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Feasibility Investigation of A Novel Natural Surfactant Extracted from Eucalyptus Leaves for Enhanced Oil Recovery of Carbonates: Experimental Study

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Abstract

After primary and secondary oil production from carbonate reservoirs, approximately 60% oil-in-place remains in the pore space of reservoir rocks. Chemical flooding is one of the promising ways to produce the remained oil. Nowadays, surfactant flooding is a low-cost and a common method generally used to improve oil recovery due to the oil-water Interfacial Tension (IFT) reduction and alteration of the rock wettability to water-wet state, leading to decrease the capillary number. In this study, a novel leaf-derived non-ionic natural surfactant, named Eucalyptus is introduced and the capability of this natural surfactant for IFT reduction and wettability alteration is analyzed. Accordingly, the natural surfactant was derived from Eucalyptus leaves and the effect of natural surfactant solution on the Oil-water IFT and carbonate rock wettability alteration was investigated. The results demonstrated that the addressed natural surfactant significantly reduced IFT value from 35.2 mN/m to 10.5 mN/m (at CMC of 3.5 wt. %) and the contact angle value from 140.6° to 60.2°. As a result, Compared to conventional chemical surfactants, the Eucalyptus natural surfactant had an excellent surface chemical activity and confirmed its performance by laboratory experiments which could be used for EOR applications.

Keywords: Eucalyptus leaves, natural surfactant, Enhanced Oil Recovery, wettability alteration, IFT reduction

Highlights

- A new natural surfactant was extracted from Eucalyptus leaves plant for EOR applications.
- Eucalyptus natural surfactant demonstrates a significatant potential in wettability alteration and IFT reduction.
- Wettability alteration and IFT reduction were mechanistically investigated.
- Comared to other conventional surfactants, Eucalyptus natural surfactant is more effective and inexpestivness.

Introduction

Carbonate rocks play a significant role in oil production due to holding a large amount of the world's proven oil and their reserves. Actually, the majority of middle eastern oil fields and reservoirs, have carbonates rocks, especially associated with the natural fractures. These carbonate reservoirs have been producing for many years, thus, they have depleted and lost the natural force and energy to produce by their own natural drive mechanism. The rapid decline behavior of the reservoirs, on the other hand, growing world and the industries, oil and energy demands and the rising oil price per barrel are the main and most satisfying factors to extract and produce more and more oil and invest in the secondary and tertiary recovery technics. After the first recovery stage, secondary recovery by external fluid injection like water and/or gas in order to reach the pressure maintenance and volumetric sweep efficiency goalsis started [1]. The ultimate oil recovery that first and secondary oil recovery mechanisms and technics can produce from the reservoirs don't exceed approximately more than 40-50% [2,3]. In order to assess the reason of why these two recovery stages are unable to produce the 50-60% of the reservoir oil in place, it should note that the most of carbonate rocks are mixed to oil wet and polar and heavy compounds are adsorbed to the rock surface and leads to oil trapping and altering the wettability state to the more oil wet [4-8]. In fact, as the production started and goes on, the pressure declines and as a matter of fact, the required force to displace the oil is lost. In other words, by production, oil trapping in small pores causes high capillary forces, wettability alteration to more oil-wet and weakness of viscous force are caused oil mobility reduction through the porous media [9]. Because of these facts and shortcomings, enormous researches and studies have been conducted by many researchers in order to produce the 50-60% underground trapped oil and they developed Enhanced Oil Recovery technics such as thermal oil recovery, microbial injection, gas injection and/or chemical flooding [2,1,10,11].

There are several chemical EOR processes, including alkaline(A), Surfactant (S), Polymer, and any combination of them [1]. One of the fundamental and effective chemical EOR processesis surfactant flooding which increases the ultimate oil recovery by IFT (interfacial tension) reduction, increase in capillary number and also wettability alteration by adsorption [1,12]. There are several factors like IFT reduction ability, ultimate oil recovery, surfactant cost, loss of surfactant in there servoir due to adsorption, environmental concernsand etc.,That affect and control the select an appropriate surfactant for flooding to meet the best results [13-16,19].

Surfactants assorted based on their headgroup ionic nature named: non-ionic, ionic, cationic and zwitterionic surfactants [1,17]. Natural surfactant is placed in the group of ionic surfactants which are marked by their environmental friendly compounds, nonvolatile, an alternative for traditional solvent, they can separate organic compounds on the rock surface which makes it a good candidate to separate the hydrocarbons from rock surface and promote them to the bulk phase [15,18]. The natural surfactant used in this study is extracted from Eucalyptus leaves that contains a substantial amount of saponin which is believed its responsible for IFT reduction, wettability alteration and increase in ultimate oil recovery. Eucalyptus is a single-stemmed tree with a crown that forms the minor portion of the tree, and the size of a mature Eucalyptus tree vary from a low shrub to a very large tree that is named the tallest flowering tree. The Eucalyptus is mainly evergreen tree with oil glands covered leaves and the flowers of the tree have numerous fluffy stamens which may be white, cream, yellow, pink, or red. The most By assessing the factors like cost, IFT reduction, environmental concerns, rock surface charge, fluids interface and surfactant structure put it in a good condition to be an effective alternative of chemical EOR [9,13-16,19].

There are several types of research and works by some researchers around the application of natural surfactants in petroleum engineering [4,15,20,21]. In 2009, Ragnao and Lionettiextracted the Quillaia Saponaria Molina natural surfactant from Chilean Solar Bark tree for the first time [22]. Pordel et al. 2012 a,b, for The first time used of natural surfactant as saponins in petroleum engineering [4,23]. In 2011 Pordel Shahr et al, illustrated and reported wettability alteration toward more water wet and IFT reduction from 48 to dyne/cm by introducing saponins extracted from Zizyphus Spina- Christi leaves to the oil-water system and interface. Deymeh et al. 2012, used a new natural surfactant, naming Seidlitzia Rosmarinus, in order to investigate the feasibility of this natural surfactant as an alternative to synthetic surfactants in chemical Enhanced Oil Recovery, and by the pendant drop method measured the IFT between oil phase and natural surfactant solution reported the IFT values reduction from 32 to 9 dyne/cm as the surfactant concentrations increased. Ghahfarokhi et al. 2015, investigated the effect of three leave extracted natural surfactants, naming Olive, Spistan,and Prosopis, on Enhanced Oil Recovery technics and extracting more oil from the pores in surfactant flooding. IFT reduction. Using pendant drop method showed the IFT values between kerosene and distilled water containing different concentrations of Olive, Spistan and Prosopis natural surfactant and the values reduced from 36.5 to 14 mNlm, 36.5 to 25.15 mN/m and 36.5 to 15.11 mN/m respectively.

In this study according to the abstract, a new leaf extracted non-ionic natural surfactant was introduced and investigated. In fact, the mechanistic behavior assessments were conducted in order to evaluate the effects of this novel natural surfactant on the oil recovery and EOR purposes. According to our information, there are no reports on the effects of this natural surfactant on the wettability alteration and the IFT and ultimate oil recovery. The experiments were conducted to evaluate the ability in IFT reduction and wettability alteration in the oil-aqueous phase containing different surfactant concentrations. Assessment of the experimental result with IFT values, wettability alteration, and economical aspects considerations, the optimized concentration was derived in order to the best performance.

Materials and methods

Materials

Aqoues phase

10 wt.% NaCl solution were prepared for IFT, contact angle and core flooding experiments.

Oil phase:

the oil was collected from mansoori oil fileld located in khouzestan, Iran.The composition of the used oil is given in Table.1.

Table 1: the composition of the oil used for experiments

Component	Mole Percent
H_2S	0.62
N_2	1.15
CO_2	3.15
C_1	34.62
C_2	8.26
C_3	3.36
iC_4	1.26
nC_4	3.35
iC_5	1.02
C_6	3.53
C_7	3.52
C_8	1.01
C_9	1.5
C_{10}	1.28
C_{11}	1.98
C_{12}^{+}	30.39
Total	100.00

Porous medium used in this investigation was collected from one of the outcrops of Iranian oil reservoirs with predominant lithology of dolomite and limestone. Porosity and permeability of shaped-samples were examined by helium and brine tests, respectively. Table.2 represents the peroperties and dimensions of as-prepared core samples.

Table 2: properties and dimensions of plugs

Core	Length (cm)	Diameter (mm)	Porosity (%)	Permeability (mD)	S_{wir}	Aqueous solution
C-1	8.25	39	17.2	23.6	8.2	Distilled water
C-2	8.3	38.70	18.3	24.9	8.6	Surfactant solution

Flat pellet of the same rock was utilizedfor solid phase for contact angle experiments. Noting that the sampleswere washed with absolute ethanol. next, they were dried in the electric oven at 100°C for 10h.

Surfactant

The leaves of Eucalyptus plant was collected from southern of Iran. After washing process, the soponin containing powder of Eucalyptus was extracted from aqoues mixture of Eucalyptus plant thorough sprat dring technique. In the end, the aqoues solution of Eucalyptus surfactant was prepared by addition certain content of exracted-powder in distilled water. Peroperties of the of the Eucalyptus surfactant are listed in Table.3.

Table.3 peroperties of leaf-drived eucalyptus surfactant powder

Product	Extracted powder of Eucalyptus
Preparation method	Spray drier
Used part	Leaves
Description	Fine powder
Color	Light green
Odor	specific odor
PH value (2 wt.% solution)	5.9
Density (kg/L) (2 wt.% solution)	1.125

Experimental procedure

The device used for measurement of interfacial tension between oil and water and contact angle experiments were measured by pendant drop apparatus (Vinci IFT-700) which consists of four main parts, namely an experimental chamber, a video capturing system, an illuminating system and a data acquisition system (Fig.1).

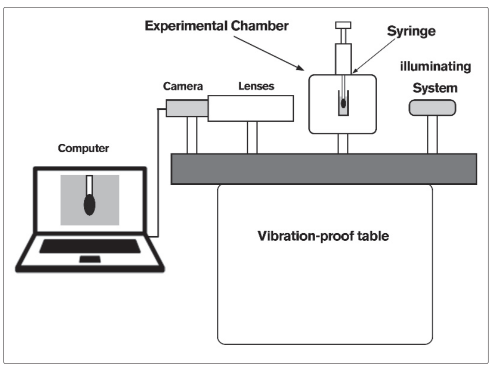

Figure 1: pendant drop tension meter

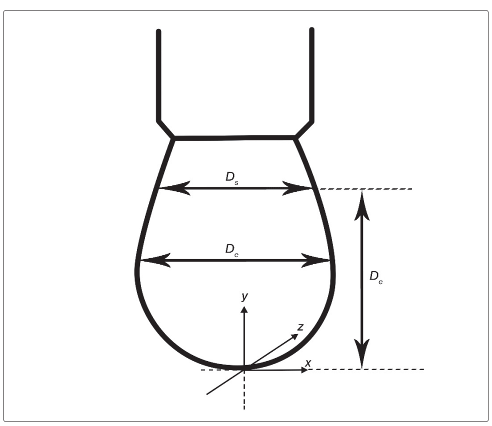

Figure 2: Drop scheme

For this aim, the brine was added into a cell; the oil droplet was then dispensed from tip of the needle, and the characteristic shape of the oil drop was analyzed to determine IFT. This method is based on the drop shape analysis. For this purpose, a ratio of maximum diameter to the horizontal diameter is defined. In fact, first, the maximum diameter, d_e, is determined by the device and then it is used to measure horizontal diameter, d_s, as shown in Fig.2. The aforementioned ratio, S, is the ratio of these diameters which is crucial to determine interfacial tension by the following relations:

$$\gamma = \frac{\Delta\rho g b^2}{\beta} \quad (2)$$

$$S = \frac{d_s}{d_e} \quad (3)$$

$$\beta = 0.12836 - 0.7577S + 1.7713s^2 - 0.5426s^3 \quad (4)$$

$$b = \frac{d_e}{2(0.9987 + 0.1971\beta - 0.0734\beta^2 + 0.34708\beta^3} \quad (5)$$

Where Δ is the difference between densities of drop material and the material by which the drop is surrounded. β, a dimensionless number, and b are calculated from equations (4) and (5) respectively.

As is clear from the formula, a measurement of density is required before the IFT determination. Density Meter Apparatus (DMA) is implemented to measure The densities of solutions with different surfactant concentrations.

Contact angel experiments were also performed via the same instrument.Ther oil droplet was released by the needle and contact angle was determined on the rock entire surface. All of the experiments were carried out at near reservoir conditions (i.e. 70°C and 2000 psi).

Result and discussion

IFT measurement

Fig.3 represents IFT values versus Eucalyptus surfactant concentration. As the consentration of surfactant increased from 0 to 3.5% the IFT value reduced from 35.2 mN/m to 10.5 mN/m. This phenomenon could be explained by the fact that hydrophilic and hydrophobic groups of surfactant result in formation of a stable interface moisles between water and oil which avoids contactness of the two phases and leads to reduce the IFT value between oil and water.

However, at the concentrations higher than 3.5 % the IFT values didn't change noticeably. It is due to thefact that at concentrations above CMC the system would not be stable anymore and the surfactant act as emulsifier. Therefore, from the obtained results, it could be said that the best point for selection of surfactant concentration is the 3.5% wt.

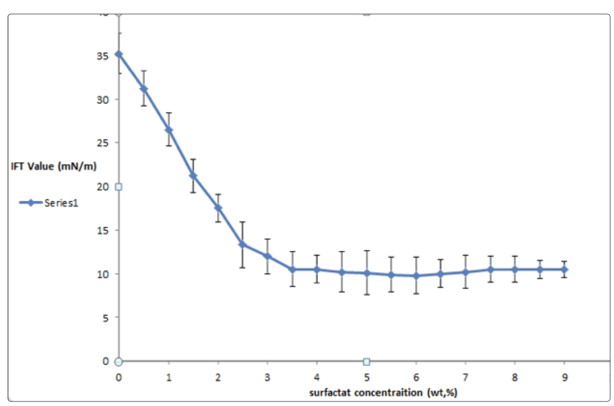

Figure 3: variation of IFT via surfactant concentration

Contact angle measurments

Fig.4 demonstrates the impacts of Eucalyptus surfactant on contact angle. As could be seen, the contact angle was decreased from 140.6° to 60.2° as the concentration increased from 0 to 9. At concentrations above CMC the reduction in contact angle was so remarkable. In contrast to cationic or anionic surfactants, non-ionic surfactants do not have strong ion-ion attraction with adsorbed organic chemichals and the mechanism is slightly different. The proposed mechanism could be explained in two ways which could occur simultaneously: (1) the weak attraction between positive- charged head of surfactant with negative adsorbed chemicals including asphaltene which leads to desorption of adsorbed chemicals. (2) The hydrophilic part of surfactant forced the surfactant to move toward the the surface of the rock which is the nearest place to the brine. The approached molecules of surfactant take the place of chemical groups and the surface becomes water-wet.

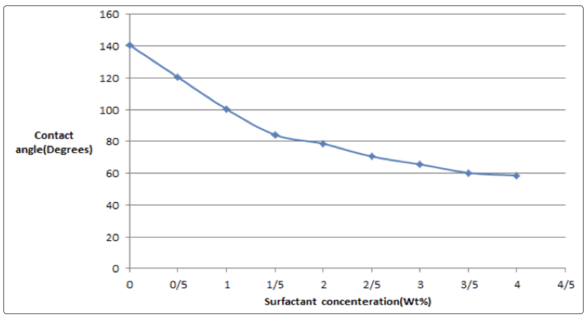

Figure 4: variation of Contanct angle via surfactant concentraition

Comparison of conventional surfactants with Eucalyptus natural surfactant

Fig.5 shows the amount of reduction in IFT of oil-water systems with increasing chemical surfactant concentrations. As could be seen, IFT reduction for Brii 72 and Step+amphoare greatest among other chemical surfactants. Among the natural surfactants, addition of glycyrrhiza glarba and sedila rosmarinos result in a considerable drop in IFT from (36.5mN/m) to (7.9mN/m) and (32mN/m) to (8.9mN/m), respectively. The reductions of IFT for natural surfactants are so close to that of the chemicals. Also, it should be mentioned that the natural surfactants have the advantages of being more environmental friendly, lower cost and availability. So using natural surfactants can lower the environmental damage and also reduce the cost of the recovery processes, and both of these are important factors for the oil industry must be consider. As a result, natural surfactants like eucalyptus and zizyphus spina Christi are new agents for enhancing oil recovery through enviormental friendly process.

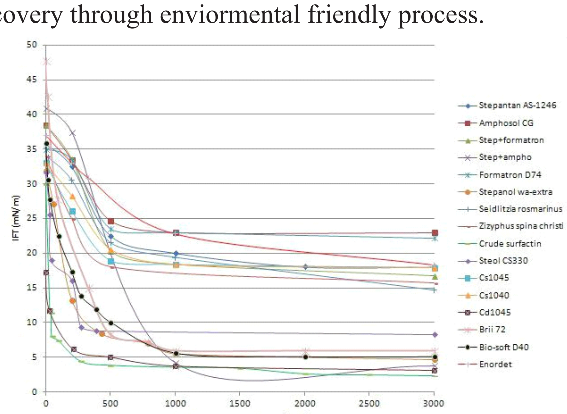

Figure 5: Comparison of IFT variation vs. surfactant concentration of chemical surfactants that used for EOR recently

Conclusion

In this investigation, a new natural surfactant named Eucalyptus was introduced. peroperties of oil used in expriments was determined. Experimental results showed that new surfactant considerably decreased oil-water IFT from from 35.2 mN/mto 10.5 mN/m. Also, Eucalyptus surfactant alternated the wettability of carbonate rock from oil-wet to water-wet and the Contact angle reduced from 140.6° to 60.2°. The CMC value of about 3.5 wt.%, which was determined from the plot of IFT versus content of Ecualyptus surfactant, can be used as the prevailing concentration in future EOR industrial application. Finally, efficiency of Eucalyptus surfactant in IFT reduction was compared with other surfactants, the results validates the fair surfactant properties of Ecualyptus as a surfactant in chemical flooding.

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