70 °C, the injection of CSBSB-G or CSBSB-R results in improved oil recovery by 10-13% OIIP compared with injection of FMB, and by 2-6% OIIP compared with CSB injection.

- Our results suggest that controlled salinity-biosurfactant brine injection should be implemented in secondary or tertiary modes to maximize oil recovery compared with CSB injection.

- The use of rhamnolipids and GreenZyme® combined with controlled salinity waterflooding is shown to be beneficial for oil recovery while at the same time the tested biosurfactants present lower hazards compared with conventional chemical surfactants used for EOR. However, further research is required to identify biosurfactants to be used in such synergetic EOR method to reduce operational costs while increasing efficiency of oil recovery.

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