[Regular Paper]

Applicability Test of New Surfactant Produced from Zizyphus Spina-Christi Leaves for Enhanced Oil Recovery in Carbonate Reservoirs

Mojtaba PORDEL SHAHRI*, Seyed Reza SHADIZADEH, and Mohammad JAMIALAHMADI

Dept. of Petroleum Engineering, Petroleum University of Technology, P.O. Box 63431, Ahwaz, IRAN

(Received March 16, 2011)

After the primary production period, water flooding is usually performed to recover more oil from reservoirs. However, water flooding recoveries are low from naturally fractured carbonate reservoirs, due in part to these reservoirs being mixed to oil-wet. Most of Iranian reservoirs are naturally fractured. Chemical process and especially surfactant flooding is an interested method because of its effect on interfacial tension (IFT) reduction and wettability alteration. Different surfactants are used for chemical flooding in the world but these chemical have high price and some detrimental effect on the environment. In this paper a new nonionic biosurfactant which is produced from the leaves of special tree called Zizyphus Spina-Christi is introduced. There is a hypothesis that this surfactant can be used in chemical flooding of fractured reservoirs because of very low cost and availability in Middle-East and Africa compared to other currently used surfactants. For this purpose surfactant is extracted from the leaves by spray dryer method. The pendant drop method is used to measure interfacial tension and critical micelle concentration (CMC) values. In order to investigate the effect of this surfactant on oil recovery two series of imbibition experiments are conducted on water-wet and oil-wet samples. It is observed that oil recovery is about ~16 % OOIP (original oil-in-place) for oil-wet cores by using this surfactant. In the same test, no oil is produced with water due to high oil wettability. After adding surfactant to the water, the oil recovery about ~7 % OOIP is obtained. Other test is done on water-wet cores which shows that addition of surfactant reduce the ultimate recovery from ~35 % OOIP to ~12.5 % OOIP. Reducing interfacial tension cause decrease in imbibition drive mechanism and lower the ultimate recovery. These results indicate that this new type of surfactant can meet the technical requirements as enhanced oil recovery (EOR) agent for chemical flooding.

Keywords

Zizyphus Spina-Christi, Imbibition, Biosurfactant, Carbonate reservoir, Oil wet

1. Introduction

Most of the world's oil reservoirs are found in carbonate rocks, many of which contain fractures with high hydraulic conductivity surrounding low-permeability matrix blocks. Evaluation of the wetting state for different reservoirs from all over the world indicates that most carbonate reservoirs seem to be mixed to oil-wet^{1),2)}. After the primary production period, waterflooding is usually performed to recover more oil from reservoirs. However, waterflooding recoveries are low from naturally fractured carbonate reservoirs, due in part to these reservoirs being mixed to oil-wet. In such reservoirs, production depends on spontaneous imbibition of water to expel the oil from the matrix into the fracture system, but this is only efficient when the matrix blocks are water-wet. Wettability is an important parameter controlling the capillary pressure^{3),4)},

which is in turn the driving force for the spontaneous imbibition process. The imbibition process is also affected by many other factors including matrix permeability⁵⁾, size and shape^{6)~8)}, heterogeneity^{3),9)}, and boundary conditions^{6),10)}. Fluid properties such as viscosities of the phases and interfacial tensions (IFT) also play a role in capillary imbibition recovery rate^{11),12)}.

Naturally fractured reservoirs are good candidates for enhanced oil recovery (EOR) processes since the matrix part of the reservoir may contain a large amount of oil. Chemical EOR methods such as surfactant flooding are used to improve the recovery from reservoirs. Surfactants can act in several ways to enhance the oil production: lowering the IFT between residual oil and injected water, changing the wettability of the surface, forming emulsions, *etc.* To enhance the spontaneous imbibition process in fractured reservoirs, surfactants are used as wettability alteration agents to modify the wettability of the reservoir rock or as interfacial tension reducing agents. Different varieties of surfactants are used for enhanced oil recovery in the world. All these

* To whom correspondence should be addressed.

* E-mail: mojtaba.pordel@yahoo.com

surfactants have high price which cause chemical process so expensive and uneconomical in some situation¹³.

In this research a new surfactant is introduced. This research evaluating and comparing the effectiveness of using a biosurfactant produced from leaves of *Zizyphus Spina-Christi* trees from south of Iran in mediating the wettability of oil-wet rocks and interfacial tension reduction. Effect of different surfactant concentration on the interfacial tension is investigated by pendant drop method. The ability of this new surfactant to enhance the spontaneous imbibition process in cleaned and crude oil-aged cores is tested.

2. Materials

2.1. Aqueous Phase

Early studies showed that biosurfactants (Saponin) will precipitate using brine as the aqueous phase, so deionized water is used in IFT and imbibition tests. A 10 g/L solution of NaCl used to avoid clay swelling. The density and viscosity of 10 g/L brine at 25 °C are 1.0026 g/cm³ and 1 cP (1 cP = 1 mPa·s) respectively.

2.2. Surfactant

Zizyphus Spina-Christi is a tree with spiny branches and small, orange-yellow fruits, commonly found in Jordan, Iran, Iraq and Egypt. Three cyclopeptide alkaloids, as well as four saponin glycosides and several flavonoids have been isolated from the leaves of *Zizyphus Spina-Christi*. All parts of the plant are used by the local Arab people to help maintain a healthy lifestyle. The plant has also been used for its soothing properties¹⁴. In Saudi Arabia it is used for the treatment of ulcers, wounds, eye diseases and bronchitis. The Bedouin use it for the treatment of wounds, skin diseases and as an anti-inflammatory. They also use it as a febrifuge and diuretic.

Zizyphus Spina-Christi is a tree indigenous to the south of Iran as shown in **Fig. 1**. The leaves of this plant, which are locally known as “Sedr” and “Konar,” have been used for washing the hair and body. Plant leaves are also used in Iranian folk medicine as an antiseptic, antifungal and anti-inflammatory agent, and for healing skin diseases such as atopic dermatitis^{15,16}. In China it has been used as a form of birth control. Aqueous leaf extract of *Zizyphus Spina-Christi* may possess antinociceptive properties in the rat and have a calming effect on the central nervous system¹⁷. It has been described as anticathartic, astringent, diuretic and tonic¹⁸.

No research has been reported about the saponin as a surfactant which can be used in petroleum engineering applications. Saponin which is a biosurfactant is produced from the leaves of *Zizyphus Spina-Christi*. The leaves of *Zizyphus Spina-Christi* were collected from south of Iran and the saponin extracted by spray dryer

Fig. 1 *Zizyphus Spina-Christi* Tree

method. The total extracted powder contains saponin and flavonoids. Powder has light brown color and soluble in water and alcohol. The density of powder is 0.103 g/cm³ and 1 % of this powder in water has a pH of 4.6-5. Saponin is a natural and biodegradable non-ionic surfactant. **Table 1** summarizes the properties of this surfactant.

2.3. Oil Phase

Kerosene was used as oil phase in all IFT measurements. The reason of choosing kerosene instead of crude oil in IFT measurements is cleanness. Kerosene density and viscosity at 25 °C are 0.8017 g/cm³ and 1.7 cP respectively. A crude oil sample is obtained from one of Iranian south oil reservoirs. Due to high viscosity of crude oil which is caused very long imbibition test, the oil was diluted with *n*-heptane in the volume ratio of 33/67 heptane/crude oil. This oil is used to modify the wettability of the outcrop cores by aging the core samples in the stabilized crude oil at elevated temperatures. Diluted oil has a density of 0.8 g/cm³ and a viscosity of 2.4 cP at 25 °C.

2.4. Core Samples

Cores were used for imbibition test are sandstone outcrop which are collected from 40 km south of Ahwaz, Iran in order to show the effect of saponin on imbibition recovery. Each core was characterized first by measuring the dimensions to get the length, diameter and bulk volume.

In order to compare the effectiveness of different treatments on the same core and to be able to restore the core state, it is important that the core can be cleaned to a repeatable initial state. Restored state analysis requires that the core be cleaned to the water-wet that existed before oil accumulated in the formation. The core is then saturated with crude oil to a capillary pres-

Table 1 Properties of Extracted Powder of Zizyphus Spina-Christi Leaves

Product	Total extracted powder of Zizyphus Spina-Christi
Used part	Leaves
Preparation	Spray dryer
Description	Fine powder
Color	Light brown
Solubility in cold water	Soluble
Solubility in alcohol	Soluble
Density	0.103 g/cm ³
pH value (1 % solution)	4.6-5
Residue at 110 °C, 6 h	96.9-98.9 %
Total ash at 800 °C, 3 h	9.9-10.5 %
Application	Personal care 0.7-1.5 % Special shampoo 0.7-2 %
Ingredient	Saponin-flavonoids

Table 2 Core Characterization

Core		S1	S2	S3	S4
Average length	[cm]	4.48	4.48	6.91	6.89
Average diameter	[cm]	4.10	4.10	4.10	4.10
Area	[cm ²]	13.16	13.16	13.16	13.16
Bulk volume	[cm ³]	58.90	58.90	90.90	90.42
PV ($S_w = 1$) calculated by weight	[mL]	8.35	8.49	11.65	11.74
PV calculated by Boyle's two cell	[mL]	9.21	9.03	15.13	15.24
Mean PV	[mL]	8.78	8.76	13.39	13.49
Porosity	[%]	14.91	14.87	14.73	14.91
Absolute permeability ($S_w = 1$)	[mD]	18	18.5	21.5	21.3

sure typical of the formation and the system allowed to equilibrate or “age” under formation conditions¹⁹. Cores had been cleaned by Soxhlet extraction using toluene and dried to constant weight before further experiments. Cleaning was carried out in a fume hood. The sandstone core types were labeled S1, S2, S3 and S4. After cleaning and drying to constant weight, cores were characterized with water to determine their pore volume, porosity, and permeability. Initially, water was used to saturate the core. Pore volume and porosity for each core was obtained from the difference in dry and water saturated weights of the core along with its dimensions. Also Boyle's two cell method was used to determine the pore volume and porosity of cores material. **Table 2** shows the result of cores characterization.

3. Results and Discussion

3.1. Interfacial Tension Measurement

Kerosene was selected as oil phase and brine with variable surfactant concentration as aqueous phase in interfacial tension measurement experiments. The reason of choosing kerosene instead of crude oil was ignoring asphaltene and other surface active agents effects in crude oil and its cleanness. In order to evaluate the interfacial tension between aqueous solution with different surfactant concentrations and kerosene using the pendant drop method it is necessary to evalu-

ate the density of the aqueous solution with different surfactant concentrations and kerosene. In this work the densities of aqueous solution with different surfactant concentrations and kerosene were measured using DMA-5000 apparatus.

Another part of tests is pendent drop experiment to investigate the effect of saponin on IFT reduction. During this experiment pendent drop cell was filled with kerosene and transfer vessel was filled with aqueous solution with different surfactant concentrations. Aqueous solution with different surfactant concentrations was injected through ISCO pump into the pendent drop cell with the very low flow rate. Although this low flow rate makes the process time consuming, but it will allow the surfactant monomers and micelles reach to the equilibrium between two layers of oil and brine. Choosing this low rate, guaranties that the aqueous phase separation from the tip is result of density difference not flow rate of injection.

According to the above mentioned method, the IFT between aqueous solution with different surfactant concentrations and kerosene was determined. The IFT values for aqueous solution with different surfactant concentrations and kerosene system were plotted against the surfactant concentration in **Fig. 2**.

As shown in **Fig. 2**, saponin decreases the IFT between brine and kerosene to about 9 mN/m which can be decreased further by addition of different salt concentration into the solution. IFT experiment did

Fig. 2 Interfacial Tensions between Different Concentrations of Surfactant (Saponin) and Kerosene

Fig. 3 Photograph of Imbibition Cell

not continued for higher concentration due to problems related to high foaming activity of this surfactant during solution preparation.

3. 2. Imbibition Test

The imbibition cell is photographically shown in **Fig. 3**. Imbibition cells are consisted of a tubular glass base into which the core was placed. The top was connected to the base *via* a ground glass joint lubricated with inert grease (silicon). The top incorporated a burette to allow the produced oil to be quantified. A magnetic stirrer bar under the core allowed for oil drops adhering to the core surface to be dislodged periodically. To prepare the imbibition cell for testing, silicon grease was smeared in the ground glass joint. The two cell pieces were twisted together several times to form a tight seal and eliminate vertical flow paths in the grease. The cell was initially filled with water contain 10 g/L NaCl by siphoning through a tube inserted in the top of the pipette and let sit for 30 min to make sure that it would hold water before starting the actual imbibition test. It was then taken apart and reassembled with the stir bar. The core to be tested placed on the core stand inside the imbibition cell, and the imbibition cell was reassembled. The imbibition cell was refilled with water or surfactant solution through the burette up to a desired height. Spontaneously produced oil was monitored and recorded *versus* time on a daily basis. All tests are conducted at room temperature. In order to

check the repeatability of tests, each imbibition profile is measured three times. It means that after each imbibition test, corresponding core is cleaned by soxhlet apparatus and then a same cycle of aging and imbibition process is performed to check the validity of data. There was no significant difference between the experimental results that shows the accuracy of the tests.

In order to show the effect of saponin on oil recovery two types of aging process are used. The outcrops which are used in this thesis are sandstone so they would be water-wet at the initial state. Also according to the cleaning process they become water-wet after cleaning process. The duration of aging process affect the amount of oil wetting. In order to investigate the effect of saponin on oil recovery in both water-wet and oil-wet rock, cores S1 and S2 were used as water-wet cores without any aging process. These cores are saturated with crude oil and used for imbibition test in water-wet state. Also, cores S3 and S4 were used for oil-wet state imbibition test. These cores were first saturated with crude oil and then immersed in a container with same crude oil for aging process. Then container and cores were put in an oven in the temperature of 60 °C. This temperature was used because there is some *n*-heptane in crude oil sample which may reach into the boiling point. After 2 weeks in this temperature cores was put in a dark place for 3 weeks at atmospheric temperature. At the start of experiment, the cores were 100 % oil saturated. Two imbibition tests were conducted for oil-wet cores S3 and S4. One with brine and one with surfactant present in brine with 8 wt%. The cores was placed vertically and surrounded by 350 cm³ of aqueous imbibition solution. The expulsion of the oil from the core surface was observed visually and the oil production *versus* time was recorded.

In the first imbibition cell core S3 is used and exposed to brine. No oil was collected in the graduated tube until 21 days. Oil was not release from the surface of the core because of high interfacial tension and high affinity to spread on the surface as shown in **Fig. 4**. In order to produce oil interfacial tension must be lowered in order to convert imbibition mechanism to gravity drive and the oil drop can be release from the rock surface. The brine in the imbibition cell was replaced with the 8 wt% surfactant solution and imbibition profiles showed a jump in oil production after the exposure to surfactant solution as shown in **Fig. 5**. Saponin resulted in a total of ~7 % OOIP recovery from the strongly oil-wet core, S3. Saponin enhanced the spontaneous imbibition by decreasing interfacial tension. Another type of experiment was done on the core S4 which has the same property as S3. The core S4 was aged with the same procedure as S3 in order to obtain same aging condition. S4 is exposed to the 8 wt% surfactant solution from the first in an individual imbibition cell. As can be seen in the **Fig. 5**, oil produced

Fig. 4 Core S3 after 21 days Exposing to Brine

Fig. 5 Imbibition Recovery for Oil-wet Cores

after three day. The oil production reached its plateau after 33 day. The amount oil produced after this period is ~16 % OOIP. In this experiment saponin is used from the beginning of the imbibition process. The visual analysis shows that in these two types of experiment, imbibition mechanism was driven by gravity due to addition of saponin. Oil droplet in the experiment released easier from the rock surface due to low interfacial tension. When the interfacial tension become lower, the imbibition mechanism convert to gravity drive in which oil is produced from the upper surface of rock.

Surface active chemical dissolved in the injected water may either change the wettability towards a more water-wet system to improve the capillary force imbibition by a counter current flow, or decrease the interfacial tension (IFT) between the water and oil to increase the ratio between the gravity force and capillary force according to the inverse of the Bond number. When the imbibition mechanism is capillary drive, oil may be produced from the lateral surface of the core by counter-

Fig. 6 Imbibition Recovery for Water-wet Cores

current imbibition. When the imbibition mechanism is gravity drive, the oil may be displaced by gravity force in a co-current flow from the core through the top surface. As shown in **Fig. 4**, oil was produced from the upper surface which is show that the imbibition mechanism is driven by gravity force relative to capillary force. Another result from the imbibition recovery curves is that, if we use saponin from the first in enhanced oil recovery process we have more oil recovery than the situation in which we inject water first and then followed by saponin. One cause of this difference is that when we used water from the beginning of imbibition process, some of the oil near the rock surface was displace with water but do not produce due to high interfacial tension between water and oil. If we use saponin after water imbibition, surfactant monomer must be passed from this water film near the rock surface which is a slow process by diffusion and cause a decrease in recovery rate and ultimate oil recovery.

Another type of experiment was done on the water-wet cores. Cores S1 and S2 were only saturated with oil and put in an imbibition cell without any aging process. Cores were sandstone type and water-wet at initial state. S1 was put in an imbibition cell surrounded by brine. In order to see the effect of saponin on water-wet rock, S2 exposed to surfactant solution in different imbibition cell. Both S1 and S2 cores have same characteristics. Imbibition recovery curves were shown in **Fig. 6**. As visual analysis, in core S1 and S2, the imbibition recovery mechanism was both capillary and gravity driven. In this cores oil expelled also from the lateral surface of cores which means capillary imbibition drive by a counter current process as shown in **Fig. 7**. When surfactant is added to the surrounded water, the interfacial tension between oil and water decreases which is cause a decrease in capillary force. Capillary force is drive mechanism in this experiment. Reducing interfacial tension cause decrease in imbibition drive mechanism and lower the ultimate recovery. Counter-current flow is developed due to the capillary

(a) 1st day, (b) 3rd day.

Fig. 7 Core S1 Exposed to Brine

forces. At low interfacial tension, the imbibition rate decreases due to a decrease in capillary force. Saponin decreases the interfacial tension between brine and oil which is resulting lower capillary force. As one can see in Fig. 6, addition of saponin to brine cause a reduction in ultimate oil recovery from ~35 % OOIP to ~12.5 % OOIP.

4. Conclusions

(1) Advantages of saponin are compared to other surfactant is availability and very low cost. Also saponin is a natural and biodegradable surfactant which has not adverse effect on the environment which is a very important characteristic of this surfactant in compared to chemical surfactants which are used in chemical flooding.

(2) Addition of saponin as a nonionic surfactant to the distilled water with 10 g/L NaCl can decrease the interfacial tension from 48 dyne/cm to 9 dyne/cm. The IFT obtained by saponin is the same as other surfactants which are used in chemical flooding process for enhanced oil recovery.

(3) In the oil-wet cores, the amount of oil produced is ~16 % OOIP if saponin is used from the beginning of the imbibition process. This recovery is due to reduction in interfacial tension and converts the imbibition to gravity drive mechanism. Also, after exposing the oil-wet core to the water from the beginning, oil was not produced due to the core wettability. In this experiment oil shown high affinity to spread on the core surface and did not released. If saponin is added after the imbibition with water for oil-wet core, the amount of oil produced is ~7 %. The difference between ultimate recoveries in these tests is due to extraction of some oil from cores by water in the imbibition test in which saponin is used after imbibition with water. Extracted oil droplet cannot release due to high oil wettability of core as shown in visual analysis. After exposing this core by saponin, there is a thin film in the some outer layer of the core that resists the interaction of saponin and existing oil. This low interaction reduces the ultimate recovery if saponin is used after water imbibition.

(4) Addition of saponin to the brine causes a reduction in ultimate oil recovery from ~35 % OOIP to ~12.5 % OOIP in water-wet cores. Decreasing in ultimate recovery is due to interfacial tension reduction. The imbibition process in water-wet cores is capillary driven as shown in visual analysis. Reducing interfacial tension cause a decrease in capillary pressure which is the driving force.

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