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Adsorption of a new nonionic surfactant on carbonate minerals in enhanced oil recovery: Experimental and modeling study

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ABSTRACT

Surfactants have ability to mobilize the residual oil trapped in porous medium and resulting higher oil recovery by altering interfacial tension between residual oil and water. However, adsorption of surfactant onto the solid surface reduces the concentration of surfactant and makes it less effective in interfacial tension reduction in enhanced oil recovery (EOR) applications. This study highlights equilibrium adsorption and kinetics of Trigoonella foenum-graceum as a newly introduced nonionic surfactant on carbonate minerals. Conductivity technique was used to measure the amount of surfactant adsorbed on crushed rock. Batch experiments were used to investigate the adsorption of surfactant on solid rock surface. The results demonstrated that increasing surfactant concentration increases the adsorption. Four adsorption isotherms (Langmuir, Freundlich, Temkin, and Linear) were introduced to resulted data and their adsorption parameters were calculated. It can be concluded that the Langmuir isotherm is the best model for describing the data. The experimental adsorption kinetic data were evaluated by three well-known models (pseudo-first-order, pseudo-second-order and intra particle diffusion models). According to correlation coefficients it was found that the pseudo-second-order model was fitted to the data very well. The results of this study can be useful in surfactant selection in EOR processes especially for chemical flooding schemes.

1. Introduction

Carbonate reservoirs contain great number of oil reserves in the world. The recovery factor from these reservoirs in primary and secondary production stages is about 45%. Tertiary recovery techniques should be used in order to mobilize the residual oil saturation and gain higher oil recoveries from these reservoirs. Surfactant flooding as part of a tertiary oil recovery can be used for achieving this goal. Surfactant can mobilize the residual oil by lowering the interfacial tension between oil and water. The main problem which often can make the process of surfactant flooding uneconomical and ineffective is surfactant loss due to adsorption of surfactant on reservoir rock surface. Surfactants consist of a hydrophilic head and a hydrophobic chain. They are generally divided into four groups namely nonionic, cationic, anionic and zwitterionic. Adsorption of surfactants is a process of transferring from bulk phase to solid/liquid interface (Najafabadi et al., 2008; Ahmadi and Shadizadeh, 2012; Ahmadi et al., 2012; Achinta et al., 2013; Weifeng et al., 2011; Zendehboudi et al., 2013).

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Nomenclature

Acronyms

CMC critical micelle concentration
EOR enhanced oil recovery
PPM part per million

Variables

B Temkin constant which is related to the heat of adsorption
C surfactant concentration in aqueous solution after equilibrium (ppm)
C_e equilibrium concentration (ppm)
C^0 surfactant concentration in initial solution before equilibrium (ppm)
h initial kinetics rate (mg/g)
K_1 pseudo-first-order rate constant (h^{-1})
K_2 pseudo-second-order adsorption rate constant (g/mg h)
K_{ad} energy of adsorption (L/mg)
K_f Freundlich constant
K_H constant in linear model (L/m^2)
K_t equilibrium binding constant corresponding to the maximum binding energy (L/mg)
$m_{Carbonate}$ total mass of crushed carbonate (g)
$m_{Solution}$ total mass of solution in original bulk solution (g)
n Freundlich constant
q adsorption capacity (mg/g-rock)
q_e equilibrium adsorption (mg/g-rock)
q_0 adsorption capacity in Langmuir model (mg/g-rock)
ΔG° change in Gibbs energy (J/mol)
ΔS° change in entropy (J/mol)
ΔH° change in enthalpy (J/mol)
R universal gas constant (J/mol K)
T temperature (K)
t time (h)

Adsorption of surfactants on solid/liquid interface contains four steps. First the surfactant is adsorbed on solid by electrostatic forces between hydrophilic head of surfactant and positive and negative charges on the solid surface. Interaction between hydrophobic parts of non-adsorbed and adsorbed surfactant takes place in second step and causes further adsorption of surfactant on solid surface. Formation of microstructures called hemi-micelle is attributed to this step. In the third step increasing surfactant concentration will cause additional adsorption by hydrophobic interactions. Since the surface of solid possesses the same charge as the adsorbing surfactant ions the process of adsorption will reach a maximum value at critical micelle concentration (CMC). In final step the adsorption will remain constant (Zhang and Somasundaran, 2006; Somasundaran and Zhang, 2006). Adsorption of surfactant on solid surface depends on the characteristics of surfactant and properties of solid surface. For negatively charged solid substrates such as quartz, anionic surfactants are of interest due to less adsorption of surfactant on solid surface as a result of repulsive electrostatic forces (Bera et al., 2013). The adsorption of different types of surfactants on different solid surfaces has been reported in literature. Ahmadi and Shadizadeh (2013) investigated the adsorption of new nonionic surfactant *Zizyphus Spina Christi* on carbonate rock and applied four isotherm models to their data to obtain the appropriate model. They conclude that the adsorption increases as the concentration of surfactant increases and after that reaches a plateau which is the saturation point. The Freundlich model was the best model for their results according to correlation coefficients. Ahmadi and Shadizadeh (2012) also investigated the effect of adding nano silica on adsorption of *Z. spina Christi* on sandstone rock. They conclude that the adsorption of surfactant decreases with increasing nano silica concentration and the hydrophobic nano silica had more potential for adsorption reduction. Literature review shows that the adsorption of new nonionic surfactant Trigoonella foenum-graecum on carbonate rock is not reported. In this study the adsorption of this surfactant at different temperatures on carbonate rock is investigated. In addition, adsorption equilibrium (Langmuir, Freundlich, Temkin and Linear models) and kinetic models (pseudo-first-order, pseudo-second-order and intra particle diffusion models) were fitted to resulted data and parameters for each model were determined. Thermodynamic parameters of the adsorption process were also calculated using adsorption thermodynamic of surfactant. Calibration conductivity curve was used for determining the amount of surfactant adsorption on rock surface. Batch experiments were used to investigate the relation between surfactant concentration and adsorption density on rock surface. Results of this test can be helpful in surfactant selection in EOR schemes.

2. Materials and experimental procedures

2.1. *Adsorbent*

In order to investigate the adsorption process of new surfactant, carbonate cores were obtained from one of Iranian southwest oil fields (Aghajari oil field). These carbonate cores were obtained from Asmari reservoir in this field. Cores were crushed to small pieces by jaw crusher and were grounded into fine grains. Laboratory sieves were used to obtain particle sizes ranging from 250 μm to 300 μm. The fine grains were then washed with distilled water and dried in an oven at 100 °C for 24 h.

2.2. *Surfactant*

Trigoonella foenum-graceum (TFG) is a plant belonging to Fabaceae family. It is widely available in southwest of Asia and Mediterranean countries such as India, Iran, China, Egypt, Italy, Greece etc. The main feature of Trigoonella foenum-graceum is that its seeds contain saponins. Saponins are located in leaves, roots, seeds and hulls of many plants. They are a group of various natural surface-active compounds. Their molecules consist of a steroid or triterpene group known as aglycone which is linked to one or two sugar molecules. The presence of both non polar (sugar moiety) and polar (steroid or triterpene) groups make saponins to have strong surface-active properties. Saponins are classified into three groups (triterpene glycoside, steroidal glycosides, or steroidal alkaloid glycosides) based on the type of aglycone they contain (Kjellin and Johansson, 2010; Hostettmann and Marston, 1995; Guglu Ustundag and Mazza, 2007; Yücekutlu and Bildacı, 2008). The new surfactant was extracted by spray drier method. The seeds were extracted by methanol for 48 h using soxhlet apparatus. Then the residue was cooled to room temperature and