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New Surfactant Extracted from *Zizyphus Spina-Christi* for Enhanced Oil Recovery: Experimental Determination of Static Adsorption IsothermMohsen SAFIAN-BOLDAJ^{†1)}, Mojtaba PORDEL SHAHRI^{†1)*}, Mohammad ZARGARTALEBI^{†1)}, and Milad ARABLOO^{†2)}^{†1)} Dept. of Petroleum Engineering, Petroleum University of Technology, Ahwaz, IRAN^{†2)} Dept. of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran, IRAN

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A fundamental chemical enhanced oil recovery (EOR) process is surfactant flooding in which the key mechanism is to reduce interfacial tension between oil and the displacing fluid and hence mobilizing the trapped oil. Surfactant loss by adsorption is one of the most important criteria that governs the economics of the surfactant flooding methods. In addition to this, detrimental effects and high price of currently used surfactants cause EOR process so expensive and unfeasible. This study is aimed to introduce a novel kind of plant based surfactant which is extracted from *Zizyphus Spina-Christi* tree. In addition, equilibrium adsorption behavior of this novel biosurfactant in aqueous solution on crushed reservoir rocks is presented. A conductivity technique was used to assess the critical micelle concentration (CMC) value in the aqueous phase. Batch experiments were used to understand the effect of adsorbent dose on sorption efficiency as well. Four adsorption models were also employed to make a quantitative description of equilibrium adsorption behavior of surfactant solution. For evaluating the ability of this novel biosurfactant on the surface properties, IFT values of Saponin solution were compared to those of commonly used chemical surfactants in petroleum industry. It is shown that availability and the low cost of the *Zizyphus Spina-Christi* extract in comparison to common chemical surfactants in petroleum industry make it economically viable for surfactant flooding.

KeywordsEquilibrium isotherm, Critical micelle concentration, Adsorption, *Zizyphus Spina-Christi*, Enhanced oil recovery**1. Introduction**

Historically, oil production from oil reservoirs has been divided into three phases. Initially, oil is produced by the native energy of the reservoir and this period is called primary production. Primary production results in 5–30 % original oil in place (OOIP) recovery¹⁾. Water flooding is used to increase the oil production beyond that of primary production and this stage is called secondary production. The water pushes the oil in front of it toward the production wells and helps to increase the total recovery to 40–60 % OOIP. At the end of secondary production there is a significant amount of oil (40–60 % OOIP) still left in the reservoir due to many factors including unfavorable wettability conditions, heterogeneity of reservoir rock and capillary-trapped oil. Hence, implementation of tertiary oil production techniques as a part of an enhanced oil recovery (EOR) scheme is inevitable to unlock this immense oil resource. Chemical EOR methods have not historically

been responsible for significant additional recovery, worldwide. Nevertheless, surfactants are being increasingly used as a well stimulation or wettability alteration agent in EOR projects. This along with the price of oil is a strong reason for scientists to continue the advancement of surfactant research in EOR^{2)–4)}. Surfactants can action several ways to enhance the oil production: lowering the interfacial tension (IFT) between residual oil and injected water, changing the wettability of the surface, forming emulsions, etc⁵⁾. Surfactant flooding has been tried for a number of conventional oil reservoirs around the world with some success stories (*e.g.*, Yates field in Texas^{6),7)} and Cottonwood Creek in Wyoming^{8)–10)}), but it has largely proved inefficient due to the cost of surfactant loss in the porous medium as well as issues with adsorption efficiency and negative reactions with the reservoir rock.

Adsorption kinetics and equilibrium of surfactants are dependent on the nature of or properties of the surfactants and also the solid-liquid surface¹¹⁾. Studies related to the application of surfactants in EOR processes indicated that surfactant lost by adsorption is only one of the several mechanisms responsible for surfactant

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retention. Other mechanisms may include precipitation by divalent ions, partitioning and entrapment in a residual (immobile) oil phase. Thus, surfactant loss by adsorption is one of the important criteria that governs the economics of the surfactant flooding methods¹². Surfactant adsorption in porous systems typically occurs through a range of complex phenomena. Surface area of the porous media has a remarkable effect on surfactant adsorption. Liu¹³ measured surfactant adsorption in three rock samples of the same carbonate porous medium but with different surface areas. He used a TC blend surfactant, 1 : 1 mixture by weight of dodecyl 3 ethoxylated sulfate and isotridecyl 4 propoxylated sulfate from Stepan. He found that the adsorptions of the TC blend on the three samples were close to each other if the adsorption was calculated by using surfactant adsorption amount per porous media surface area. Surfactant adsorption is strongly affected by the redox condition of the system. Laboratory cores typically have been exposed to oxygen and are in an aerobic state. Wang¹⁴ showed that the surfactant adsorption in anaerobic conditions was lower than that in aerobic conditions. Regarding the surfactant type and rock type, nonionic surfactants have much higher adsorption on a sandstone surface than anionic surfactants¹³. However, Liu's¹³ initial experiments indicated that the adsorption of nonionic surfactant on calcite was much lower than that of anionic surfactant without the presence of Na_2CO_3 and was of the same order of magnitude as that of anionic surfactant with the presence of Na_2CO_3 . The role of salinity is much less important, but the temperature effect is much more important for nonionics than for anionics¹⁵. Hurd¹⁶ patented a method of desorbing and reusing surfactant by flooding a saline surfactant solution using less saline water. More factors that affect adsorption were discussed by Hanna and Somasundaran¹⁷.

While surfactant is adsorbed, surfactant molecules transfer from bulk solution to the surface. It can happen if the surface is energetically more favored by the surfactant than the bulk solution^{11,18,19}. If the adsorption is too high, the large amount of surfactants would be required to produce small amount of extra oil.

Although the adsorption of chemical surfactants at pure solid-liquid interface has been investigated intensively in the literature, an investigation on equilibrium behavior of natural biosurfactant has not been studied, in spite of their great importance. With this aim, this study is focused on investigating the micellar formation concentration and static equilibrium behavior of a novel plant based natural surfactant on crushed reservoir rock. The adsorption mechanism of *Zizyphus Spina-Christi* on the surface of rock is not yet reported in the literature. Earlier researches on this novel natural surfactant in petroleum industry have been presented by Pordel Shahri *et al.*^{20,21} and Arabloo *et al.*^{22,23}. This

Fig. 1 *Zizyphus Spina-Christi* Distribution around the World

paper highlights the adsorption behavior of *Zizyphus Spina-Christi* extract in solution as a new natural surfactant to be implemented in EOR process. Adsorption of the studied surfactant was evaluated using a conductivity technique for aqueous phase. Batch experiments were also conducted to investigate the influence of adsorbate dose on sorption efficiency of this novel surfactant. Four adsorption models are also employed to make a quantitative description of equilibrium adsorption behavior of surfactant solution and then applicability of each model is examined in detail.

For evaluating the ability of *Zizyphus Spina-Christi* extract on the surface properties, IFT values of this new biosurfactant were compared to those of commonly used chemical surfactants in petroleum industry.

2. Experiment

2.1. Experimental Materials

2.1.1. Surfactant

Zizyphus Spina-Christi is widespread in tropical and subtropical regions with spiny branches and small, orange-yellow fruits. The genus *Zizyphus Spina-Christi* is widely distributed because it is cultivated and has been naturalized across a large area from N. Africa east to Afghanistan and NE India. In UAE found in wadis, different landscape, and it is widely cultivated all over the UAE. **Figure 1** shows countries where the species has been planted.

Native: Chad, Djibouti, Eritrea, Ethiopia, Kenya, Libyan Arab Jamahiriya, Mali, Mauritania, Nigeria, Pakistan, Senegal, Somalia, Tunisia, Turkey, Zimbabwe.

Exotic: Algeria, Comoros, Egypt, India, Iran, Iraq, Jordan, Madagascar, Morocco, Netherlands, Saudi Arabia, Syrian Arab Republic, United Arab Emirates, Zanzibar.

Zizyphus Spina-Christi, locally known as Cedar, is a multipurpose tree species belonging to the botanical family Rhamnaceae that grows wild in Asia and tropical Africa. It is a genus of about 100 species of deciduous or evergreen trees and shrubs distributed in the tropical and subtropical regions of the world. For example, *Zizyphus mauritiana* and *Zizyphus jujuba*, occur on nearly every continent, whereas other species, like *Zizyphus ummularia*, *Zizyphus Spina-Christi* and

Zizyphus mucronata, are restricted in their distribution to distinct areas. *Zizyphus* species can grow either as trees and shrubs or exclusively as small shrubs or bushes²⁴. Previous phytochemical studies on the different species of the genus *Zizyphus* led to the isolation and characterization of cyclopeptide alkaloids, flavonoids, sterols, tannins, and triterpenoid saponins²⁵. Saponins are generally known as non-volatile, surface active compounds that are a structurally diverse class of compounds occurring in many plant species, which are characterized by a skeleton derived of the 30-carbon precursor oxidosqualene to which glycosyl residues are attached. Traditionally, they are subdivided into triterpenoid and steroid glycosides, or into triterpenoid, spirostanol, and furostanol saponins²⁶.

The chemical composition of the oil of *Zizyphus Spina-Christi* wild leaves obtained by hydro distillation were examined by capillary GC and GC/MS. Thirty-four components were characterized, representing 92.2 % of the oil. The main components in the oil were geranyl acetone (14.0 %), methyl hexadecanoate (10.0 %), methyl octadecanoate (9.9 %), farnesyl acetone C (9.9 %), hexadecanol (9.7 %) and ethyl octadecanoate (8.0 %). The free sugars fructose, raffinose, sucrose, glucose, galactose, rhamnose have also been isolated from different parts of the plants²⁷.

Saponin, a biosurfactant is produced from *Zizyphus Spina-Christi* leaves. Different studies investigated the properties of this novel surfactant. For further information on other physico-chemical properties of *Zizyphus Spina-Christi* interested readers can refer to Amin²⁸, Mahran²⁹, Nafisy³⁰ and Pordel Shahri *et al.*³¹.

2. 1. 2. Core Samples

Rock samples were taken from Asmari sandstone outcrop. Based on the petrographic observations, the rock composition of the Asmari reservoir varies between silica clastic and carbonates lithologies. In this reservoir, quartz and dolomite are dominant minerals where calcite, anhydrite, clay minerals, potassium feldspar and iron oxides are among other abundant minerals. In order to increase experiment accuracy all of the rock samples were taken from one block of rock with the same properties.

2. 2. Experimental Method

2. 2. 1. Preparation of Surfactant Solution and Core Samples

Depending on the required concentration of the solution, specific amount of surfactant powder was poured into specific volume of distilled water. Early experimental studies showed that Saponin will precipitate using this brine as the aqueous phase, so deionized water was used in all tests. The distilled water used was reverse osmosis (RO) water produced in our lab. The water-Saponin solution was then stirred on a magnetic stirrer and simultaneously heated to overcome temperature of solubilizing or Krafft temperature for one hour.

Each solution is prepared separately to eliminate the error caused by stock solution.

The rock samples were then crushed into small parts by jaw crusher and then grounded into fine particles. The particles were then washed with distilled water to remove dusts. After exposing the samples to free air, a laboratory oven operating at 140 °C was employed to dry the rock powder. Dried rock samples were sieved to obtain particles with diameter lower than 700 µm and bigger than 600 µm.

It should be mentioned here that, clay swelling may affect surfactant adsorption due to excess surface provided. This affection is more severe for cationic surfactant according to negative charges on the rock surface. Non-ionic surfactant adsorption on the other hand may also face infinitesimal influence by clay swelling. Regarding the facts that Asmari formation clay content is not high and the surfactant used at this study is a non-ionic surfactant; clay swelling influence on the adsorption can be neglected.

2. 2. 2. Critical Micelle Concentration (CMC) Measurement

In this study, the conductivity method was used to determine the CMC measurements. Concentration of the surfactant solution samples used was on the wide range of 1000-120,000 ppm. The conductivity of the different solutions was determined from high to low concentrations. The conductivity meter, Sartorius professional meter PP-20 with the accuracy of 1E-2 µs/cm was used. The conductivity meter was calibrated by using a standard solution. The conductivity of the solution was measured by immersing the probe in the solution. The electrode was washed with distilled water before and after every test to ensure accuracy of the conductivity measurements.

2. 2. 3. Adsorption Measurement

Adsorption isotherms are determined by batch equilibrium adsorption procedures. To measure the amount of adsorption of surfactant on rock samples, a ratio of 5 : 1 (v/w) of surfactant solution and rock is agitated on an orbital shaker at 80 rpm for 24 h to be sure the adsorption process is complete. Different centrifuging speed and time is tested to find optically the optimum conditions in which all rocks deposit in the solution. The optimum condition was the speed of 7000 rpm for 15 min. Conductivity measurements were then carried out on aqueous solutions of Saponin. All the adsorption experiments were performed with two replicates at 25 ± 1 °C to obtain the accurate results.

Amounts of adsorbed were obtained by measuring surfactant concentrations before and after equilibrating with crushed rock. The amount of surfactant adsorbed (adsorption density) was expressed as the unit mass of surfactant adsorbed per 1 gram of rock (mg/g). Adsorption values were determined by the following material balance equation:

$$\Gamma = \frac{M_s \times (C_i - C_e)}{M_R} \times 10^{-3} \quad (1)$$

Where,

Γ = amount adsorbed (mg_{surfactant}/g_{rock})

M_s = mass of surfactant solution (g)

C_i = initial surfactant concentration before equilibrated with rock (ppm)

C_e = surfactant concentration in surfactant solution after equilibrated with rock (ppm)

M_R = total mass of the crushed rock (g)

Adsorption isotherms were generated by varying the initial surfactant concentration in solution and plotting amounts adsorbed *versus* the equilibrium concentrations.

3. Equilibrium Adsorption Isotherms

An adsorption isotherm shows the amount of surfactant adsorbed on the substrate *versus* the equilibrium surfactant concentration. In other words, it shows the dependence of adsorption amount on the equilibrium surfactant concentration in the bulk phase. The four well-known general adsorption isotherms were employed to describe the equilibrium adsorption behavior of surfactant solution.

3.1. Linear Isotherm

The simplest type of adsorption isotherm is the linear increase described by the Henry equation³²:

$$\Gamma = k_H C_e \quad (2)$$

Where Γ is the amount of solute adsorbed per unit mass of adsorbent under equilibrium condition, C_e is the equilibrium concentration, and k_H is a constant for this model in units of L/m².

3.2. Freundlich Isotherm

An empirical equation was established by Freundlich³³) to describe the adsorption equilibrium process, assuming the adsorbent has a heterogeneous surface with different categories of adsorption sites. This isotherm model best describes the adsorption on heterogeneous surfaces with the high affinity regions (sites) being occupied first, which accounts for the steep increase in low concentrations. The lateral repulsion between the adsorbed molecules could result in a decrease in adsorption value. The Freundlich isotherm model is given as:

$$\Gamma = k_f C_e^{1/n} \quad (3)$$

Where Γ is the amount of solute adsorbed per unit mass of adsorbent under equilibrium condition, C_e is the equilibrium concentration, and k_f and n are the Freundlich constants. Equation (3) can be rearranged in the linear form by taking the logarithm of both sides as:

$$\log \Gamma = \log k_f + \frac{1}{n} \log C_e \quad (4)$$

The intercept and the slope of the linear plot of $\log \Gamma$ *versus* $\log C_e$ at a given experimental conditions provide the values of k_f and n , respectively.

3.3. Langmuir Isotherm

The Langmuir adsorption isotherm has been widely applied to many adsorption processes. It has produced good agreement with a wide variety of experimental data for adsorption of a solute from a liquid solution. A basic assumption of the Langmuir theory is that the sorption takes place at specific homogeneous sites in the adsorbent. Moreover, when a site is occupied by a solute, no further adsorption can take place at that site. The Langmuir equation is expressed as:

$$\Gamma = \frac{\Gamma_0 k_1 C_e}{1 + k_1 C_e} \quad (5)$$

Where, Γ_0 and k_1 represent the adsorption capacity and adsorption equilibrium capacity in the Langmuir model, respectively. The constants Γ_0 and k_1 can be determined by plotting $1/\Gamma$ *versus* $1/C_e$ and rewriting Eq. (5) as:

$$\frac{1}{\Gamma} = \frac{1}{\Gamma_0 k_1} \frac{1}{C_e} + \frac{1}{\Gamma_0} \quad (6)$$

Obviously, model parameters simply could be determined by intercept and slope of linear curve fitting.

3.4. Temkin Isotherm

The Temkin isotherm is generally expressed in the following linear form:

$$\Gamma = A \ln k_t + A \ln C_e \quad (7)$$

Where A and k_t are the Temkin constant and equilibrium binding constant, respectively.

4. Results and Discussion

4.1. Evaluation of Surfactant's Critical Micelle Concentration (CMC) Value

Study of the properties of solutions containing surface-active materials has shown that the bulk solution properties can change dramatically over small changes in concentration of surface-active materials. These sudden changes in a property of solution can be interpreted as a significant change in the nature of the solute species in the solution. These observations serve as proof for the formation of aggregates or micelles in surfactant solutions. It is one of the characteristic properties of surfactant solutions to spontaneously form aggregates in aqueous phase.

Quantifying the critical micelle concentration (CMC) is important to understand the active surface chemistry of Saponin in the solute. The conductometric method followed for the determination of CMC, was based on

Fig. 2 Conductivity vs. Saponin Concentration for Determination of CMC

the one suggested by Williams^{(34),(35)}. For surfactant concentrations below the CMC, the addition of surfactant to the solution causes an increase in the number of charge carriers and consequently, an increase in the conductivity. Above the CMC, further addition of surfactant increases the micelle concentration while the monomer concentration remains approximately constant (at the CMC level). Since a micelle is much larger than a surfactant monomer it diffuses more slowly through solution and so is a less efficient charge carrier. A plot of conductivity against surfactant concentration thus expected to show a break at the CMC. Conductivity values *versus* surfactant concentrations were plotted in order to obtain the CMC magnitude from the inflection point of the data shown in Fig. 2. Two lines were simply drawn before and after the break of the curve and the CMC value was determined applying linear fitting to the two linear portions separately. The correlation coefficient values were higher than 0.99 for the two regressions and the CMC value obtained based on this method is about 5 wt%.

4.2. Adsorption Isotherms

Most static adsorption studies have employed the surfactant depletion method with the results being presented as isotherms which are simply plots of the amount of surfactant adsorbed per gram of solid *versus* the equilibrium surfactant concentration at a constant temperature. Figure 3 shows the results of adsorption of *Zizyphus Spina-Christi* extract onto the rock sample using a wide range of surfactant concentration from below to above the CMC. Adsorption isotherm of Saponin solution on rock surface exhibits a pronounced sigmoidal shape, *i.e.*, a low-affinity initial region followed by a region in which the adsorption increases steeply and reaches a plateau after the critical micelle concentration (CMC).

Generally, a typical isotherm will show four regions. At low concentrations, designed as region I (see Fig. 3), the adsorption is due to electrostatic interaction between the head group of the surfactant and charged sites on the rock surface. A gradual increase of ad-

Fig. 3 Equilibrium Adsorption of *Zizyphus Spina-Christi* Extract by Conductivity Method

sorption with increase in Saponin concentration is observable in this region. The surfactant molecules which are adsorbed on the surface do not interact with each other. The mechanism dominating adsorption in region II (see Fig. 3) was described by Gaudin and Fuerstenau⁽³⁶⁾ as forming surface aggregates (known as “hemi-micelles”) of the surfactant molecules of the adsorbent surface. In other words, the CMC of hemi-micelle formation also called critical aggregation concentration (CAC) that is lower than CMC of surfactant⁽³⁷⁾ in which a two dimensional aggregation is formed on the rock. This phenomenon generates an additional driving force, and with the still existing electrostatic attraction, makes the adsorption isotherm curve in this stage exhibit a sharp increase.

Adsorption of surfactant is proposed to occur with a reduced slope after region II. Some literature^{(11),(18)} defines this region as region III. This type of behavior was not noticed in our experiments. It should be noted that the shape of the isotherm will be dependent on some factors including the type of surface, and the presence or absence of additional compounds such as electrolytes, co-surfactants, and alcohols⁽³⁸⁾. A plateau of the adsorption isotherm, shown as region IV, is characterized by little or no increase in surfactant adsorption with increasing surfactant concentration.

The adsorption value of *Zizyphus Spina-Christi* extract at CMC point was found to be 6.8 mg_{surf}/g_{rock}. Muherei *et al.*⁽³⁹⁾ evaluated the adsorption of sodium dodecyl sulfate (SDS), TX100 and their mixtures onto local shale and sandstone outcrops. It was determined that the amounts of TX100 adsorbed to shale (7.5 mg/g) are greater than those adsorbed to sandstone (1.5 mg/g). While adsorption of TX100-SDS mixtures on shale reduced to 4.5 mg_{surf}/g_{rock}. Thus this value is in the range of other chemical surfactants.

To perform an optimized design for a sorption process, it is essential to consider the most proper correlations for equilibrium curves. To this end, four adsorption models namely, linear, Freundlich, Langmuir, and Temkin isotherm models were employed to make a quantitative description of equilibrium adsorption be-

havior of Saponin.

In the linear model, the simplest isotherm model, a graph of the amount adsorbed per unit mass of the adsorbent, Γ , versus equilibrium concentration, C_e , has a slope of k_H for the linear isotherm as shown in Fig. 4. Figures 5-7 show the equilibrium adsorption behavior of the Saponin solution on the sandstone samples, based on the Freundlich, Langmuir, and Temkin isotherm models, respectively. The values of the all equilibrium isotherm model studied in this work are listed in Table 1. Based on the reported values in Table 1, the equilibrium isothermal adsorptions of the *Zizyphus Spina-Christi* are better represented by the two models of linear and Langmuir. Both of the models produce similar magnitude of correlation coefficient ($R^2 = 0.978$,

and $R^2 = 0.964$ for linear and Langmuir model, respectively). Moreover, the calculated correlation coefficient for Temkin model is 0.766 which is much less than R^2 value of the plots obtained from the Freundlich, Langmuir, and linear isotherm equations.

4.3. Applicability of *Zizyphus Spina-Christi* for EOR

The success of surfactant flooding depends on many factors such as formulation, cost of surface active agent, availability of chemicals, and oil price. Between these factors, selection of proper surfactants and oil prices in market are two key factors in chemical EOR applications. *Zizyphus Spina-Christi* is a natural surface active substance found in N. Africa east to Afghanistan

Fig. 4 Adsorption Equilibrium Data Based on the Linear Isotherm Model

Fig. 5 Adsorption Equilibrium Data Based on the Freundlich Isotherm Model

Fig. 6 Adsorption Equilibrium Data Based on the Langmuir Isotherm Model

Fig. 7 Adsorption Equilibrium Data Based on the Temkin Isotherm Model

Table 1 Adsorption Models and the Calculated Parameters

Isotherm model	Equation	Constant parameter [s]	Correlation coefficient (R^2)
linear	$\Gamma = k_H C_e$	$k_H = 0.199$	0.978
Freundlich	$\Gamma = k_f C_e^{1/n}$	$k_f = 0.878$ $n = 1.582$	0.941
Langmuir	$\Gamma = \frac{\Gamma_0 k_1 C_e}{1 + k_1 C_e}$	$\Gamma_0 = 3.080E-3$ $k_1 = 83.609$	0.964
Temkin	$\Gamma = A \ln k_t + A \ln C_e$	$A = 4.253$ $k_t = 0.563$	0.766

Fig. 8 Comparison of Interfacial Tension of *Zizyphus Spina-Christi* vs. Chemical Surfactants

and NE India. It is easy available. Since *Zizyphus Spina-Christi* is freely available with lower cost compared to commercial synthetic surfactants, it is expected to be a viable candidate for chemical EOR methods.

From the other point, the proposed surfactant is natural and biodegradable. Thus, causes minimal or no harm to the environment compared to common chemical surfactants in petroleum industry. One of the key parameters controlling the economics of any chemical EOR process is the amount of surfactant loss due to adsorption. The adsorption value of *Zizyphus Spina-Christi* extract at CMC point was found to be $6.8 \text{ mg}_{\text{surf}}/\text{g}_{\text{rock}}$. This value is on the range of other chemical surfactants.

One of the key mechanism in surfactant flooding is to reduce interfacial tension (IFT) between oil and the displacing fluid. As IFT is reduced, the capillary number is increased, leading to reduced oil residual saturations⁴⁰. Thus the ability of surfactant to lower the IFT between the aqueous solution and oil phase is one of the most significant aspects during a chemical EOR process. IFTs for common chemical surfactants in petroleum industry and *Zizyphus Spina-Christi* extract in the presence of an oil phase are shown in Fig. 8. It should be noted that IFT data for alkyl poly glycosides, alkyl sulfates⁴¹ and *Zizyphus Spina-Christi* extract²⁰ were determined by the pendant-drop method against kerosene oil, while in the case of Sodium dodecyl benzene sulfonate and Sodium laureth sulfate, IFTs obtained by ring tensiometer against Saltrol 130⁴². This figure shows that IFT decreases with increasing surfactant concentration and minimum values of IFT are obtained (IFT = 5.5, 8.5, 9, 14.5, 17.5 mN/m, for Sodium dodecyl benzene sulfonate, Sodium laureth sulfate, *Zizyphus Spina-Christi* extract, alkyl poly glycosides, and alkyl sulfates, respectively). *Zizyphus Spina-Christi* gives the lower values of IFT comparing to alkyl poly glycosides, and alkyl sulfates. At concentration of 10 wt%, the reduction of IFT in the system kerosene oil-Saponin solution is similar to the IFT value obtained with 0.2 wt% of Sodium dodecyl benzene sul-

fonate, or Sodium laureth sulfate. These results indicate that there is no much difference in the interfacial tension reduction provided by the proposed surfactant compared to Sodium dodecyl benzene sulfonate and Sodium laureth sulfate, especially considering the fact that the manufacture cost of the Saponin is much lower than the cost of the commercial surfactants. In addition to this, lower IFT may be achieved by adding alkaline or salt to the solution. As previously noted, the ability to lower the surface tension between aqueous solutions and other phases is one of the most significant aspects of surfactants that raise their applicability in industries. Therefore, this new natural surfactant can meet the technical and economical requirements as EOR agent in chemical flooding in sandstone as well as carbonate oil reservoir.

5. Conclusions

Zizyphus Spina-Christi is plentiful in Middle East and North Africa especially in Iran, Iraq, Jordan and Egypt and can be a good selection for use in this region's reservoirs, but has not yet attended as surfactant for EOR process. The equilibrium adsorption behavior of *Zizyphus Spina-Christi* extract on Asmari outcrop was investigated. The adsorption value of *Zizyphus Spina-Christi* at CMC point was found to be $6.8 \text{ mg}_{\text{surf}}/\text{g}_{\text{rock}}$. Adsorption isotherm of *Zizyphus Spina-Christi* solution on rock surface exhibits a pronounced sigmoidal shape, i.e., a low-affinity initial region followed by a region in which the adsorption increases steeply and reaches a plateau after the critical micelle concentration (CMC).

Results of fitting experimental adsorption data to four isotherm model showed that equilibrium isothermal adsorptions of the *Zizyphus Spina-Christi* are better represented by the two models of linear and Langmuir whereas the Temkin model does not give a good validity.

Comparison of IFT data of *Zizyphus Spina-Christi* with some commonly used chemical surfactants in petroleum industry showed that proposed new natural surfactant more favorably reduce IFT. Also, availability and the low cost of the *Zizyphus Spina-Christi* make it economically viable for surfactant flooding. Moreover, the newly introduced biosurfactant poses minimal or no harm to the environment compared to common chemical surfactants in petroleum industry. Therefore, this new natural surfactant can meet the technical and economical requirements as EOR agent in chemical flooding in sandstone as well as carbonate oil reservoirs.

Nomenclatures

A	: constant of Temkin isotherm model	[-]
C _e	: equilibrium solution concentration	[ppm]

C_i	: initial surfactant concentration before equilibrated with the carbonate rock	[ppm]
C_f	: surfactant concentration in surfactant solution after equilibrated with the rock	[ppm]
k_f	: constant of Freundlich isotherm model	[-]
k_H	: constant of linear isotherm model	[-]
k_l	: constant of Langmuir isotherm model	[-]
k_t	: constant of Temkin isotherm model	[-]
M_R	: total mass of the crushed rock	[g]
M_s	: mass of surfactant solution	[g]
<Greek>		
Γ	: amount adsorbed	[mg _{surfactant} /g _{rock}]

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