Effect of Natural Leaf-derived Surfactants on Wettability Alteration and Interfacial Tension Reduction in Water-oil System: EOR Application

Mehdi RAHMATI, Milad MASHAYEKHI, Reza SONGOLZADEH, and Amin DARYASAFAR *

Petroleum Dept., Petroleum University of Technology, P.O.Box 6198144471, Ahwaz, IRAN

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In this study, two types of plants based natural cationic surfactants, named Mulberry and Henna are introduced and the application of these natural surfactants in wettability alteration of reservoir rock and reducing the interfacial tension of water-oil system is investigated. For this purpose, two natural-based surfactants were extracted from the leaves of the trees of addressed plants and then the interfacial tension (IFT) values between oil and natural surfactant solution and also the contact angle values between natural surfactant solution and rock sample were measured. The results demonstrated that Mulberry extract was able to lower the interfacial tension between oil and distilled water from 43.9 to 4.01 mN/m, while Henna extract could reduce the IFT from 43.9 to 3.05 mN/m. These natural surfactants were also able to reduce the contact angle of rock/fluid system which shows the wettability is altering to water wet system and so it may increase recovery factor by reducing residual oil saturation and Henna extract could reduce the contact angle more than that of Mulberry leaf extract. According to these results in addition to the low price of generating natural surfactants, the feasibility of using these kinds of surfactants in future oil recovery processes is of major concern.

Keywords
Surfactant flooding, Natural cationic surfactant, Interfacial tension reduction, Wettability alteration, Mulberry leaf extract, Henna leaf extract

1. Introduction

Enhance oil recovery (EOR) techniques are used for decreasing oil trapping within the pores of reservoir rock. In subject of EOR, one of the proven methods is surfactant flooding which its objective is to decrease oil trapping by reducing the interfacial tension (IFT) of water and oil system and altering wettability of crude oil/brine/rock system and so can improve the water flooding sweep efficiency1)–3). Surfactant solutions have two important effects on the rock/fluid system. The first effect is reduction of IFT between injected aqueous phase and the trapped oil and therefore mobilization of trapped oil. The second effect is the alteration of the wettability of the rock which shows the wettability is altering to water wet system and would increase the brine imbibition rates.

Surfactant flooding can be affected by different parameters for example surfactant cost, IFT reduction, wettability alteration, oil recovery and etc. to be an economical process5). Nowadays because of environmental fates, natural based surfactants can be used instead of industrial surfactants and many researchers have studied on these kinds of surfactants in recent years. The first natural surfactant was Quillaja Saponaria Molina that was extracted from a Chilean Soar bark tree5). Shahri et al.6) used Amott cell to extract a natural surfactant from Zizyphus Spina-Christi and introduced the application of this surfactant in oil recovery. After that, Ahmadi and Shadizadeh7),8) investigated the adsorption behavior of this surfactant onto carbonate rocks at different conditions; this adsorption will cause further changes in rock wettability. Ahmadi et al.9) formulated a micro-fluid using micro-sized particles of Mulberry leaf and studied the effect of Mulberry leaf-derived surfactant on the IFT between oil and water at different surfactant concentration. They demonstrated that a micro-fluid containing 1 wt% of Mulberry leaf particles could reduce the IFT between distilled water and kerosene by 60 %.

In this paper, two new natural cationic surfactants produced from the leaves of Mulberry and Henna, are introduced. Massive efforts have been put forth to study the effect of these surfactants on wettability alteration of reservoir rock and also IFT reduction of water/oil system. For this purpose, surfactants were extracted from the leaves of the trees of addressed plants and pendant drop method was then employed to measure the
IFT between the surfactant solution and oil. Finally, contact angle goniometer was used to measure the contact angle between surfactant solution and rock sample.

2. Materials

2.1. Aqueous Phase
In experiments, deionized water is used since natural surfactants will precipitate in brine.

2.2. Surfactant

2.2.1. Mulberry Leaf-derived Surfactant
The Mulberry tree has abundant branches and is a deciduous tree and rarely exceeds 6-9 m in height. It has leaves (Fig. 1) which are alternately arranged, simple, often lobed and have a rough upper surface, while they are pubescent underneath, about 7-12.5 cm long.

The Mulberry tree has originally been come from Persia, but is now been widely available in several regions for example southwest Asia and eastern North America. Table 1 shows the chemical composition of the dry material of Mulberry, in the form of elemental and gross composition.

| Gross composition | [%] | Elemental analysis | [%] |
|-------------------|-----|--------------------|-----|
| Dry matter        | 25  | Calcium            | 3.6 |
| Organic matter    | 90  | Potassium          | 1.75|
| Crude protein     | 23  | Sodium             | 0.2 |
| Neutral detergent fiber | 26.2 | Phosphorus       | 0.75|
| Acid detergent fiber | 16  | Magnesium          | 0.72|
| Acid detergent lignin | 7   |                    |     |
| Hemicelluloses    | 10.2|                    |     |
| Ash               | 10  |                    |     |

Surfactant is a substance consists of amphipathic molecules. Amphipathic molecule has both a hydrophilic portion and a lipophilic portion. The combination of these portions in a molecule makes a surfactant to have a specific behavior in a solution. Cationic surfactants are a kind of surfactants which the hydrophilic end contains a positively-charged cation. Typical examples are benzalkonium chlorides or bromides and trimethylalkylammonium chlorides. Both Mulberry and Henna surfactants are cationic surfactants which their portion bears a positive charge; 2,2’-azino-bis-(3-ethylbenzthiazoline-6-sulphonic acid) (ABTS) radical cation for Mulberry extract and RNH₃⁺Cl⁻ for Henna extract. In this study, we investigate the effect of these two different surfactants on IFT reduction and wettability changes.

2.2.2. Henna Leaf-derived Surfactant
Henna is a small tree, standing 6 to 25 ft tall. It is multi-branched, with spine-tipped branchlets. Its leaves (Fig. 2) are glabrous, sub-sessile and long and wider in the middle and have depressed veins on the dorsal surface. The Henna plant is native to northern Australasia, western and southern Asia and northern Africa. The leaves gradually yellow during cool intervals.

Geetex N. Z. Ltd. analyzed the composition of Henna leaf, the results are as follows: moisture and volatile matter 4.53 %, cold water extract 27.53 %, crude fiber 11.75 %, mineral matter 9.81 %, acid insoluble ash 4.23 %, extraneous sand 2.53 %, pigments 1.26 %, paraphenylenediamine (PPD) nil, hydrogen peroxide nil and ammonia nil.

Surfaceactant is a substance consists of amphipathic molecules. Amphipathic molecule has both a hydrophilic portion and a lipophilic portion. The combination of these portions in a molecule makes a surfactant to have a specific behavior in a solution. Cationic surfactants are a kind of surfactants which the hydrophilic end contains a positively-charged cation. Typical examples are benzalkonium chlorides or bromides and trimethylalkylammonium chlorides. Both Mulberry and Henna surfactants are cationic surfactants which their portion bears a positive charge; 2,2’-azino-bis-(3-ethylbenzthiazoline-6-sulphonic acid) (ABTS) radical cation for Mulberry extract and RNH₃⁺Cl⁻ for Henna extract. In this study, we investigate the effect of these two different surfactants on IFT reduction and wettability changes.

2.3. Oil and Rock Sample
In IFT experiment, kerosene was used as the oil phase since in IFT measurements, the oil phase is better to be clean.

In contact angle measurement experiment, heavy oil of Asmari formation in Azadegan oil field with viscosity of 35 cP (1 cP = 1 × 10⁻³ Pa s) and gravity of 28° API (American Petroleum Institute) was used. The sample of sandstone rock was also used in this experiment.

3. Experimental Procedures

3.1. Extract Preparation
The leaves of two types of plants (Mulberry and Henna) were hand-picked from trees, dried at ambient condition. Powder of dried leaves was inserted in Soxhlet extractor (Fig. 3) and after about 12 h, a viscous solution was appeared in the chamber of the Soxhlet extractor. The viscous solution was then put in oven with temperature of 65°C so the little amount of remained water could be vaporized without damaging the extract. We used the obtained extract of each plant to make solutions with known concentration for investi-
gating the effect of different quantities of the derived extract in the surfactant’s ability in lowering IFT and altering wettability of reservoir rock.

3.2. CMC Measurement

Conductivity method was used in this study to measure critical micelle concentration (CMC). For this purpose, conductivity of natural surfactant solutions was determined using a conductivity detector which is from Crison Co. At first the conductivity detector was calibrated using standard solution and the probe was washed up with distilled water for accuracy of solutions conductance. The value of CMC can be figured out from the turning point in the plot of conductivity versus concentration. Surfactant ions or molecules will start to be micelles when surfactant solution concentration increases to a certain value, this cause a change in trend of curve. Figures 4 and 5 are the plots of conductivity versus solution concentration for Mulberry and Henna, respectively.

Mulberry-derived surfactant has a critical micelle concentration of about 2.6 % by weight, while Henna-derived surfactant has CMC of about 2.8 wt%.

3.3. Method Implementation in Measuring IFT

Pendant drop method was used for IFT measurements using the Captive Drop Instrument. Density values of surfactant solution and oil are needed for measuring the IFT between oil and natural surfactant solution by pendant drop method. The densities of different percent weights of aqueous solutions of Mulberry and Henna extracts are illustrated in Tables 2 and 3, respectively. Kerosene was used as the oil phase. The pump of the pendant drop instrument must be adjusted that the low flow rate ensures that releasing the oil drop is the result of density difference. In this study, an accurate method described by Herd et al. [1] was used to calculate the IFT.

The IFT is:

\[
\sigma = \frac{\Delta \rho g R_0^2}{\beta} \quad (1)
\]

Where \(\sigma\) is the IFT, \(\Delta \rho\) is the density difference between two phases and \(g\) is the acceleration due to gravity. \(\beta\) and \(R_0\) are determined as follows:

\[
\beta = 0.12836 - 0.7577S + 1.7713S^2 - 0.5426S^3 \quad (2)
\]
\[
\frac{d}{2R_0} = 0.9987 - 0.1971\beta - 0.0734\beta^2 + 0.34798\beta^3 \quad (3)
\]

S is the drop shape factor and equals to \(d/D\). \(D\) is the maximum diameter of the drop and used in the calculation of the drop’s horizontal parameter, \(d\), (Fig. 6).

3.4. Method Accomplishment in Measuring Contact Angle

Since the factor which had to be measured was contact angle, the first step in this laboratory investigation was to prepare pellets of rock from the sample of sandstone outcrop. Rotary sidewall cores (Fig. 7) was used to obtain cylinders with small diameter from rock sample and then, the cylinder was transformed into small well-smoothed pellets of sandstone. The next step was to wash the rocky pellets. It was done through Soxhlet extractor by a solvent like toluene.

The clean pellets must be aged with oil so we could achieve an oil-wet reservoir rock sample. In this step heavy oil of Asmari formation in Azadegan oil field in

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Fig. 3 Soxhlet Extractor

Fig. 4 Conductivity of Aqueous Solution of Mulberry Extract vs. Surfactant Concentration

Fig. 5 Conductivity of Aqueous Solution of Henna Extract vs. Surfactant Concentration

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south-west of Iran was used. The pellets were fully drowned in oil for three weeks in atmospheric pressure and room temperature. The obtained extract could be used to make solutions with known concentration. In this investigation the concentrations were 2, 4, 6, 8 and 10 % by weight which would be used in final step for calculating the contact angle and its changes on reservoir rock.

At last the contact angle goniometer (Fig. 8) was used to measure contact angle of different solutions on a sample of sandstone rock so the wettability changes could be observed at specific concentration. In contact angle goniometry, the drop is imaged from the side and the drop shape is then analyzed with image analysis software. Images were taken using a planar CCD camera. The CCD camera and the water dispensing system are controlled from a computer. Measured contact angle would change if different samples of pellets used in the experiment since some properties of rocky pellets like heterogeneity and smoothness are different from one pellet to another and these properties may affect the measured contact angle. In this experiment we used 2 pellets at each concentration and the average contact angle was considered so we can consider other parameters affecting wettability and by this procedure the accuracy of results will increase.

| Concentration [wt%] | Density [g/cm³] | Conductivity at room temperature [mS/cm] | IFT [mN/m] |
|--------------------|----------------|------------------------------------------|------------|
| 0                  | 0.9938         | 0.01                                     | 43.9       |
| 0.5                | 0.9957         | 0.58                                     | 33.19      |
| 1                  | 0.9978         | 1.18                                     | 17.8       |
| 1.5                | 0.9992         | 1.79                                     | 13.02      |
| 2                  | 1.0008         | 1.88                                     | 11.43      |
| 2.5                | 1.0021         | 2.44                                     | 9.62       |
| 3                  | 1.0037         | 2.74                                     | 8.73       |
| 5                  | 1.0103         | 3.10                                     | 6.98       |
| 8                  | 1.0197         | 3.23                                     | 5.21       |
| 10                 | 1.0267         | 3.45                                     | 4.01       |

Table 2 Characteristics Related to Different Concentrations Aqueous Solution of Mulberry-derived Surfactant

| Concentration [wt%] | Density [g/cm³] | Conductivity at 24.2 °C [mS/cm] | IFT [mN/m] |
|--------------------|----------------|---------------------------------|------------|
| 0                  | 0.9938         | 0.01                            | 43.9       |
| 0.5                | 0.9965         | 0.63                            | 31.75      |
| 1                  | 0.9986         | 1.24                            | 27.87      |
| 1.5                | 1.0002         | 1.81                            | 10.32      |
| 2                  | 1.0025         | 1.93                            | 8.23       |
| 2.5                | 1.0043         | 2.56                            | 7.46       |
| 3                  | 1.0059         | 2.84                            | 5.89       |
| 5                  | 1.0114         | 3.16                            | 4.58       |
| 8                  | 1.0205         | 3.41                            | 3.79       |
| 10                 | 1.0284         | 3.59                            | 3.05       |

Table 3 Characteristics Related to Different Concentrations Aqueous Solution of Henna-derived Surfactant
4. Results and Discussion

Two types of plants based natural cationic surfactants, named Mulberry and Henna, were used to reduce the IFT of water-oil system and kerosene was used as the oil phase to eliminate the surface active agents present in crude oil.

As the surfactant concentration increases, the IFT between the drop and the surrounding oil phase decreases. This is due to the surfactant absorption at the interface between oil and water. The IFT values between the aqueous solution of addressed natural surfactants and kerosene were calculated using pendant drop method. In Fig. 9, IFT values for the aqueous solution of Mulberry-oil have been plotted versus surfactant concentration. As shown by this graph, 10 wt% of Mulberry extract have decreased the IFT between kerosene and water from 43.9 to 4.01 mN/m.

The plot of IFT values for the aqueous solutions of Henna-oil against surfactant concentration is shown in Fig. 10. As indicated by this figure, 10 wt% of Henna extract could reduce the IFT of water-kerosene system from 43.9 to 3.05 mN/m.

As shown in the above figures, little change is observed in the value of IFT beyond the critical micelle concentration point of each natural surfactant since surfactant added in excess of CMC cannot increase the concentration at the water-oil interface and hence participates in micelle formation.

Enhanced oil recovery processes would have a better recovery at concentrations above CMC since surfactants can reduce IFT values significantly but it must be noticed that higher concentrations suffer from problems regarding deposition and non-stability of surfactant particles.

The addressed natural leaf-derived surfactants were also used to investigate the effects of natural surfactant solutions with known weight concentrations on wettability of reservoir rock sample by measuring contact angle of droplets of solutions on pellets of sandstones aged with heavy oil. The device used for measuring contact angle was goniometer. The solutions were used in five concentrations of 2, 4, 6, 8 and 10 % by weight for both Mulberry leaf-derived extract and Henna leaf-derived extract. Two tests for each concentration were conducted which are reported in Table 4 for Mulberry and Table 5 for Henna extract, respectively.

In Fig. 11, measured average contact angle values between the aqueous solutions of Mulberry extract and rock sample have been plotted versus surfactant concentration. It is obvious that the higher the Mulberry leaf concentration the lower the contact angle. This figure shows that Mulberry leaf extract can alter the wettability to water wet system and may increase recovery factor and 10 wt% of this extract can reduce the average contact angle from 62.5 to 48.5. As written before, the measured contact angle would change if other sample of pellet used in the experiment since some properties of these rocky pellets like heterogeneity and smoothness affect the measured contact angle. Because of this, at each concentration, 2 pellets were examined.

The trend between 4 % and 6 % was obviously reversed. This is probably because of pellets heterogeneity and error that is occurred; as it is clear in 8 %
and 10%, the trend is normal again. The general trend is what was written before. This figure gives a good view of Mulberry leaf extract effect on wettability changes. For concentrations more than 10%, solid particles make separation hard and without separation, these particles may plug the pores and throats which cause permeability reduction and formation damage.

The average contact angle values between the aqueous solutions of Henna leaf-derived extract and rock sample against surfactant concentration is plotted in Fig. 12. As indicated by this figure, 10 wt% of Henna extract can reduce the average contact angle from 66 to 37.

As the trend shows, higher concentration results in lower contact angle which shows the wettability is altering to water wet system and so it may increase recovery factor by reducing residual oil saturation ($S_o$).

From Figs. 11 and 12, it is obvious that Henna extract is able to lower the contact angle more than that of Mulberry leaf extract.

The results show the performance of the mentioned plants on wettability alteration and IFT reduction. In other words, Mulberry and Henna leaf-derived extracts act as surfactants. This means that they contain both hydrophilic groups and hydrophobic groups. Therefore, Mulberry and Henna extracts contain both a water insoluble component and a water soluble component and because of this, they can be absorbed at the interface between water and oil and hence, lower the IFT between two liquids. Wettability alteration is mainly controlled by the adsorption of chemicals on surface of rocks. Adsorption and wettability changes are determined by surface properties of the rock, chemical structure of the surfactants, composition of the oil and etc. Mulberry and Henna extracts have the ability to be adsorbed on surface of rocks and change the rock wettability.

5. Conclusions

Some herbs may contain extract in their leaves or their other parts that may affect some properties of fluid and reservoir rock for instance IFT and wettability, as investigated in this paper, which leads to useful changes in properties and finally preparing the situation to an in-

| Concentrations [wt%] | First measured contact angle | Second measured contact angle | Average measured contact angle |
|----------------------|-----------------------------|-------------------------------|-------------------------------|
| 0                    | 61                          | 64                            | 62.5                          |
| 2                    | 58                          | 61                            | 59.5                          |
| 4                    | 55                          | 49                            | 52                            |
| 6                    | 52                          | 57                            | 54.5                          |
| 8                    | 52                          | 52                            | 52                            |
| 10                   | 48                          | 49                            | 48.5                          |

Table 5 Concentration and Contact Angles Measured by Goniometer for Henna Leaf-derived Extract

| Concentrations [wt%] | First measured contact angle | Second measured contact angle | Average measured contact angle |
|----------------------|-----------------------------|-------------------------------|-------------------------------|
| 0                    | 66                          | 66                            | 66                            |
| 2                    | 62                          | 61                            | 61.5                          |
| 4                    | 55                          | 51                            | 53                            |
| 6                    | 52                          | 50                            | 51                            |
| 8                    | 49                          | 54                            | 51.5                          |
| 10                   | 32                          | 42                            | 37                            |

![Fig. 11 Average Contact Angle vs. Mulberry Leaf Concentration](image1)

![Fig. 12 Average Contact Angle vs. Henna Leaf Concentration](image2)
crease in production and oil reserve.

In this study, two new natural based cationic surfactants produced from the leaves of Mulberry and Henna were studied for their ability in reducing IFT and altering the wettability of a reservoir rock sample. Based on the results obtained from this research, following conclusions can be drawn:

(1) The results demonstrated that a surfactant solution containing 10 wt% of Mulberry extract could reduce the IFT between kerosene and distilled water from 43.9 to 4.01 mN/m, while the same amount of Henna extract lowered the IFT from 43.9 to 3.05 mN/m.

(2) Mulberry-derived surfactant has a critical micelle concentration of about 2.6 % by weight, while Henna-derived surfactant has a CMC of about 2.8 %. The CMC values of these natural surfactants can be used in future oil recovery studies.

(3) The results demonstrated that a surfactant solution containing 10 wt% of Mulberry extract could reduce the contact angle between the aqueous solution and reservoir rock pellet from 62.5 to 48.5, while the same amount of Henna extract lowered the contact angle from 66 to 37. For concentrations more than 10 %, natural surfactant will precipitate in aqueous phase and this precipitation causes permeability reduction and formation damage in porous media.

(4) Immiscible displacement processes like water flooding are extremely controlled by wetting properties of pore surfaces within reservoir rocks. As the results show, using the addressed natural surfactants can alter the wettability of rock sample to water wet system and so, increase the brine imbibition rate which causes more oil exploitation in water flooding.

(5) Henna leaf-derived surfactant could lower the IFT of a water-oil system and reduce the contact angle of a rock/fluid system more than that of Mulberry leaf-derived surfactant.

(6) Mulberry and Henna plants are now widely available in several regions, so that high surface activity surfactants can be obtained. According to this in addition to the low price of generating plant-derived surfactants, the feasibility of using these kinds of surfactants in future oil recovery processes is of major concern.

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