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Toward mechanistic understanding of natural surfactant flooding in enhanced oil recovery processes: The role of salinity, surfactant concentration and rock type

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ABSTRACT

Surfactant flooding has emerged as an interesting enhanced oil recovery (EOR) process due to wettability alteration and reduction of oil-water interfacial tension (IFT). Environmental concerns and high cost, cause synthetic surfactant flooding to become expensive and uneconomical in some circumstances. Natural surfactants are environment-friendly and less expensive than synthetic surfactants which recently have been proposed as alternatives for synthetic surfactants in EOR processes. However, the exact mechanism behind natural surfactant flooding as EOR process is an unsettled and complex issue that has not been completely understood. In this communication, the use of natural surfactants as an alternative for synthetic surfactants for wettability alteration of oil-wet rocks in EOR processes was investigated. Through the wide range of experiments, the performance of a natural surfactant named Cedar in the wettability alteration of carbonate and sandstone rocks was deeply studied. Moreover the effect of natural surfactant on oil-water interfacial tension was compared with common used synthetic surfactants. The results showed that Cedar is very efficient in wettability alteration of both carbonate and sandstone rocks and its effect is comparable with common used synthetic surfactants. In addition, it was found that the cationic surfactant is more effective than anionic surfactants in wettability alteration of carbonate reservoirs. On the other hand, the anionic surfactants are very effective in sandstone rocks. In addition, two distinct trends were observed for wettability alteration of surfactants at different salt concentrations. When the head of surfactant and rock surface carries the same charge, there is an optimum salinity for wettability alteration. Finally, the core flooding experiments demonstrated that natural surfactant can increase oil recovery efficiently.

1. Introduction

Primary recovery refers to the initial production of hydrocarbons from an underground reservoir accomplished by the use of natural reservoir energy. The natural energy of a hydrocarbon reservoir is sufficient to produce only a small fraction of the initial hydrocarbons in place (normally around 5–15%). Even in the secondary recovery stage, with methods like water and gas flooding, total oil recovery is still far behind the initial oil in place. The remaining oil is a large and attractive target for enhanced oil recovery (EOR) techniques in the oil fields.

Capillary number and mobility ratio are two main variables that have a direct impact on EOR processes. EOR methods attempt to increase oil recovery by reducing mobility ratio and/or increasing capillary number. Low interfacial tensions can increase capillary number and have been shown to be favorable to extract residual oil [1]. Surfactants are widely used for this purpose [2–4] and it is proposed that correctly designed surfactant systems together with the crude oil, can create micro-emulsions at the interface between crude oil and water; thus, reduces the interfacial tension, which consequently will mobilize the residual oil and result in improved oil recovery [5]. Furthermore, surfactants can alter surface wettability from oil-wet to water-wet [6–11] which is favorable for oil recovery.

Surfactants, in general, are classified into four main classes of anionic, cationic, nonionic and amphoteric or zwitterionic based on their dissociation in water [12]. Wettability alteration of anionic [9,11,13–15], cationic [9,10,16–18] and nonionic [19–23] surfactants has been widely investigated and their effectiveness in wettability alteration of oil-wet rocks is well-established.

The major limitation of synthetic surfactants is their cost. Synthetic surfactants are expensive, which causes surfactant flooding processes to become quite expensive and uneconomical in some circumstances. Moreover, in terms of environmental issues, there are ever increasing concern about the effects of the surfactant on the environment [24]. One alternative for synthetic surfactants is natural surfactants. Natural

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Table 1
General specifications of the crude oil.

Specification	Unit	Value
Gravity of dead oil	API	27.9
Viscosity of oil at room temperature	m.Pa.Sec	3.34
H_2S	(Mole fraction)	0
CO_2	(Mole fraction)	0
C_1	(Mole fraction)	0
C_2	(Mole fraction)	0.0008
C_3	(Mole fraction)	0.0172
iC_4	(Mole fraction)	0.0070
nC_4	(Mole fraction)	0.0265
iC_5	(Mole fraction)	0.0179
nC_5	(Mole fraction)	0.0179
C_6	(Mole fraction)	0.0927
C_7	(Mole fraction)	0.0752
C_8	(Mole fraction)	0.0919
C_9	(Mole fraction)	0.0740
C_{10}	(Mole fraction)	0.0557
C_{11}	(Mole fraction)	0.0466
C_{12}^+	(Mole fraction)	0.4766
C_{12}^+ molecular weight	–	418
Sp.Gr. of C_{12}^+ fraction @ 15/15 °C	–	0.9459
Saturation pressure of live oil @ 43.3 °C	MPa	6.98
Solution gas oil ratio of live oil @ 43.3 °C	M^3/M^3	59.48

Fig. 1. Samples of rock slices with 0.5 cm thickness and 3.79 cm diameter which has been cut from the selected core samples.

surfactants are environment-friendly and less expensive than synthetic surfactants.

Natural surfactants are taken directly from natural sources such as plants or animal origin which can be obtained with a separation procedure like extraction [25]. Saponins are the main source of plant based natural surfactants. Saponins are high-molecular-weight glycosides and considered as natural surface-active materials which have detergent properties and can produce stable foam in water [26]. More recently, potential of several natural surfactants for decreasing oil-water interfacial tension was evaluated [27–29]. Shadizadeh and kharrat [25] introduced *Matricaria chamomilla* as a new natural surfactant for reducing oil-water interfacial tension. In other studies, Arabloo and coworkers investigated the application of saponin-surfactants in different area of petroleum industry [21,30]. Very recently, Arabloo et al. [31] studied the adsorption behavior of a natural surfactant onto

Table 2
Physical and geometrical properties of the core samples.

Permeability (mD)	Porosity (frac.)	Length (cm)	Diameter (cm)
61	0.21	6.53	3.79

sandstone rocks. They evaluated the performance of isotherm and kinetic models for the natural surfactant. However, the effect of natural surfactants on wettability alteration of oil-wet rocks is rarely evaluated. Type and concentration of surfactant, oil composition, brine salinity and type of the rock are main variables in the wettability alteration with surfactants [32].

To the best of the authors' knowledge, very few researches delved into the performance of natural surfactant in wettability alteration of different rocks. In this study, the performance of a natural surfactant extracted from leaves of Zizyphus Spina-Christi trees (Cedar) in wettability alteration of different rocks, including calcite, dolomite, and sandstone, is compared with synthetic surfactants at various surfactant concentrations and brine salinities. To this end, contact angle is measured on different rock slices. In addition, an axisymmetric drop shape analysis (ADSA) is utilized to measure the equilibrium IFT between different surfactants and crude oil. Afterward, the IFT behavior and wettability alteration of a natural surfactant is compared with conventional surfactants (three common used synthetic surfactants, Cetyl Trimethyl Ammonium Bromide (CTAB) as a cationic surfactant, Sodium Dodecyl Sulfate (SDS) and Sodium Alpha Olefin Sulfate (AOS) as anionic surfactants) in a wide salinity range (0 to 15 wt%). Finally, the performance of different kind of surfactants (both synthetic and natural) on increasing oil recovery in an oil-wet carbonate core sample is investigated using core flooding experiments.

2. Experimental section

2.1. Materials

2.1.1. Crude oil

In all experiments, stock tank oil of one of Iranian oil reservoir was used as oleic phase which its general properties are given in Table 1.

2.1.2. Brine solution

Sodium chloride (NaCl), with purity of 0.99 which was supplied by Merck Company, is used to prepare different concentrations of the aqueous phase in the experiments.

2.1.3. Surfactants

Three common used synthetic surfactants, Cetyl Trimethyl Ammonium Bromide (CTAB) as a cationic surfactant, Sodium Dodecyl Sulfate (SDS) and Sodium Alpha Olefin Sulfate (AOS) as anionic surfactants and a natural surfactant which was extracted from leaves of Zizyphus Spina-Christi trees (Cedar) are used in this study. Zizyphus Spina-Christi is a tree generally grown in dry parts of tropical regions of Asia and Africa and contains high concentration of saponins [33].

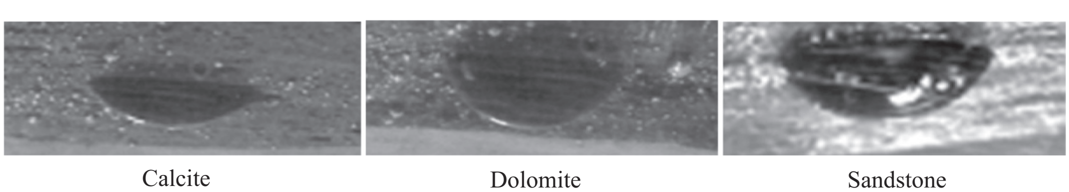

Fig. 2. Wettability status of rock surfaces after aging.