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Simultaneous Evaluation of Capillary Pressure and Wettability Alteration based on the USBM and Imbibition Tests on Carbonate Minerals

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Abstract

Wettability alteration would play a significant role in the hydrocarbon displacement as it can improve oil recovery factor both in conventional and unconventional reservoirs. Therefore, accurate prediction of this parameter would be of importance in displacement sweep efficiencies. In this paper, we aimed to experimentally investigate wettability changes in the presence of a nonionic natural surfactant (Cedar) for different carbonate mineral samples. To do this, Imbibition and USBM tests were taken into consideration to predict capillary pressure and how it affects oil production rate. It is observed that the presence of Cedar had a profound impact on the wettability and capillary pressure for calcite and dolomite samples. Due to the different composition of rock minerals, Cedar has a good effect on both core sample (calcite and dolomite), whereas the oil recovery for dolomite cores is more than calcite cores. This change for calcite cores corresponding oil-wet to neutral-wet or slightly water-wet and for dolomite samples become to water-wet. In addition, the most S_{or} decreasing occurs in dolomite samples particularly in D1 (14%). Moreover, the oil recovery for reservoir samples is less than mineral samples.

Keywords; USBM test, Imbibition Test, Nonionic Natural Surfactant, Capillary Pressure, Wettability Alteration

1. Introduction

Credible evaluation of wettability in reservoirs is vitally essential because it has a great impact on the displacement of hydrocarbons through the porous medium (Amott 1959; Anderson

1985; A. Davarpanah et al. 2019; A. Davarpanah and Mirshekari 2020; Han et al. 2019; Hirasaki and Zhang 2004; Y. Hu et al. 2020; Jadhunandan and Morrow 1995; Jarrahan et al. 2012; Newgord et al. 2020). Moreover, the variation of wettability have a huge impact on the capillary pressure, irreducible water saturation and residual oil saturation (Anderson 1985; A Davarpanah 2018; A Davarpanah et al. 2019; A Davarpanah and Mirshekari 2019a, 2019b, 2019c; Han et al. 2019; Xiao Hu et al. 2020; Jadhunandan and Morrow 1995). It has been proved that the most of the carbonate reservoirs act as oil-wet due to the interaction of components crude oil and the kind of this rock (Afshin Davarpanah 2020; Afshin Davarpanah et al. 2018; Geyssant 2019; Hirasaki and Zhang 2004; Xiaoyong Hu et al. 2020; Jarrahan et al. 2012; Kafashi et al. 2020; Zhou and Davarpanah 2020). The composition of rock minerals plays a significant role in the adsorption of added surfactants, reservoirs and their influences on wettability (Hamid Esfandyari et al. 2020; Giraldo et al. 2013; Pan et al. 2020; Somasundaran and Zhang 2006). Wettability is mainly estimated by experimental methods that can be done for core samples extracted from hydrocarbon reservoirs. These laboratory procedures usually have consisted of spontaneous and forced fluid displacement. The Imbibition and the USBM method are practical examples of these tests for measuring wettability (Donaldson et al. 1969; Sjørgård and Seland 2020). The priority of USBM to Amott test is its more sensitivity to near-neutral wettability and it can determine an average wettability value for the investigated core samples. Although USBM method is also faster, its limitation has contained the use of plug-size core samples as they should be utilized in the centrifuge (Salehi et al. 2008). The imbibition method has been known as one the most popular qualitative methods for measuring the spontaneous imbibition because there is no need to complicated instrument and it represents a rapid but rough idea about the wettability (Anderson 1986). Different techniques such as chemical flooding have been utilized to raise water imbibition into the carbonate reservoirs (Gomari et al. 2006; Seethepalli et al. 2004). Within chemical flooding methods, the surfactant can enhance oil

production via diminishing the IFT, reducing residual oil saturation, increasing sweep efficiency, and wettability alteration. This scenario is feasible if there is adsorption interaction between surfactants and reservoir rock (Ahmadi and Shadizadeh 2013a; Buckley 2001; A Davarpanah 2018; Freer et al. 2003; Hassenkam et al. 2011; Rai et al. 2015).

Esfahani and Haghighi (2004) evaluated the wettability of Iranian reservoir rocks and they found that there is not a good harmony outcome between the USBM and the Amott–Harvey indexes by centrifuge. Moreover, these measurements have the same outcomes using the core flooding system (Esfahani and Haghighi 2004). Bennetzen et al. (2014) elucidated the oil recovery from limestone rock using various surfactants. They concluded that 14.7–28% of OOIP were produced by utilizing these surfactants (Bennetzen et al. 2014). Amirpour et al (2015) worked on the wettability alteration in sandstone and carbonate rock by surfactant during capillary pressure measurements. They concluded that utilizing T-X100 and cedar can alter the wettability of core samples from oil-wet toward water-wet, but, the results of contact angle and USBM methods have not had good concordance (Bennetzen et al. 2014).

Sharma et al. (2013) run a set of experimental tests to investigate the wettability changes of carbonate rock by using three sorts of surfactant. They concluded that, by spontaneous imbibition, the mixture of surfactants could recover the oil approximately 70-80%. Additionally, using surfactant during secondary water flooding caused to increase the oil recovery remarkably rather than the water flooding spontaneously (from 29% to 40%) (G. Sharma and Mohanty 2013). Esfandiyari et al. (2020) tried to elucidate the impact of amphoteric and cationic surfactants on relative permeability and wettability changes. They found out HTMAB is more impressive than HABSA as it has better ability to improve oil recovery and modify the wettability toward water-wet (H. Esfandiyari et al. 2020).

Due to the environmentally friendly property of natural surfactants, in this paper we concentrated on the investigation of Cedar impact on different sorts of carbonate rocks

wettability in mineral scale. During USBM and Imbibition tests, capillary pressure is investigated in various kinds of calcite and dolomite samples and drainage and imbibition's cycles are gained by centrifuge. The main reason for choosing this nonionic surfactant is, firstly, there are many Zizyphus Spina Christi trees and it can be extracted conveniently and without extra unnecessary expenditures of surfactant productions. Secondly, it is a natural and non-hazardous surfactant and does not have any detrimental effect on the reservoir and environment. Additionally, utilizing two excellent and precise methods (USBM and Imbibition tests) on several carbonate core plugs give the best and comprehensive view about the relationship between mineralogy and capillary pressure, wettability and EOR processes. It is due to the composition of the rock mineralogy has a huge impact on the interaction between fluids and rock in the reservoir, wettability and finally mobility ratio. Therefore, the first pace in EOR processes might be recognition the various sorts of minerals in reservoir which can be achieved in this work by USBM and Imbibition tests.

2. Materials and methods

2.1. Materials

Surfactant: In these experiments, cedar (Zizyphus Spina Christi) dry extract (powder) was used as a surfactant. Zizyphus is a category of about 40 species buckthorn family, spread in the warm and subtropical places across the world. The name of this tree in Arabic is Cedar and in Iran, its pounded leaves are usually called "Cedar". The fruit of this tree is also called Kunar and is edible. The Kunar leaves (cedar) contain tannin and phytosterols such as $-\beta$ Sitosterol and $-\beta$ Sitosterol Glycoside and also a saponin Ebelinlacton. The saponin in cedar is the foaming agent in the Kunar leaf. Cedar is a natural nonionic and biodegradable surfactant (Pordel Shahri et al. 2012). It was easily gained from trees, and it is an environmentally-friendly surfactant (Hamid Esfandyari et al. 2020). Saponin consists of the hydrophobic (triterpenoid or

steroid) and hydrophilic (remnants of saccharides) sectors (Ahmadi and Shadizadeh 2013a; Stanimirova et al. 2011). According to preliminary studies on this surfactant and its critical micelle concentration (Ahmadi and Shadizadeh 2013b), these experiments used plant surfactants containing 8% wt. of cedar dry extract. The chemical structure and properties of this powder are stated in Figure 1 and Table 1.

Fig. 1. Zizyphus Spina Christi (Hamid Esfandyari et al. 2020).

Table 1. Powder properties extracted from the Kunar leaf (cedar)

Product	Powder extracted from the Kunar (cedar)
Part used	Leaves
CMC	8%
Compounds	Saponins - flavonoids
Color	light brown
Solubility in cold water	Soluble
Solubility in alcohol	Soluble
Viscosity	2.9466 cP
Density	1.0253 gr/cm ³

Core samples: Core samples of extracted from calcite and dolomite reservoir rocks. The first series of calcite sample is lumachelle type (sample C1). Lumachelle is a group of high purity calcium carbonate that is approximately 98%. The second type of calcite (sample C2) is a reservoir sample with a purity of about 96%. Dolomite samples, D1 and D2, are also mineral and reservoir samples. The characteristics and compositions of plugs used in the imbibition and centrifuge tests are shown in Table 2 and Figure 2. The purity of these two plugs more than 96%. The XRD tests prove that these plugs have a high percentage of calcite and dolomite and all the percentages were obtained from XRD tests. The main reason of choosing these lengths of samples is the most length can be utilized is 7 cm because of centrifuge instrument.

Table 2. The petrophysical plugs properties.

core	L [cm]	D [cm]	Vb [cm ³]	PV [ml]	Φ [%]	K [mD]
C1	5.6	3.8	63.51	21.8	34.33	13.72
C2	4.6	3.8	52.17	3.85	7.37	8.34
D1	4.1	3.8	46.5	6.75	14.51	12.25
D2	4	3.8	45.36	3.20	7.05	6.85

A

B

C

D

Fig 2. The results of XRD tests; A) C1, B) C2, C) D1, D) D2

Fluid properties: the crude oil was provided from Ahvaz oil field in Iran. The surfactant solution was prepared according to previously mentioned studies (containing 8% wt. of cedar dry extract). Besides, because of precipitation of bio-surfactant in the brine solution, the distilled water was utilized in these tests (Hamid Esfandiyari et al. 2020). The viscosity and density of solutions were measured precisely by SVM300 instrument (Anton Paar Company). The outcomes of these measurements were depicted in Table 3.

Table 3. Fluid properties used in experiments.

Fluid	Fluid color	Viscosity (cp)	Density(gr/cm ³)
crude oil	black	84.524	0.8737
Surfactant solution	Brown	2.9466	1.0253

High-speed core analysis centrifuge: According to Fig. 3, a high-speed core analysis centrifuge (BECKMAN-L8M, the maximum speed of 12000 rpm) was used in this research. Within these measurements, the standard rotor was used to measure the drainage curve and the inverted rotor was used to measure imbibition curves (Fig. 4). During the tests, the change of the fluid level in the receiving cells indicates the effluent fluid volume. Before the capillary

pressure measurement, a calibration test was performed first to determine the effluent fluid amount. Rotational speeds gradually increased from 1000 rpm to 10000 rpm approximately (Luo and Li 2017). The capillary pressure can be calculated by Eq. 1:

$$P_c(r) = \frac{1}{2} \Delta\rho \omega^2 (r_1^2 - r_2^2) \quad (1)$$

Where P_c is the capillary pressure at core inlet, dynes/cm², ω is the angular velocity ($=2\pi N/60$), where N is revolutions per minute, r_2 and r_1 are outer and inner radii of centrifuge and $\Delta\rho$ is the different density of water (ρ_w) and oil (ρ_o) (Chattopadhyay et al. 2002).

Fig. 3. High-speed centrifuge.

Fig. 4. Schematic of capillary pressure experiments in centrifuge tests (Luo and Li 2017).

Initially the saturated sample with a fluid and immerses in a second fluid. During the rotation, the inner fluid is forced out of the core plug (Fig. 5). Finally, in various speeds of the centrifuge,

the average saturation of a specimen and produced fluid can be collected and measured (Hopkins et al. 2017).

Fig 5. Schematic of the centrifuge method [29].

By centrifuge apparatus and Eq. 1, average saturation ($\bar{S}$) and capillary pressure $P_c(r)$ at the inner rotation radius, r_1 can be measured, while for earning the diagram of capillary pressure (P_c), we have to calculate S_w inlet based on the Forbes method and its modification (Andy Chen and Ruth 1993).

Imbibition cell: Figure 6 schematically shows the experimental apparatus in the cylindrical system. In this Imbibition Flask, the core was placed into the lower part and at the upper part; the quantity of oil leaving is measured. After placing the core at the bottom of the cell, to ensure that the fluid is kept inside the cell, the two parts of the cell were coated with silicone grease, and the two parts were rotated several times to eliminate airways and complete sealing. Moreover, rubber bands were utilized to hold the pieces of this cell together (Johnson et al. 2007). All experiments were performed at reservoir temperature (about 60 °C) because of condition of reservoirs in Iran and instruments restrictions. In addition, the aim of this experimental work is elucidate of reservoir mineralogical composition and there is no need to higher temperatures. Moreover, there are several restrictions during these tests such as breaking rocks at high centrifuge speeds, the limitation of temperature condition, and test are so time consuming.

Fig 6. The imbibition cell used in experiments.

2.2. Methods

2.2.1. Sample preparation

As was mentioned, four core plugs have opted for these tests. Firstly, the thin section was cut from each sample to find out and analyze the lithology and mineralogy of them, by employing a microscope and XRD apparatus (Esfahani and Haghighi 2004). Then, the core plugs were cleaned by Soxhlet extractor and dried by a furnace for 24 hours. For this achievement, the toluene was utilized as a solvent. Dried core plugs were vacuumed by Hassler-type coreflooding instrument for 4 hours and then saturated with distilled water (Amirpour et al. 2015). Besides, by using the coreflooding instrument, the porosity, permeability and irreducible water saturation (S_{wi}) were recorded. After immersing these core plugs in the crude oil, the ageing samples were gained by placing them in the oven for at least 100 h (at 60 °C).

2.2.2. USBM Method

This section aims to estimate the relationship between wettability and capillary pressure curves. One of the quantitative methods used to achieve this goal is the USBM test by centrifuge [18]. In the USBM method, the forces related to the work required for displacement of fluids by each other are measured. Moreover, it has been proved that these amounts of the forces are obtained by calculating the areas under the capillary curves (M. M. Sharma and Wunderlich 1987). The USBM wettability index can be calculated with Equation 2:

$$\text{USBM Wettability Index} = I_w = \log\left(\frac{A_1}{A_2}\right) \quad (2)$$

Where A_1 and A_2 are the areas under the oil and brine drive curves, respectively (Fig. 7). The core is water-wet when I_w is greater than zero, the cores are oil-wet when I_w is less than zero, and the core is neutrally wet when I_w is near zero. The larger value of I_w demonstrates the greater level of wetting predominance. In principle, I_w can vary from $-\infty$ to $+\infty$, but in practice, the range of values is about -1 to +1 (Denekas et al. 1959).

Fig. 7. Wettability measurement by USBM method (Morrow 1976).

Due to obtaining this curve, after the saturation of the core plug, the core is located in a centrifuge core holder that it is filled by oil. This core holder is rotated at a certain speed to gain the S_{wi} (primary drainage) (Figure 7). After that, this procedure is done by inverted core

holder where the brine is permitted to imbibe into the core spontaneously. Afterwards, the plug is centrifuged at incremental speeds (forced imbibition). In the next step, secondary drainage is gained by placing the core plug into the core holder that it is filled with oil. Finally, the areas under the two curves are determined.

2.2.3. Imbibition Method

By using this test, the capability of the wetting phase for displaces the non-wetting phase under static conditions is measured. In an imbibition test, an aged core plug at S_{wi} was saturated by crude oil with core flood apparatus, is first submerged in the cell contains brine or surfactant solution, and the quantity of oil recovered is measured during brine imbibition. This oil collected in the neck of the glass cell and then, it is reported as the recovered oil (G. Sharma and Mohanty 2013). If the large amounts of brine are quickly imbibed, the sample rock is strongly water-wet, while the lower rates and little volumes depict a more slightly water-wet core. If there is on water imbibition into the core, it implies that it is either oil-wet or neutrally wet (Anderson 1986). Finally, Imbibition curve can be achieved by plotting oil production versus time. Therefore SI test; it is supposed one of the most reliable measurements of wettability alteration.

3. Results and discussion

3.1. Capillary Pressure Results

The samples included 4 plugs (C1, C2, D1, and D2). Each test was implemented 2 times for achieving precise data and the mean of these two series measurements were used as results. The quantitative experiment (USBM method) is fulfilled by the centrifuge apparatus. All steps in these USBM tests were performed according to Fig.7. By using an ultra-centrifuge and this procedure, all capillary pressures can be achieved. According to Fig. 8, all S_w is measured at reservoir temperature (60 °C) and different centrifuge speeds (from 100 rpm to 10000 rpm) for C1 plug. As can be seen, one experiment was done by brine and another one performed by

surfactant solution (8% wt). By putting a saturated core plug with brine in the core holder is filled with crude oil, in speed 10000 rpm, the S_{wi} is obtained ($S_{wi} = 16\%$). in the next pace, the core placed in the core holder full of crude oil for approximately 24 hours for doing spontaneous imbibition. After this time, the S_w reach 22% and then by force imbibition the S_{or} is gained 27% (curve II). After the spontaneous drainage (24 hours), the oil saturation becomes 35% and finally, the secondary drainage is obtained. The core plug should be spun at each rpm for about 1 hour to ensure equilibrium

In the next experiment, all these steps were done by C1 plug and surfactant solution by centrifuge. Zizyphus Spina Christi at 8% wt utilized as wetting fluid. Firstly, C1 plug saturated with a surfactant solution, placed in core holder full of crude oil and in 10000 rpm speed $S_{wi}=21\%$ is achieved. The spontaneous imbibition was performed after 24 hours where the core plug is determined in Zizyphus Spina Christi, ($S_w= 26\%$). The $S_{or}=19\%$ at the end of force imbibition was recorded and the amount of oil saturation reached to 30% within spontaneous drainage. Finally, the secondary drainage curve is gained.

Fig. 8. Drainage and imbibition capillary pressure curves for core plug C₁.

According to the above procedure and centrifuge instrument, capillary pressure curves of core plugs C₂, D₁ and D₂ are achieved (Fig. 9). As can be depicted for core plug C₂, S_{wi} and S_{or} by water are 14 % and 32 %. These amounts when surfactant used as aqueous are 20 % and 26 % respectively. Besides, this information for core plug D₁ and D₂ are shown in Fig 9.

Fig. 9. Capillary pressure curves for USBM method of other samples.

All of the calculated indexes for core plugs using the centrifuge are illustrated in Table 4. In each test, as can be seen, there are 13 recorded spots from speed 100-10000 rpm in the centrifuge method. Based on Table 4, the USBM Index for all calcite and dolomite plugs were tested by using water indicate that they are oil-wet or slightly oil-wet. However, performing these complicated experiments with centrifuge apparatus shows this nonionic surfactant (cedar) has a great impact on changing I_{USBM} and finally improving the wettability, capillary pressure and enhance oil recovery. For sample C_1 the wettability changes from oil-wet to weakly water-wet after utilizing surfactant, where I_{USBM} alters from -0.228 to 0.097 and the amount of reduction of S_{or} is 8% (from 27% to 19%). The wettability alteration in core sample C_2 indicates that it becomes neutral-wet and I_{USBM} changes from -0.179 to 0.025 and S_{or} decrease 6% after force imbibition by surfactant. It seems that this nonionic surfactant has more impact on dolomite samples. The results demonstrate that the wettability shift from oil-wet to water-wet (the variation of wettability indexes are from -0.150 to 0.142 and -0.138 to 0.157 for D_1 and D_2 respectively). Also for D_1 and D_2 S_{or} reduce 14% and 12% respectively.

Finally, these measurements prove that the mineralogical composition of rock plays a significant role in wettability alteration. Zizyphus Spina Christi is practical and beneficial surfactant for decreasing wettability and S_{or} in carbonate reservoir, particularly in dolomite rock type. Besides, this improvement for mineral samples (C_1 and D_1) is more than reservoir samples (C_2 and D_2). The main reasons of difference in figures are differences in mineralogical composition, pore size distribution, capillary force and wetting behavior.

Table 4. Experimental centrifuge measurements for core plugs

Core Plug	Aqueous Phase	S_{wi}	S_{or}	I_{USBM}
C1	water	16	27	-0.228
	Surfactant	21	19	0.097
C2	water	14	32	-0.179
	Surfactant	20	26	0.025
D1	water	15	30	-0.150
	Surfactant	23	16	0.142
D2	water	12	36	-0.138
	Surfactant	19	24	0.202

3.2. Imbibition test results

In this section, the results of the imbibition tests are shown. The two carbonate minerals, calcite and dolomite have been utilized for these experiments. The CMC of Zizyphus Spina Christi (8%) that used in the centrifuge method was then utilized for imbibition tests on core plugs. The spontaneous imbibition (SI) test firstly was immersed in water and then placed surfactant solution as the imbibing phase. Because of Imbibition tests are so time-consuming and the results are obtained from them approximately precise and unique, these experiments were performed once.

In this section, two various calcite samples have been tested and the results are described separately in each case. In Fig. 10 the result of oil recovery during imbibition tests for core

plugs C_1 and C_2 are depicted. As can be seen, the recovery rate of sample C_1 by water has reached 26.7% after 10 days while at the end of 101 days the oil produced has become 30%. It means that after approximately 90 days the recovery increased by only 3.3 %. In the next experiment, surprisingly, when data was recorded in presence of *Zizyphus Spina Christi* solution, the oil recovery has reached 42% after 138 days. 36 % of this value is related to the first 40 days. In other words, just 6 % of oil recovery occurred within about 80 days.

The difference in oil recovery for core plug C_2 is 9 %, where the percentage of oil produced in presence of water and surfactant solution is 28 % and 19% respectively. According to Fig 10, the recovery rate of C_2 by water has reached to 18 % after 40 days from zero and it has remained constant until the end. On the other hand, the rate of oil production of C_2 by utilizing surfactant rose gradually until the end of the spontaneous imbibition test. Finally, the effect of *Zizyphus Spina Christi* on sample C_1 is greater than sample C_2 .

Fig. 10. Imbibition profiles for calcite samples.

In Fig 11, the results of the series of dolomite (Samples D_1 and D_2) are illustrated. Firstly, based on figures of oil recovery of core sample D_1 , after using surfactant within spontaneous

imbibition test, the oil recovery increased noticeably from 18.4 % to 31 %. These amounts of recovery are gained in 37 and 43 days respectively. The oil production of D₁ by water reached to 18.2 % after 18 days while the oil produced of this plug by surfactant obtained gradually during 43 days. The experiments for core sample D₂ continue until 42 days. These measurements show that the oil recovery in the first condition (by water) reached smoothly to 13 % after this period, while by utilizing the surfactant, this oil produced increased a significant amount (10 %). Therefore, the surfactant had a relatively greater effect on D₁ than D₂ sample.

Fig. 11. Imbibition profiles for dolomite samples.

3.3 Summary of the result of Spontaneous Imbibition test and USBM method

Wettability of the rock, mainly the composition of the rock minerals has a great impact on the capillary pressure and phase behavior. Due to the different composition of rock minerals, the behavior of core plugs changes in presence of water and surfactant. It means that Zizyphus Spina Christi has a good effect on both of sorts (calcite and dolomite), whereas the oil recovery for dolomite cores are more than calcite cores. Moreover, the oil recovery for reservoir samples

is less than mineral samples. By comparison of the results, it can be concluded that the wettability changes is at the same in both of these methods (Table 5). In other words, for example, for C₁ plug the I_{USBM} changes from oil-wet to neutral-wet or slightly-wet after usage of surfactant and the oil recovery by spontaneous imbibition test approximately demonstrate the same outcome. Besides, for D₁, because the alteration of I_{USBM} is more than C₁, then the oil recovery of D₁ is also more than C₁.

Table 5. Comparison of imbibition and USBM measurements for core plugs.

Core plug	Method	ΔS_{or}
C1	USBM	8%
	Imbibition	12%
C2	USBM	6%
	Imbibition	9%
D1	USBM	14%
	Imbibition	12.6%
D2	USBM	12%
	Imbibition	10%

Based on the achieved results and plotted diagrams, it can be found that, this research gives an excellent view on wettability and its relation with capillary in porous media in compare to previous researches in this area. Some experimental works have been implemented in this matter to conclude that what is the best relation between wettability alteration, capillary forces, the composition of reservoir rock and the chemical additives to reservoir. Esfandiyari et al. [8], Amirpour et al. [32]. Saxena et al. [aaaa], Ahmadi and Shadizadeh [15], Esfahani, Haghghi [21] and some scientists focoused on investigation of wettability behaviour or capillary forces in carbonate rocks in precence different surfactants especially natural ones. In addition, by our

research, the act of various minerals constitutive of carbonate reservoir were more accurately elucidated rather than others because of utilizing the two incomparable and decent methods by unique natural environmentally friendly surfactant(Saxena et al. 2019).

4. Conclusions and Remarks

Wettability alteration is one of the most outstanding matters in oil recovery and critical traits of rock–fluid systems. The understanding behavior of the liquid in contact with the solid surfaces and capillary force are key factors for EOR processes. The intent of this study is elucidating the effects of different types of carbonate minerals on wettability changes and capillary force using the imbibition and centrifuge tests and natural surfactant (cedar). Based on the experimental results, the following conclusions are depicted:

- The presence of this nonionic natural surfactant had a distinct influence on the wettability and capillary force on all of calcite and dolomite samples, particularly, on dolomite core plugs.
- For core plug C_1 the wettability changes from oil-wet to slightly water-wet (I_{USBM} alters from -0.228 to 0.097). The I_{USBM} variation for core sample C_2 is from -0.179 to 0.025. It means that the wettability changes from approximately oil-wet to neutral-wet.
- In dolomite series, these changes are more than calcite samples. For D_1 and D_2 plugs, the I_{USBM} variation is from -.015 to 0.142 and -.138 to 0.202 respectively. In other words, the wettability changes from oil-wet to water-wet for both of them.
- According to the results of the centrifuge, the most reduction for S_{or} belong to D_1 (14%) and then D_2 (12%). The decrease of S_{or} for C_1 and C_2 are 8% and 6% respectively.
- This surfactant is so useful for enhancing oil recovery in different kinds of carbonate rocks. By spontaneous imbibition test, the oil recovery for samples C_1 and C_2 are 12% and 9% respectively. The most effective of cedar surfactant is related to D_1 core plug where this oil recovery after utilizing surfactant is 12.6%. The impact of surfactant after imbibition test for D_2 is also suitable (10%).

- By comparison of all the outcomes of these experiments, it can be found that the composition of rock has a huge effect on wettability and capillary pressure and finally it is an inseparable parameter of EOR processes.
- Zizyphus Spina Christi is an excellent and practical natural surfactant during EOR processes. As mentioned, it has the most impact on carbonate rocks, particularly in dolomite reservoirs. Besides, it can be extracted cheap and easy from many trees in the south of Iran.
- The centrifuge and imbibition tests are so precise and practical methods to elucidate the role of capillary and gravity forces within wettability alteration and oil recovery. These procedures are so difficult and time-consuming but they give a good view of the interaction between rock and fluid phase in the porous environment.
- Each of USBM and Imbibition methods approximately have the same outcome in the field of the effect of Zizyphus Spina Christi on wettability and capillary pressure and therefore it can be concluded that these results validate each other.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Abbreviations

S_{or} ; Residual oil saturation

EOR; Enhance oil recovery

COBR; Crude oil/brine/rock system

SDBS, Sodium Dodecyl Benzene Sulfonate

S_{wi} ; Initial water saturation

USBM method; (U.S. Bureau of Mines) method

OOIP; Original oil-in-place

IFT; Interfacial tension

XRD test; X-Ray Diffraction test

P_c ; Capillary pressure

ω ; Angular velocity

IW; USBM Wettability Index

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