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Full Length Article

Wettability modification, interfacial tension and adsorption characteristics of a new surfactant: Implications for enhanced oil recovery

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HIGHLIGHTS

- Physico-chemical characteristics of a new eco-friendly surfactant is studied.
- Freundlich model can better describe the equilibrium adsorption data.
- Multilayer coverage of surfactant onto the sandstone particle surfaces is more probable.
- Adsorption data are better represented by the pseudo-second order kinetic model.
- Kinetics of adsorption is a multi-step process.
- Both intraparticle diffusion and film diffusion mechanisms are involved.
- Studied surfactant could modify the wettability of reservoir rock.

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ABSTRACT

This paper concerns with the interfacial tension (IFT), wettability modification and adsorption behavior of a new plant-based surface active agent, Zizyphus Spina Christi, onto sandstone minerals which has been rarely attended in the available literature. Both kinetics and equilibrium adsorption data were obtained from batch mode tests. It was revealed that Freundlich isotherms matched better fit to the equilibrium data which implied that multilayer coverage of Zizyphus Spina Christi onto the sandstone particle surfaces was more likely to occur. Analysis of experimental kinetic data based on intraparticle diffusion model disclosed that the intraparticle diffusion mechanism is not the only rate limiting step and the boundary layer diffusion or surface adsorption also contributes to the rate-controlling step. The reservoir rock wettability modification was evaluated on sandstone-oil phase–water system by change of surfactant concentration, time and solution salinity. The results of this work help toward a clearer understanding the impact of various influencing parameters on the efficiency of a surfactant flooding project.

1. Introduction

During the primary stage of oil recovery, natural drive energy of the reservoir declines and considerable amount of oil is remained uncovered [1]. Injection of water and/or gas as the external driving energy is aimed to maintain reservoir pressure and push more oil through reservoir toward production wells. However, primary and secondary recovery processes usually recover about one-third of the initial oil in place [1]. In order to mobilize the residual oil, most of the enhanced oil recovery approaches rely on decreasing the interfacial tension (IFT) between injection water and reservoir oil [2–5]. Examples of EOR (Enhanced Oil Recovery) methods employing surface active agents include, surfactant/polymer, alkaline/surfactant/polymer and foam flooding [2,4–6]. Addition of surfactant to the injected water reduces the oil/water IFT and change wettability of reservoir rock and thus enhances oil recovery [1]. Both processes are capable of increasing oil production. Surfactant-based chemical injection has been applied for several oil reservoirs around the world [7–11]. However one of the main issues encountered during a flooding process involving surfactant is the adsorption onto reservoir rock [3]. The loss of surfactant from the main chemical slurry affects technical and economic efficiency of flooding process [12,13]. Therefore, attainment of a deep and thorough data regarding the retention behavior

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Nomenclature

AARE	average absolute relative error
ARE	average relative error
b	parameter in Temkin isotherm model
B	constant in Temkin isotherm model
C_e	equilibrium concentration of adsorbate in solution
C_t	concentration of adsorbate at time, t
CMC	critical micelle concentration
C_0	initial concentration of adsorbate in solution
EC	electrical conductivity
exp	experimental
I	constant in intraparticle diffusion model
k_1	rate constant of pseudo-first order kinetic model
k_2	pseudo-second order adsorption rate constant
k_{ip}	intraparticle diffusion rate constant
k_f	Freundlich isotherm constant
k_l	Langmuir isotherm equilibrium binding constant
k_t	Temkin isotherm constant
m_{sol}	mass of solution (g)
m_{sand}	mass of sandstone (g)
n	exponent in Freundlich isotherm
Q_0	theoretical monolayer capacity of Langmuir isotherm
q_e	amount of adsorbate adsorbed at equilibrium
q_t	amount of adsorbate adsorbed at time, t
R	universal gas constant
R^2	coefficient of determination
t	time (min)
T	absolute temperature (K)

Greek symbols

α	initial sorption rate in Elovich model
β	desorption constant in Elovich model

of surfactant based fluid in the porous media is essential for having an optimized and successful EOR project.

During the past decades several authors have been focused on the determination of adsorption mechanisms and the various parameters involved in the surfactant adsorption [14–19]. The general conclusion is that the surfactant adsorption can be greatly affected by surfactant type as well as mineralogical characteristics of porous medium [3,20]. In between, several authors have examined the role of presence of electrolyte in the solution [21–23].

In addition to problems associated with surfactant loss, detrimental environmental effects as well as economic aspects of currently used chemical surfactants have resulted chemical based EOR process so expensive and in some case impracticable [24,25]. Although the adsorption behavior of chemically synthesized surfactants has been previously reported by many researchers, an investigation on the interpretation of adsorption data of bio-surfactants has not been well understood. Thus, there is a need to identify and study the physico-chemical characteristics of biosurfactant which is potentially good candidate for application in petroleum industry. Applications of naturally occurring surfactants in various areas of petroleum industry have been debated by some researchers [24,26–29]. However, a little attention has been paid on modeling of equilibrium and kinetic adsorption of biosurfactant onto reservoir rocks despite its practical significance. Surprisingly, very limited works have been carried out to elucidate the behavior responsible for wettability alteration of sandstone surface in the presence of plant-based surfactant solutions. Therefore, the primary objective of this article is to study the adsorption behavior of a special kind of plant-based surface active agent onto sandstone rock and also to monitor its effectiveness in modifying surface properties of the reservoir rock. The kinetic and equilibrium models involved in the sorption process were evaluated in detail. Thus this article is organized as follows: in the following section, the details of experimental works are illustrated. In Section 3, the experimental results are presented. In this section we will discuss the detailed studies on the wettability alteration, interfacial tension and adsorption behavior of plant-based surfactant solutions. Finally, key findings of the present study are outlined in Section 4.

2. Experimental

2.1. Saponin

The plant's saponins are naturally occurring triterpene or steroid glycosides that hold some pharmacological and biological activities. They contain either a steroidal or a triterpenoid aglycone to which one or more glycoside chains are attached [30]. Zizyphus Spina Christi (Rhamnaceae) is a native tree to the subtropical and warm-temperate regions of the Mediterranean, North Africa, tropical America, Australia, Middle East and southern Asia [24,31]. In our study, the leaves of this tree were collected from trees growing at the south of Iran and the saponin was extracted by spray drying technique [32,33]. Spray drying is a widespread technique in industry to produce a dry powder by drying the liquid slurry by hot air [32]. In this process, the liquid input stream is sprinkled or showered by a nozzle into a hot vapor stream. When the slurry solution is exposed to the hot air, moisture is evaporated from the particle surface and thereby a particle forms and falls to the bottom of the drum. Then, the accumulated powder in the drum is recovered from the exhaust gas. This process is a relatively low cost, flexible and leads to production of stable and high quality particles [32,33]. In our study, the extract powder is light brown and is soluble in alcohol and water. Some physico-chemical characteristics of Zizyphus Spina Christi are given in Table 1. Fig. 1 shows a representative molecular structure of surface active agent in the extract of Zizyphus Spina Christi [34].

2.2. Sandstone rock sample

The used rock sample was provided from a local formation in south of Iran. Then, it was crushed and sieved in a standard way for adsorption tests.

2.3. Preparation of testing solutions

Surfactant solutions were prepared by adding Zizyphus Spina Christi powder in 30 ml of deionized water. After addition of Zizyphus Spina Christi, all of the solutions were sonicated for optimum time of 30 min in a sonicator. A stock solution was prepared

Table 1
Physico-chemical characteristics of extract powder of Zyziphus Spina Christi.

Characteristics	
Color	Light brown
Solubility	Soluble in water; Soluble in alcohol
Density	0.13 (g/cm^3)
pH (8.0 wt.% solution)	5.1
Loss on drying @ 110 °C after 6 h	8.5%
Total ash @ 550 °C after 4 h	15.62%