

Synthesis and CO₂ EOR Applications of Foaming Surfactants

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Abstract

CO₂ philic surfactants as foaming agent have the potential to overcome CO₂ mobility issues. A study has been conducted to synthesize and evaluate the CO₂ philic surfactants for the CO₂ mobility control. The synthesis process was optimized. The foam durability experiments in the presence and absence of the crude oil were conducted. The mobility reduction factor was found 2.93. In addition, 93.25% oil recovery was achieved. It was observed that the CO₂/water IFT appreciably decreased from 30 mN/m to 5.21 mN/m by using the surfactant in 0.5 % concentration. Results showed that CO₂ philic surfactant significantly reduce the mobility of the injected CO₂.

Keywords: Surfactants; Mobility reduction factor; Interfacial tension

Introduction

Injection of CO₂ into the deep reservoirs is well developed and currently practiced by petrochemical industries for enhanced oil recovery (EOR) [1]. Additional oil can be recovered by the EOR process and a significant amount of CO₂ injected remains permanently stored in the reservoir. Injection of CO₂ into the reservoirs as a mean to mobilize the oil and to reduce the residual oil saturation is the most prominent among other oil recovery methods [2,3]. The mobility ratio is confronting the efficiency of the CO₂ usage for displacing the fluid from reservoir. However, CO₂ viscosity is much lower than crude oil. The relative huge difference of viscosity and density between the CO₂ (injected fluid) and the reservoir fluids is provoking the unfavourable mobility ratio. The primary issues of CO₂ EOR process are the flimsy displacement due to the mobility ratio of the CO₂, crude oil and brine [3]. Viscous fingering and gravity overriding effects are commonly results from high value of mobility ratio, leading to an early breakthrough of injected CO₂. In order to minimize drawbacks of CO₂ flooding, foam is generated to reduce mobility of gas phase and hence, sweep efficiency is improved by decreasing mobility ratio. Foam can effectively be used as CO₂ mobility reducing agent to overcome the CO₂ mobility issues [4,5]. The foam generation in addition to produce stable and good quality foam are the prime challenges during foam flooding at reservoir temperature especially in the presence oil [6]. Previously, the surfactants used for foam generation were comprised of ineffectual tolerance with salinity and inducing the adsorption on carbonate rocks [7]. The CO₂ philic surfactants provides valuable scheme for the generation of stable foam for CO₂ mobility control applications. CO₂-philic surfactants recently introduced due to their excellent performance in CO₂ gas injection [8,9]. CO₂ philic surfactants are renowned to produce good quality and stable foam for EOR applications. These surfactants effectively reduce the interfacial tension between CO₂ and water. Therefore, lowering of IFT between CO₂ and aqueous surfactant solution which in turn increases the mobility reduction factor (MRF) value of CO₂ by generating stabilize foam lamellae. This incredible capability of foam stability reduces the high mobility effect of CO₂ by increasing the CO₂ viscosity and relative permeability [10]. Hence, optimizing the viscous fingering, gravity overrides and gas channelling through the un-swept zones and mobilizes the trapped oil with improved proficiency [11].

This study presents the impact of CO₂ philic surfactant on interfacial tension of CO₂/brine systems at a wide range of pressure

and salinity conditions. In addition, foam stability and CO₂ mobility reduction performance of surfactant package is also reported.

Materials and Methods

Raw material and chemicals

Methallyl chloride, sodium bisulphite, Hyamine 1622 (standard 0.004 M solution) were purchased from Fisher Scientific Malaysia. Nonyl phenol ethoxylate alcohol was obtained from OPTIMAL.

Synthesis of surfactant

The surfactant was synthesized by following the method discussed in one of our previous article. The Williamson reaction for synthesis was executed by mixing of ethoxylate alcohol (0.5mol) and sodium metal in three neck flask (1000 mL). The flask was placed in oil bath and the desired temperature of reaction 90°C was achieved. Methallyl chloride (0.5 mol) was charged into the flask after four hours. The reaction was continued for next eight hours. The product was centrifuged and solid salt produced during the reaction was separated. The obtained product was sulphonated by using sodium bisulphite as sulphonating agent. For the sulfonation of the produced product mole ratio of 1:1.2 of intermediate to sodium bisulphite in 500 mL water and equal amount of ethanol was refluxed for 24 hours. Titration of material against standard Hyamine (0.004N) solution was performed to measuring anionic contents (%) for the monitoring of sulfonation process. The process was optimized by classical method.

IFT experimetns

IFT measurement of CO₂ and surfactant solution inferred the CO₂

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philicity of newly synthesized surfactant. The pendent drop method was used for the IFT analysis. The IFT between, CO₂/brine and CO₂/surfactant in brine were evaluated by using the Vinci IFT 700 system. The CO₂ and aqueous solutions were loaded in their respective accumulators and left for a while to achieve equilibrium at specified conditions of temperature and pressure. A fine pendent drop was made and a snapshot was taken by camera to calculate the IFT.

Static foam endurance test

Initially, the foam ability and foam stability of the developed surfactants were analyzed using the Dynamic foam analyzer (DFA100) instrument at room temperature by using air as the gas source. The tests were performed without crude oil. Betaine (betadet S20) in 40% molar ratio was incorporated in order to boost up the foam quality and quantity

The foam stability was also measured in presence of oil using 1000 mL graduated cylinder. A volume of 200 mL of 0.5% surfactant solution in a 20 mL of crude oil were mixed in the cylinder. The mixture was heated in a water bath until reaching the desired temperature of 90°C. The dispersion tube was dipped in the solution and the CO₂ supply was started. The flow of CO₂ was fixed during all of the experiments for the initial screening of the in-house developed surfactants. The continuous flow was provided until the foam height reached 1000mL. The endurance time of the foam was noted until 20% of the foam was left. The replicate measurement was noted for all of the surfactants and their respective concentrations. These tests were also repeated for AOS, as an industrial bench mark surfactant.

Dynamic foam test in porous media and Oil recovery

Berea sandstone core samples (10 mD, 15.05 cm length, 3.78 diameter, porosity 17%) as porous medium. Initially, the core was saturated with brine until steady state conditions were achieved at the flow rate 0.22 cc /min. Neat CO₂ was injected to obtain CO₂ mobility base case (0.22 cc/min flow rate) in specified porous media (Berea core). The pressure drop data were collected. The core was saturated with 0.5 % surfactant solution. After surfactant saturation the CO₂ was injected to note down the mobility resistance produced by surfactant. The CO₂ was flow at the same conditions as in base line case of CO₂ flow. This experiment was also repeated for AOS using same conditions. The pressure drop data of CO₂ flow in the porous media in the base case and after the surfactant flow were used to calculate mobility resistance factor (MRF). The MRF was calculated by using following equation.

$$MRF = \frac{\Delta p(\text{In presence of foam})}{\Delta p(\text{In absence of foam})}$$

The actual oil recovery synthesized surfactant was calculated after the SAG injection by following equation.

$$\text{Oil Recovery} = \frac{V_{op}}{V_{or}}$$

where V_{op} was the total produced oil volume, and V_{or} was the residual oil volume

Results and Discussions

Synthesis and process optimization

Optimisation of the williamson reaction: The reaction parameters, such as agitation speed, reactants mole ratio, temperature and reaction time, were optimized by using the classical optimization method.

The findings by using di propylene ter-butyl alcohol are discussed in subsequent sections.

Effect of the stirring speed: In order to investigate the effect of the stirring speed, an alcohol to methallyl chloride mole ratio of 1:1 was used at the reaction temperature of 80°C and for a reaction time of 200 minutes. It was found that the reaction efficiency was low at low stirring speeds and became higher at high stirring speeds when the reaction time and temperature were kept constant as shown in Figure 1. No improvement was noticed in the conversion efficiency with a stirring speed in excess of 1000 rpm. Therefore, stirring speed of 1000 rpm was maintained throughout the course of the conducted studies.

Effect of the reaction temperature: The effect of the reaction temperature was directly associated with the reaction time as indicated in Figure 2. A reaction time of 200 minutes was used for all of the investigations with a fixed stirring speed of 1000 rpm. The yield of the Williamson reaction was low at 30°C and 60°C. It was observed that the maximum yield was obtained at a reaction temperature of 90°C. A higher reaction temperature was not possible due to the boiling point of the mixture. For investigation of the effect of the reaction temperature, an alcohol to methallyl chloride mole ratio of 1:1 was used. A better yield was obtained at the reaction

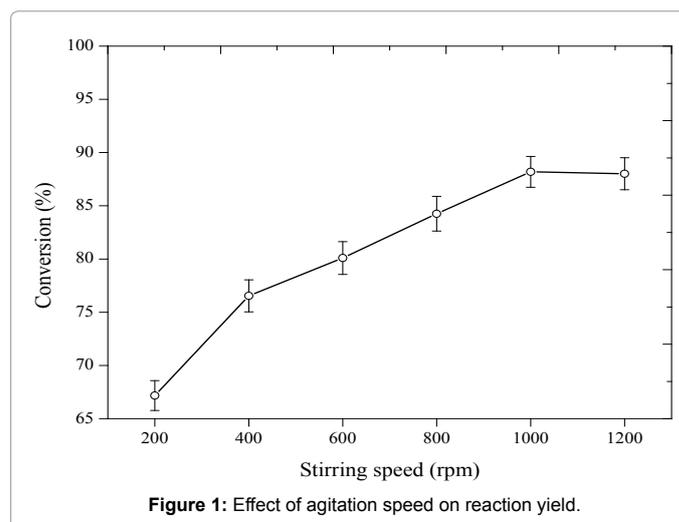


Figure 1: Effect of agitation speed on reaction yield.

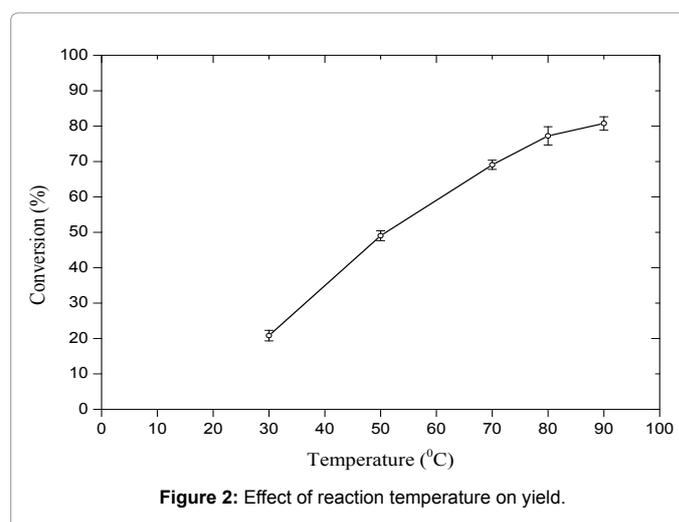


Figure 2: Effect of reaction temperature on yield.

temperature of 80°C; however, it required a relatively longer reaction time.

Effect of the mole ratio: A stoichiometric amount of alcohol for one mole of methallyl chloride is 1 mole. Therefore, increasing the amount of the alcohol beyond this limit is not feasible. Varying alcohol to methallyl chloride mole ratios was used to study the effect of the alcohol amount on the reaction efficiency. The reaction temperature of 90°C for a reaction time of 200 minutes was used with a fixed stirring speed of 1000 rpm. However, any increase in the methallyl chloride amount beyond the stoichiometric moles did not produce a significant effect. Therefore, the optimum amount of alcohol was selected as 1:1.

Effect of the reaction time: As discussed earlier, reaction time depends upon the reaction temperature. At a high temperature, the reaction was fast. To investigate the effect of the reaction time, an alcohol to methallyl chloride mole ratio of 1:1 was used. A reaction temperature of 90°C was used for all of the investigations with a fixed stirring speed of 1000 rpm. It was found that at 60°C, the reaction was completed in 800 minutes. Whilst at 90°C, the reaction was completed in 360 minutes; therefore, the optimum reaction time was found to be 360 minutes at 90°C as shown in Figure 3.

Optimised reaction conditions and yield: The Williamson synthesis process achieved the attachments of methallyl chloride with alcohols. The process was optimised for the best reaction condition. The optimised reaction conditions involve a reaction temperature of 90°C, time of 360 minutes, agitation speed of 1000 rpm and a stoichiometric molar ratio of the reactants

Optimisation of the sulphonation reaction conditions

The reaction parameters studied for the optimization included the reaction temperature, the reaction time and the molar ratio of the Sodium Bisulphite to the double bond. These parameters were optimized for the maximum yield of the sulphonated product. The product was analyzed by employing the two-phase titration to assess the produced surfactants. The amount of the active matter present in the sample showed the progress of the reaction during the synthesis process.

Effect of the reactant mole ratio: Five different molar ratios of the reactant to Sodium Bisulphite in the range of 1 -2.0 were studied. However, it was noted that a higher concentration of Sodium Bisulphite

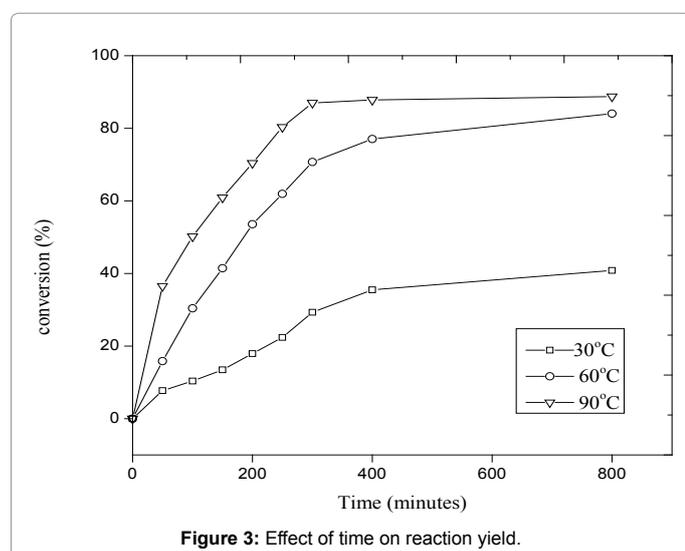


Figure 3: Effect of time on reaction yield.

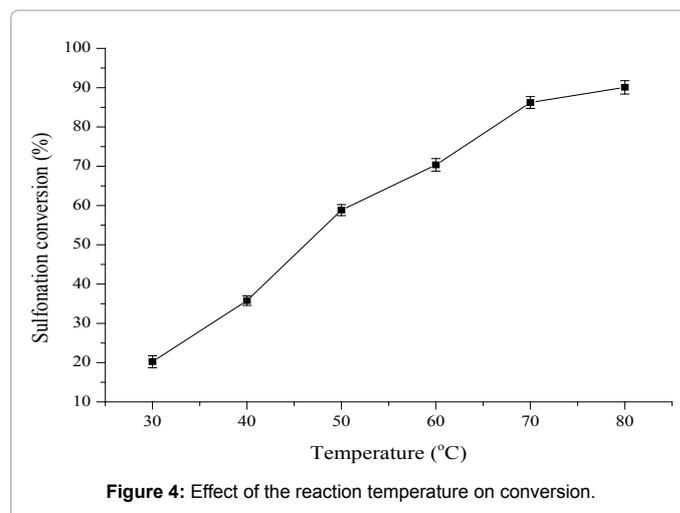


Figure 4: Effect of the reaction temperature on conversion.

was detrimental for the yield and quality of the product.

The excess Sodium Bisulphite can lead to a low yield. It was due to the different behavior of the Sodium Bisulphite at different concentrations. It was concluded from the experimental results that the sulphonation yield was maximum when a 1:1.2 mole ratio ester: NaHSO₃ was used. However, with a diluted solution is favorable as the diluted solution promotes the formation of sulphonate.

Considering the fact that the sulphonation process proceeds rapidly when form A was maximized, it was concluded that at the double bond of the alkenes the addition of the sulphonate group could be promoted by: (i) using diluted solutions and (ii) using Bronsted bases, like amine, to shift the equilibrium towards form A.

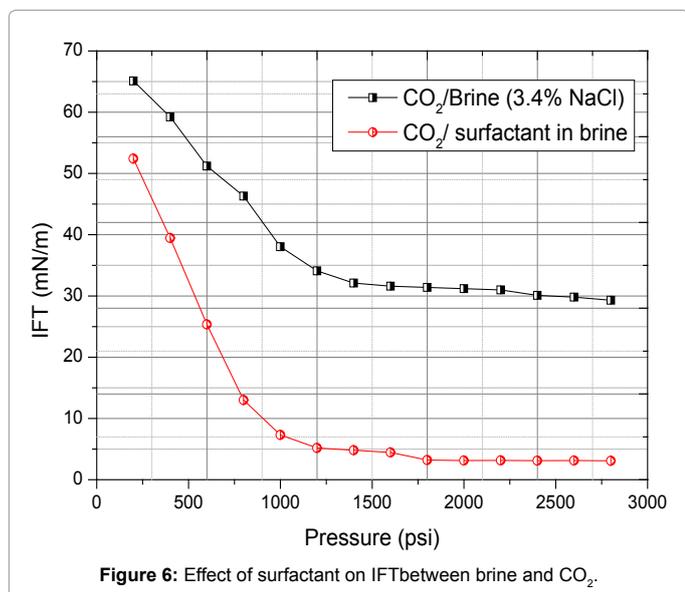
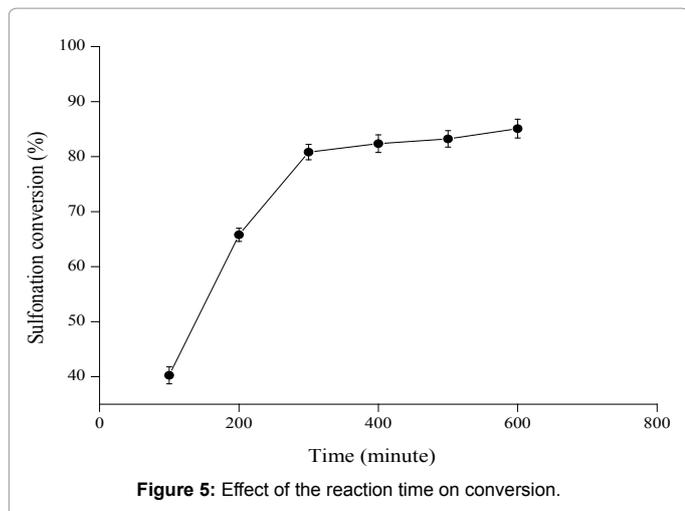
Effect of the Reaction Temperature: The sulphonation reaction was also studied for the optimisation of the reaction temperature as the reaction is temperature dependent. The reaction was studied at five different temperatures. When the reactants were delivered to the reactant flask, the flask temperature was increased to observe the effect of the temperature on the reaction. It was noted that low temperatures beyond 313K was not effective as the obtained yield was very low as shown in Figure 4. The maximum yield was obtained at the refluxing temperature of the solvents, i.e., ethanol and water. These two solvents were added in 50:50 ratios as described in the material methods. Therefore, the reaction temperature was set at which the solution started the reflux.

Effect of time: The sulphonation reaction was optimised for the reaction time as it is an important factor in reaction condition optimisation studies. It was observed that the sulphonation yield was drastically affected if the reaction proceeded for less time. The sulphonation reaction using Sodium Bisulphite required a much longer time to complete. The maximum yield was obtained using 600 minutes as shown in Figure 5.

Optimised reaction conditions and the yield of the head group synthesis: The optimised reaction conditions for the sulphonation reaction were 1.2 moles of the Sodium Bisulphite against the 1 mole of reactant. The reaction time was 600 minutes at the refluxing reaction temperature of the mixture.

IFT measurements

Figure 6 shows the affinity of CO₂ with surfactant solution. The IFT



between CO₂/brine and CO₂/surfactant /brine solution was analysed to determine the CO₂ affinity with newly developed surfactant. IFT value between CO₂ and brine was about 65mN/m, which reduced to 30 mN/m by applying pressure more than 1070 psi. The change in IFT was not apparent after this range of pressure. IFT measurement between CO₂ and water provided a fundamental scheme in this study matched with literature values as described in previous studies. It was seemed that the addition of brine tends to increase the IFT between CO₂ and as shown in Figure 6. The effect of pressure on IFT between CO₂/brine is shown in Figure 6. A substantial lowering of IFT was observed until the pressure of 1070 psi (CO₂ critical pressure) was attained. The significant decrease in IFT value of 5.21 mN/m by the addition of 0.5% surfactant was observed. Thus, IFT lowering reveals that the surfactant interfacial activity at CO₂/water interface is quite significant.

Foam stability by foam analyzer

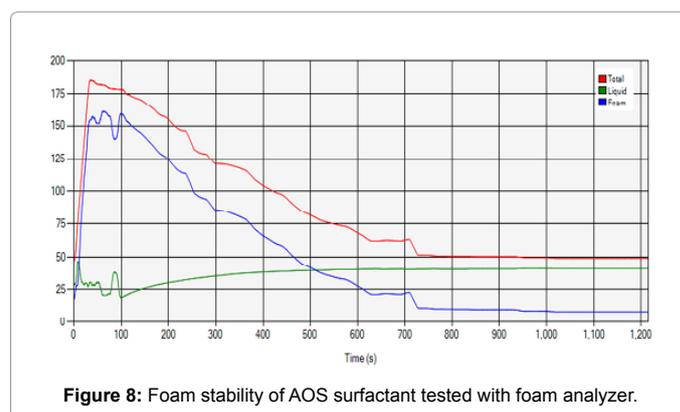
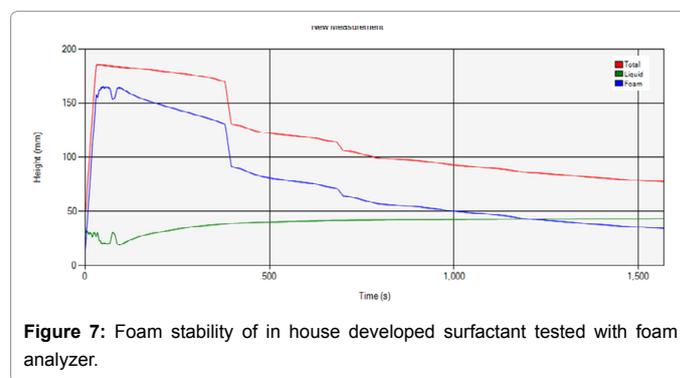
Static foam stability was measured by using DFA 100 instrument. The foam analysis results are shown in Figure 7. According to the foam decay measurements, the foam generation can be characterized in four major steps. First step was injection (a vertical line up to 160 mm

height), second was the stability at maximum height up to the foam height of 150 mm and Drop line (the line drops quickly to the x-axis). This takes about 425 seconds for foam decay so the bubble coalescence is negligible in retention phase. Rapid drainage line from 130 mm to 100 mm is the third step where the foam drained so quickly and takes 60 seconds only. Finally, the fourth stage was accounted slow drainage in foam height and bubble coalescence. This process continued for more than 1000 second until the foam height of 50 mm is reached. The stability of foam at maximum level was excellent. The maximum stability retention line of foam generated by newly developed surfactant (foam holding portion) was lasted up to 420 seconds.

The foam stability of AOS (C₁₆₋₁₈) was comparatively poorer than newly developed surfactant as shown in Figure 8. The foam started collapsing immediately after generation of lamellae from 160 mm to 100 mm it only takes 250 seconds. The drop portion was unstable and very steep. The foam collapsing time until 50 mm height for the surfactant was 450 seconds. Using foam analyzer it was concluded that in-house synthesized surfactant produced excellent quality foam at 90°C.

Foam stability by cylinder test in presence of crude oil

In presence of Dulang crude oil the surfactant attained high stability of foam. The foam stability time up to 20% remaining height was 11minutes in 1000 mL cylinder, which was excellent as compared to AOS (5minutes). The newly designed surfactant had outstanding foaming properties because the surfactant structure comprised of more number of branching and the methyl groups, tert butyl tip, presence of minimum number of methylene groups. All these structural factors are known to increase the CO₂ affinity with surfactant and lower down the IFT between CO₂/water which results in generation of stable foam film.



CO₂ mobility control and oil recovery

The mobility reduction factor (MRF) value used to measure the CO₂ flow resistance produced by the developed surfactants in the porous media.

The pore volume injected (PVI) versus the pressure drop data for mobility control test conducted from core flood experiments. The pressure drop measurement quantified that the pressure drop was 3-4 time increased with the addition of 0.5% surfactant solution as compared to the absence of surfactant in porous media. This was due the generation of stable foam inside the porous media. From the pressure drop data, it is concluded that the mobility of CO₂ was successfully reduced by employing surfactant as compared to clean CO₂. The surfactant had the potential of resistance to CO₂ flow in porous media by foam generation and caused lowering of the CO₂ mobility issues. The results are shown in Figure 9. The mobility resistance factor (MRF) value was also calculated and was found 2.93. The test was also repeated for AOS using same experimental conditions and MRF was found to be 1.3.

The overall oil recovery after surfactant flooding was 93.25% of residual oil in place (ROIP). The surfactant mainly comprised of different side chains, carbonyl and other aided groups in comparison with conventional surfactant, which were capable to generate stabilized CO₂ foam. The oil recovery results revealed that the surfactants produced highly stable foam was effectively improved the performance of oil recovery; the results are shown in Figure 10. It is, therefore, summarized that the hydrocarbon structure of surfactant had great influence on oil recovery, while the hydrophilic group impact on the solution issues, for example salinity and temperature tolerances. The much better performance of tested newly develop surfactant in term of oil recovery was due to the foam stability and surfactant structure relationship. The CO₂-philic properties of the hydrocarbon chains of this surfactant improved the foability and foam stability, which tends to enhanced the oil recovery [12]. The temperature stability of this surfactant caused by the sulphonate group as it is stable group at more than 100°C making this surfactant more promising for enhanced oil recovery formulations.

Conclusions

A low IFT value of 5.21 mN/m between CO₂ / brine was attained

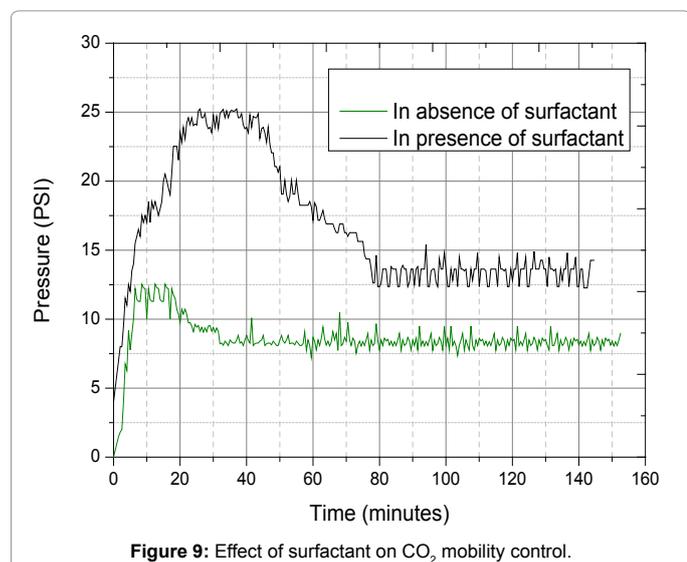


Figure 9: Effect of surfactant on CO₂ mobility control.

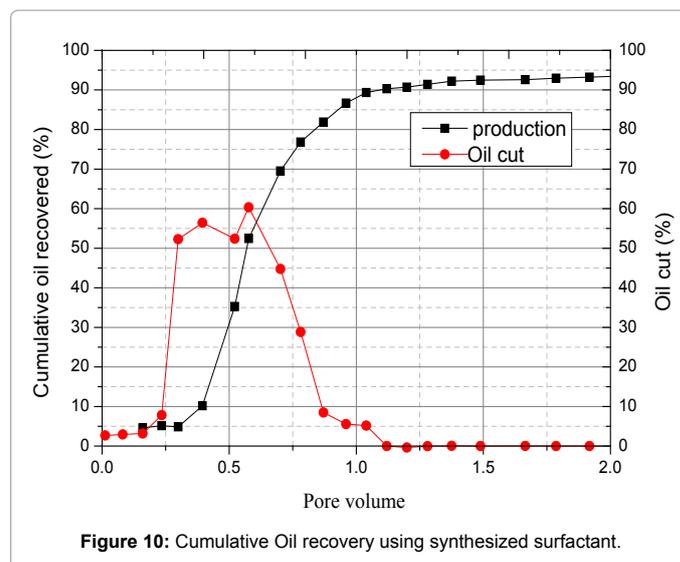


Figure 10: Cumulative Oil recovery using synthesized surfactant.

by using synthesized surfactant. The foam endurance tests were also conducted in absence and presence of oil in CO₂ environment at high temperature. It was found the developed surfactant generate good stable foam with CO₂ gas which stayed for 1000 seconds in worse reservoir conditions of high temperature, high salinity and in presence of oil. The foam stability of AOS was only 400 seconds in said conditions. The performance of surfactants in term of mobility reduction was also conducted. By employing 0.5% of surfactant the MRF value obtained were 2.93. AOS was able to provide MRF value of 1.3. Oil recovery achieved by using developed surfactant was 93.25% of ROOIP. The generation of stable foam as well as mobility reduction assets of the in-house developed novel CO₂ philic surfactant has a great prospective for CO₂-EOR applications as well for CO₂ sequestration.

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