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A comparative study of surfactant adsorption by clay minerals

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ABSTRACT

The adsorption of surfactants from aqueous solutions in porous media is essential in enhanced oil recovery (EOR) from oil reservoirs. Surfactant loss that is due to adsorption by the reservoir rocks weakens the efficiency of the chemical slurry that is injected and decreases the oil–water interfacial tension (IFT). This project investigated the effect of the mineralogical composition of adsorbents on adsorption. The experiments were conducted in batches. Adsorbents were composed of various combinations of quartz sand and clay minerals at various percentages and were exposed to nonionic and anionic surfactants. The amount of surfactant that was adsorbed was quantified by subtracting the concentration of surfactants after adsorption from the initial concentration. We observed a direct relationship between the adsorption of the nonionic surfactant and the amount of clay minerals in the adsorbents as the amount of surfactant that was adsorbed by the adsorbents increased when the percentage of clay minerals in adsorbents increased (from 5% to 20% in the mixture). The rank order of adsorption power of clay minerals for the nonionic surfactant was montmorillonite $\gg$ illite $>$ kaolinite. Adsorption of the anionic surfactant by all adsorbents was negligible.

1. Introduction

Surfactant flooding is a method for the additional recovery of oil from partially depleted reservoirs. The mechanism of action of the surfactant system in a porous medium that is partially filled with oil and brine is poorly understood. For example, in water–wet systems, after water flooding, the oil consists primarily of isolated oil drops within the pores. To mobilize the residual oil that is trapped by capillary forces in oil reservoirs, many enhanced oil recovery (EOR) methods rely on reducing the oil–water interfacial tension (IFT) to extremely low values, e.g. 10^{-4} dyne/cm or lower (Curbelo et al., 2007). Therefore, it is important to maintain low IFT for prolonged periods of time.

The complexity of the surfactant system in the porous media increases with the effects of other parameters such as heterogeneity of the rock, interaction of the surfactants with reservoir fluids, and coalescence of the oil drops and surfactant adsorption (Curbelo et al., 2007). The surfactant flooding process, however, faces problems due to the loss of high-cost surfactant in the forms of adsorption and retention in the porous media.

The loss of surfactant from the principal chemical slurry during surfactant flooding is a primary determinant in both process performance and economy. It has been shown that the nature of the adsorption isotherm depends to a large extent on the type of surfactant that is used, the morphological and mineralogical characteristics of the rock, the type of electrolytes present in the solution, and the presence of cosurfactants and alcohols. The adsorption of surfactants can be influenced by the charge on the rock surface and fluid interfaces (Liu et al., 2004).

Recently, several authors, including Rodríguez–Cruz et al. (2005), Sánchez–Martin et al. (2008) and Zhu et al. (2003) attempted to investigate the effect of the mineralogical composition of the clay fraction on surfactant adsorption. However, the surfactant adsorption cannot be predicted based upon adsorbent attributes (Muherei, 2009). Therefore, investigating the adsorption of surfactants to rocks that vary in their lithological characteristics (e.g. mineralogy, grain size, texture, and other physical properties) is a necessary prerequisite for assessing the effectiveness of the proposed EOR.

This research was primarily focused on the experimental study of the adsorption quantity of a single surfactant by adsorbents with various mineralogical compositions in static conditions. The results of this study will provide additional insight into the feasibility of surfactant-enhanced flushing for reservoir rock (e.g. sandstone) systems and supply valuable information for the development of effective and safe surfactant-EOR technologies.

2. Materials and methods

2.1. Surfactants

One anionic surfactant (sodium dodecyl sulfate) and one nonionic (triton X-100) surfactant were used. Triton X-100

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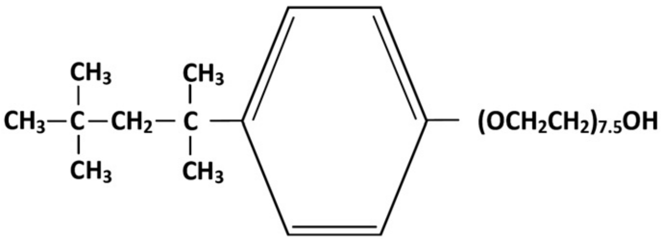

Fig. 1. Chemical structure of TX-100.

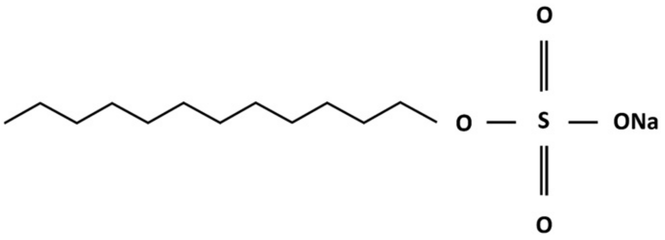

Fig. 2. Chemical structure of SDS.

(TX-100) was purchased from Scharlau, Spain, and sodium dodecyl sulfate (SDS) was supplied by Molekula, India, with a high grade of purity (99%). All chemicals were used as received without further purification. Chemical structures of these surfactants are shown in Figs. 1 and 2.

2.2. Preparation of testing fluids

The surfactant solutions were prepared in standard 1000 ml volumetric flasks. Surfactants were weighed out and subsequently dissolved in a clean volumetric flask and then, distilled water was added slowly until the proper volume is reached. Following the preparation of the stock solution, it was diluted to desired concentration. TX-100 and SDS solutions were prepared at different concentrations ranging from 0.005 wt% to 1 wt%.

2.3. Mineral samples

The samples comprise of minerals with the majority quartz, kaolinite, illite and montmorillonite. Quartz sand was collected from Teluk Ramunia, Johor, Malaysia. Kaolinite and illite were collected from Jamaluang, Johor, Malaysia, and Kuala Rompin, Pahang, Malaysia, respectively. Montmorillonite was supplied from the UK. Samples' mineralogical composition was determined by X-ray diffraction (XRD) measurements. XRD results and chemical composition of minerals are shown in Tables 1 and 2.

2.4. Surface tension measurements

The critical micelle concentration (CMC) values in different combinations of surfactant systems were determined by applying the surface tension technique. The surface tension was measured with Krüss tensiometer at constant temperature (25 ± 1 °C) (Muherei et al., 2009). In the tensiometer which operates on the Du Nouy principle, a platinum–iridium ring is suspended from a torsion balance, and the force (in mN/m) required to pull the ring off the surface film is measured. The tensiometer calibration and surface tension measurement were carried out according to the methods described in ASTM Designation: D1331-89.

Table 1
XRD results of quartz sand and clay minerals samples.

Sample no.	Mineral composition					Total
	Quartz	Kaolinite	Feldspar	Illite	Montmorillonite	
Quartz–Std	~100	–	–	–	–	~100
Quartz–Smp	~100	–	–	–	–	~100
Kalin–Std	~5	~90	–	~5	–	~100
Kalin–Smp	~27	~40	~3	~30	–	~100
Illite	~35	~20	–	~45	–	~100
Montmorillonite	~5	–	–	~5	~90	~100

Abbreviations: Std = standard; Smp = sample.

Table 2
Chemical composition of quartz and clay minerals.

Minerals	General chemical formula	Chemical structure
Quartz	SiO_2	SiO_4 tetrahedra, with each oxygen being shared between two tetrahedra, giving an overall formula SiO_2
The kaolinite group	$Al_2Si_2O_5\ (OH)_4$	Silicate sheets (Si_2O_5) bonded to aluminum oxide/hydroxide layers ($Al_2(OH)_4$) called gibbsite layers (s–g)
The illite group	$(K, H)Al_2(Si, Al)_4O_{10}(OH)_2-xH_2O$	Silicate layers sandwiching a gibbsite layer in between (s–g–s)
The montmorillonite group	$(Ca, Na, H)(Al, Mg, Fe, Zn)_2(Si, Al)_4O_{10}(OH)_2-xH_2O$	Silicate layers sandwiching a gibbsite layer in between (s–g–s)

Surface tension value was taken when constant reading was acquired for a given surfactant concentration by at least three consecutive measurements having nearly the same value. The average of a series of consistent readings for each sample was then corrected to account for the tensiometer configuration, yielding a corrected surface tension value (Zuidema and Waters, 1941). A correction factor, F, is multiplied by the average dial reading in order to obtain the corrected value for surface tension (Muherei and Junin, 2007). Zuidema and Waters (1941) proposed the following empirical correlation (Eq. (1)) to calculate the correction factor:

$$F = 0.725 + \sqrt{\left[\frac{9.075\times 10^{-4}(ST or IFT)}{\pi^3 \Delta\rho g R^3} - \frac{1.679r}{R} + 0.04534\right]} \tag{1}$$

where, F is the correction factor; R the radius of the ring, in cm; r the radius of the wire of the ring, in cm; ST the apparent value or dial reading, in m N/m; $\Delta\rho$ the density difference between the lower and upper phases, in g/cc; g the acceleration due to gravity, 980 cm/s^2. This equation is applicable only when $0.045 \le \Delta\rho g R^3/(ST) \le 7.5$.

2.5. CMC determination by surface tension measurements

Following the surface tension measurement, the surface tension values were plotted versus the surfactant concentration so as to determine the CMC. The CMC matches to the concentration where the surfactant first shows the lowest surface tension (Muherei and Junin, 2007). The surface tension remains relatively constant after this point.

2.6. Adsorption study

The quartz sand and clay minerals were mixed together on mass basis following the weight percentages presented in Table 3. A 60-ml solution containing varying amounts of surfactant and 10 g of the sand and clay mixture was added to a 250-ml flask and then shaken on a gyratory to achieve equilibrium. After