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Research note

Experimental investigation of *Seidlitzia rosmarinus* effect on oil–water interfacial tension: Usable for chemical enhanced oil recovery

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Abstract In this paper, a new plant based natural cationic surfactant, named *Seidlitzia rosmarinus*, is introduced, and the viability of using this natural surfactant as an alternate to synthetic surfactants for chemical enhanced oil recovery is investigated. For this purpose, the interfacial tension values between natural surfactant solution and oil are measured by using the pendant drop method. The results show that *Seidlitzia rosmarinus* decreased the interfacial tension values from 32 to 9 mN/m. Results confirm the fair surface activity of *Seidlitzia rosmarinus* in comparison with other natural and synthetic surfactants. Accordingly, this natural surfactant can be used as a surfactant for chemical enhanced oil recovery.

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1. Introduction

Surfactants are used to lower the oil/water interfacial tension (IFT) and modify the wettability of the reservoir rock [1]. Furthermore, they are employed to form emulsions in order to ease the fluid transport in the reservoir [2]. The world's first natural surfactant was a saponin extracted through a spray drying method from a Chilean Soap bark tree, which is called Quillaja Saponaria Molina. It holds the surfactant property in cosmetic products and detergents to affect purifying, emulsifying, foaming and softening characters [3]. Saponins are surface active compounds with detergent, wetting, emulsifying, and foaming properties [4].

Here, a new natural cationic surfactant, which is produced from the leaves and stems of *Seidlitzia rosmarinus*, is introduced. The *Seidlitzia rosmarinus* genus belongs to the Chenopodiaceae family, which is rich in saponin [5]. *Seidlitzia rosmarinus* is low priced and abundantly accessible in the Middle East and Central Asia, compared with synthetic surfactants. There is a hypothesis

that the saponin-containing powder of *Seidlitzia rosmarinus* can be used in the chemical flooding of conventional oil reservoirs. For this purpose, the powder was extracted from the leaves and stems of the *Seidlitzia rosmarinus* plant by using the spray dryer method. The pendant drop method was then employed to measure interfacial tension values between the surfactant solution and oil.

2. Materials and experimental procedure

2.1. Materials

2.1.1. Aqueous phase

Deionized water is used in most interfacial tension measurement experiments, since early studies indicated that natural surfactant will precipitate, when using brine as the aqueous phase [6]. The used distilled water was Reverse Osmosis (RO) water produced in our laboratory.

2.1.2. Surfactant

Similar to Quillaja Saponaria Molina, the saponin-containing powder of *Seidlitzia rosmarinus* was extracted from an aqueous solution of the *Seidlitzia rosmarinus* plant by means of a spray drying apparatus. The aqueous solution of *Seidlitzia rosmarinus* was prepared by mixing the distilled water and the dry material of the plant. Table 1 shows the chemical composition of the dry material of *Seidlitzia rosmarinus*, in the form of gross

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Table 1: Chemical composition of the dry material [7].

A: Chemical composition of the dry material in the form of gross composition.							
DM (%)	CP (%)	CF (%)	NDF (%)	ADF (%)	TA (%)	EE (%)	GE (cal/g)
93.6	7.9	33.2	60.5	38.3	24.5	0.5	3511
DM = dry matter, CP = crude protein, CF = crude fiber, NDF = neutral detergent fiber, ADF = acid detergent fiber, TA = total ash, EE = ether extract, GE = gross energy							
B: Chemical composition of the dry material in the form of elemental analysis							
Ca (%)	P (%)	Mg (%)	K (%)	Fe (mg/kg)	Mn (mg/kg)	Zn (mg/kg)	Na (%)
1.38	0.15	18.7	0.4	13	125	210	1.2

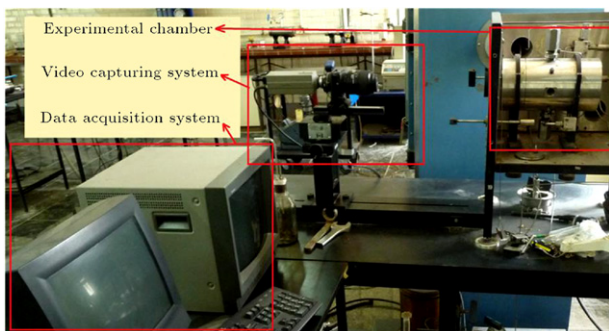


Figure 1: Pendant drop apparatus.

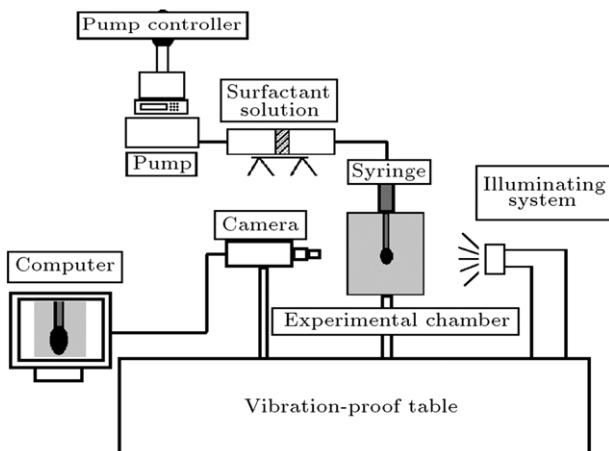


Figure 2: The schematic diagram of the experimental apparatus.

composition and elemental analysis. The density of the powder is 2639 kg/m^3 and 1% solution of this powder has a pH of 8.6.

2.1.3. Oil

Kerosene was used as the oil phase in interfacial tension measurements. By refluxing the distilled kerosene through the column multiple times, its purity was increased. The density of kerosene at a test temperature of 35°C was 801.7 kg/m^3 .

2.2. Experimental procedure

2.2.1. A typical pendant drop apparatus

As shown in Figure 1, the pendant drop apparatus typically consists of three components: an experimental chamber, a video capturing system together with an illuminating system, and a data acquisition system. A schematic diagram of the experimental apparatus set up is also shown in Figure 2.

Table 2: Densities and interfacial tensions related to different percent weights of aqueous solution of *Seidlitzia rosmarinus* with 10 kg/m^3 NaCl.

Concentration (% weight)	Density (kg/m^3)	D_e (mm)	D_s (mm)	γ (IFT) (mN/m)
0	1.0029	3.86	2.02	32
0.01	1.00297	3.83	2.01	31.6
0.02	1.00266	3.80	2.00	31.3
0.05	1.00299	3.77	1.99	31.1
0.075	1.00313	3.74	1.98	30.6
0.1	1.003547	3.71	1.97	29.2
0.2	1.00389	3.66	1.96	27.8
0.25	1.00401	3.62	1.94	25.7
0.4	1.00456	3.52	1.93	24.1
0.5	1.00487	3.43	1.92	22.3
0.75	1.00581	3.36	1.90	18.5
1.5	1.00742	2.96	1.76	14.6
3	1.00963	2.7	1.69	12.5
5	1.01820	2.68	1.74	10.2
8	1.01978	2.45	1.62	9.7
10	1.02741	2.21	1.50	8.9

2.2.2. Method implementation in measuring interfacial tension

To apply the pendant drop method, prior to getting the interfacial tension between natural surfactant solution and oil, it is crucial to find the densities of the surfactant solution and oil. The densities of different saponin solution were measured through Density Meter Apparatus (DMA). Table 2 shows the densities of different percent weights of aqueous solution of *Seidlitzia rosmarinus* with 10 kg/m^3 NaCl.

Axisymmetric Drop Shape Analysis (ADSA) is a surface tension measurement technique based on the shape of drops or bubbles. A hanging drop of surfactant solution is produced at the end of a capillary tube. The other end of the capillary tube is connected to an injection syringe. By varying the force over the syringe, direct control over the drop volume was acquired. The droplet profile was recorded in a PC with a Charged Couple Device (CCD) lens camera at suitable time intervals. The acquired image was digitized, as shown in Figure 3, and its geometrical parameters, D_e and D_s , were determined. Values of D_e and D_s were tabulated in Table 2.

In this study, as described by Herd et al. [9], a highly accurate and plain method was used to calculate the interfacial tension from the fluid properties and drop shape [9].

The interfacial tension is:

$$\gamma = \frac{\Delta\rho \cdot g \cdot R_0}{\beta}, \quad (1)$$

where γ is interfacial tension. $\Delta\rho$ shows the density difference between drop material and external phase, and g is the acceleration due to gravity. Values of β and R_0 are determined from:

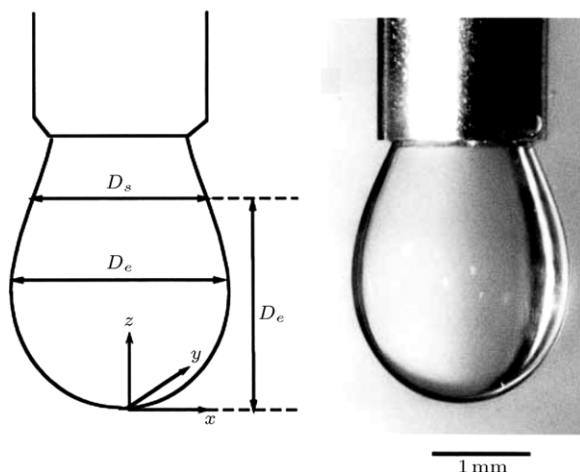


Figure 3: Geometry and the equilibrium shape of the pendant drop [8].

$$\beta = 0.12836 - 0.7577 \left(\frac{D_s}{D_e} \right) + 1.7713 \left(\frac{D_s}{D_e} \right)^2 - 0.5426 \left(\frac{D_s}{D_e} \right)^3, \quad (2)$$

$$\frac{D_e}{2R_0} = 0.9987 - 0.1971 * \beta - 0.0734 * \beta^2 + 0.34798 * \beta^3, \quad (3)$$

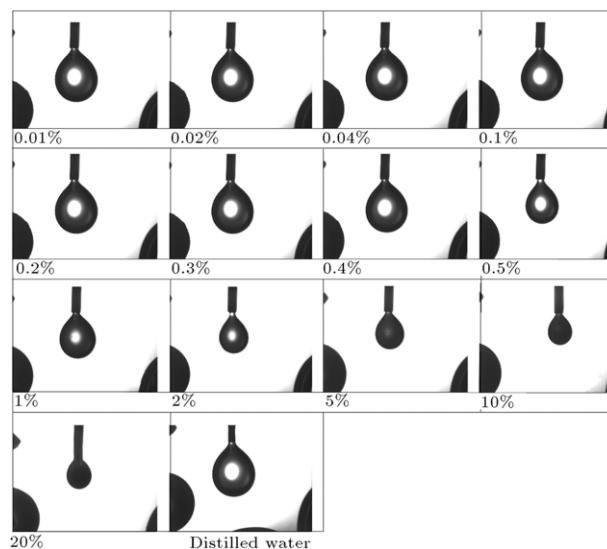
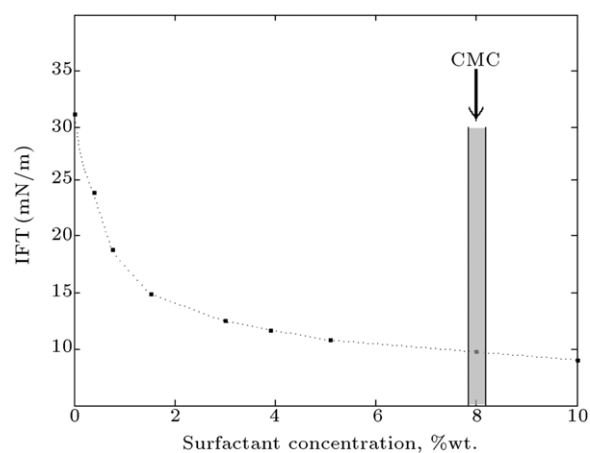
where D_e is the maximum diameter of the drop, and D_s is the horizontal dimension of the drop.

3. Results and discussion

The droplet profiles at the moment of falling, for different aqueous solutions of *Seidlitzia rosmarinus*, inside the oil phase are presented in Figure 4. As the surfactant concentration gets higher, the resistance to drop, i.e. the interfacial tension between drop and the surrounding phase is decreased. The IFT values between the aqueous solution of *Seidlitzia rosmarinus* and oil were calculated, as discussed in the above method. The plot of IFT values for the aqueous solution of *Seidlitzia rosmarinus*/oil against the aqueous solution of *Seidlitzia rosmarinus* concentration is shown in Figure 5. The increase in surfactant concentration causes the oil/water interfacial tension to decrease. As shown in Figure 5, beyond a critical point called Critical Micelle Concentration (CMC) of about 8% by weight, little change in interfacial tension is observed. This is due to the fact that surfactant added in excess of CMC participates in micelle formation and does not increase the concentration at the water/oil interface. At concentrations above CMC, the chemical flooding process would have a better recovery because of the significant decrease occurred in interfacial tension values.

3.1. Comparison of *Seidlitzia rosmarinus* with other common surfactants

There are several synthetic surfactants available in the literature, which are prepared in several different formulations, to improve the surfactant interfacial activity. These surfactants are quite common in the oil industry and some are presented for the purpose of comparison, as illustrated in Figure 6. Here, Surfactin, a biosurfactant derived from waste water and agricultural residues [10], and Zyziphus Spina Christi, a natural

Figure 4: Drop shape before falling of aqueous solution of *Seidlitzia rosmarinus* hanging drop.Figure 5: Interfacial tension for different aqueous solution of *Seidlitzia rosmarinus* concentrations at 32 °C and 14.504 psi.

surfactant derived from a Middle-eastern plant with a similar name [11], were also compared with *Seidlitzia rosmarinus*.

As shown in Figure 6, there is a good agreement between the measured interfacial tension values of *Seidlitzia rosmarinus* and the values for some common surfactants. This confirms the validity of the apparatus and employed method. As the concentration of *Seidlitzia rosmarinus* solution increases, a considerable reduction in oil/water interfacial tension values is observed. At a concentration of just 3000 ppm *Seidlitzia rosmarinus* causes the interfacial tension to be reduced by half. This reduction in interfacial tension is larger than the reduction caused by surfactant solutions of Amphosol CG, Formatron, Enordet, Stepantan, CS 1045, CS 1040, Stepantan and Formatron, and Zyziphus Spina Christi. Therefore, this validates the fair surfactant properties of *Seidlitzia rosmarinus* as a surfactant in chemical flooding.

4. Conclusions

1. Addition of the saponin-containing powder of *Seidlitzia rosmarinus*, as a natural cationic surfactant, imposes a considerable decrease in oil/water interfacial tension.

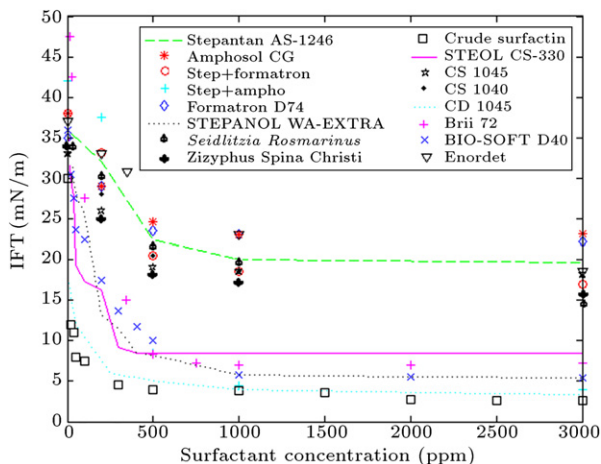


Figure 6: Comparison of IFT variation vs. surfactant concentration with some common surfactants: STEOL CS-330 or Sodium laureth sulfate, STEPANOL WA-EXTRA or Sodium dodecyl sulfate, BIO-SOFT D40 or Sodium dodecylbenzene sulfonate, Crude Surfactin done over Soltrol 130 [12], CD1045, CS 1045, CS 1040, Amphosol CG, Stepantan AS1246, Formatron D74, Enordet, Ampho [13], Brij 72 [14], Zizyphus Spina Christi [2].

- The *Seidlitzia rosmarinus* plant is widely available in desert areas of the Middle East and Central Asia, so that a high surface activity surfactant can be obtained at a low price. Accordingly, the feasibility of using this surfactant in the chemical enhanced oil recovery processes of the petroleum industry is of major concern.
- The CMC value of about 8% by weight, which was obtained from the plot of interfacial tension versus concentration of *Seidlitzia rosmarinus*, can be used as the prevailing concentration in future oil recovery feasibility studies.

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