



# Influences of hydrophilic and hydrophobic silica nanoparticles on anionic surfactant properties: Interfacial and adsorption behaviors

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## ABSTRACT

Regarding the novel applications of nanoparticles in enhanced oil recovery, the objective of this study is to investigate if nano-sized silica particles have the potential to introduce enhancement in several aspects of surfactant properties particularly its interfacial and adsorption behaviors. Two types of hydrophilic and slightly hydrophobic fumed silica nanoparticles are used in conjunction with sodium dodecyl sulfate. Extensive series of interfacial tension and adsorption measurement experiments are performed. The results indicate that surfactant interfacial and adsorption properties are interestingly influenced by the addition of silica particles. Inclusion of both nanoparticles into surfactant solution causes contrasting interfacial behaviors in low and high surfactant concentrations. The adsorption of surfactant molecules on the rock surface is generally reduced in the presence of nanoparticles except for some highly concentrated surfactant solutions.

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## 1. Introduction

Application of nanotechnology has been very limited in petroleum industry. However, in recent years, the importance of nanoscience to develop conventional methods in several branches of petroleum engineering has been highlighted. Lately, several aspects of the likely benefits of novel nano-tech based agent in smart fluid design for various oil field applications have been described, particularly for a new generation of drilling (Sensoy et al., 2009), fracturing (Crews and Huang, 2010; Huang and Clark, 2012), completion and stimulation fluids (Crews and Huang, 2008; Huang et al., 2011).

Reservoir engineering, however, has received the most attention for nanotechnology applications. Several experiments have been conducted to investigate flow behavior of nanoparticle suspensions through porous media. Rodriguez et al. (2009) investigated the migration of concentrated surface treated silica nanoparticles in sedimentary rocks. Kanj et al. (2009) identified the usable size of nanoparticles in reservoir rocks through Nano-fluid core flooding experiments. Using hydrophilic/hydrophobic synthesized nanoparticles, Zhang et al. (2011) made oil in water emulsions and stabilized CO<sub>2</sub> foams with quite high stability.

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Despite the considerable surveys investigating different applications of nanotechnology in reservoir engineering and enhanced oil recovery techniques, far too little attention has been paid to utilization of surfactant/nanoparticle systems as a novel surface-modifier chemical agent in chemical flooding and the studies usually subsume interfacial behavior of various types of surfactants in the presence of nanoparticles. Esmaeilzadeh et al. (2014) have investigated the influence of ZrO<sub>2</sub> on interfacial behavior of surfactant solutions. According to their results inclusion of nanoparticles augments the surface activity of negatively charged surfactant, sodium dodecyl sulfate (SDS), below its critical micelle concentration (CMC) and as a result it decreases the interfacial tension between oil and water. Ma et al.'s data (Ma et al., 2008), accordingly, presents interfacial tension reduction of anionic surfactant, SDS, in the presence of silica nanoparticles. They introduced the electrostatic repulsion between similarly charged particles and surfactant as the main reason for such behavior. The inclusion of silica nanoparticles in cationic surfactant solution, on the other hand, increases interfacial tension in liquid–air and liquid–liquid media (Ravera et al., 2006). This behavior is ascribed to the adsorption of nanoparticles in specific concentrations and formation of nanoparticle augmented surfactant layer. This result is inconsistent with observations of Lan et al. (2007) in which they studied the effect of silica nanoparticles on cetyltrimethyl ammonium bromide's surface activity. Their result has been heralded as the lowering impact of nanoparticles on interfacial tension which is attributed to electrostatic attraction between negative nanoparticles and positive surfactant.

Although the studies conducted on interfacial behavior of surfactants in the presence of nanoparticle are quite valuable, a mechanistically engineering approach considering alteration of dominant factors in surfactant flooding in the presence of nanoparticle is still missing.

This paper is aimed at studying SDS anionic surfactant solution properties in the presence of hydrophilic and slightly hydrophobic silica nanoparticles. The main focus is on surfactant interfacial and equilibrium adsorption behaviors since a successful chemical flooding entails having favorable fluid–fluid and fluid–rock behavior. Several hypotheses describing various interface phenomena are used to explain the obtained results.

## 2. Experimental work

This section contains the information about materials and experimental procedures used in this study. All the experiments were performed at ambient conditions (temperature of 30 °C and atmospheric pressure).

### 2.1. Materials

The following materials were used in the experiments.

#### 2.1.1. Surfactant

The surfactant used in this study was an anionic surfactant named Sodium Dodecyl Sulfate (SDS) bought from Merck Company. The CMC value of anionic surfactant was determined to be approximately 2200 ppm using conductivity measurement technique. The CMC value was relatively close to those given in literature (Atkin et al., 2003).

#### 2.1.2. Nanoparticles

Two types of nanoparticles, hydrophilic and slightly hydrophobic silica nanomaterials, were used. Both nanoparticles were supplied by Degussa industries (Evonik). Well-characterized fumed Silica, AEROSIL 300 (A300), was the hydrophilic nanoparticle. These colloidal particles are prepared by hydrolysis of silicon tetrachloride in which silanol groups (Si–OH) are generated on silica surface. The second nanoparticle used was slightly hydrophobic type commercially named AEROSIL R816. AEROSIL R816 is fumed silica (AEROSIL 200) after treated with hexadecylsilane (C16H33) hydrophobic groups. Table 1 represents some physico-chemical properties of nanoparticles used in this study. It must be mentioned that both nanoparticles have amorphous structures and are approximately spherical in shape and their average size is of order of few nanometers as observed in TEM images represented in Fig. 1.

#### 2.1.3. Rock sample

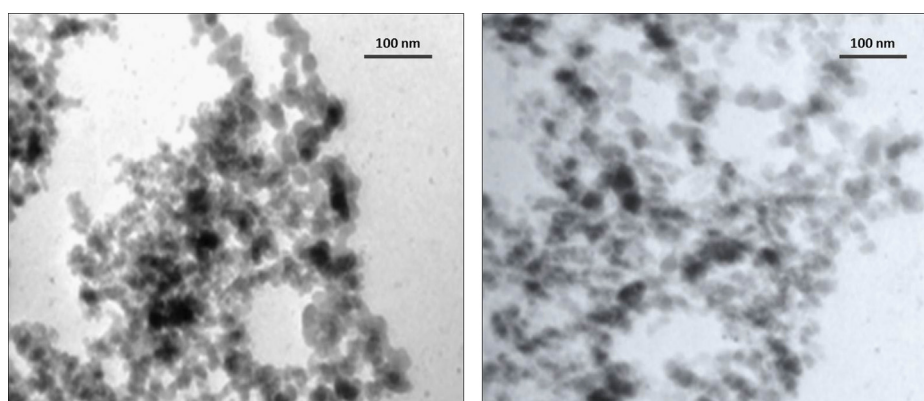
Sandstone samples of one of Middle East reservoirs were used. Based on petrographic studies, the rock mainly consisted of quartz, feldspars and minor amount of accessory minerals like zircon and sphene. Sand rocks were initially crushed into small rock fractions into single grains using a mortar and pestle. The resulting sand was sieved using meshed sieves under the agitation of a Ro-Tap Testing Sieve Shaker. The sand grains of appropriate size (400–500 µm) were gathered and carefully washed with distilled water and dried in an oven at 150 °C for three hours.

### 2.2. Experiments

Several experiments were conducted which are explained below.

**Table 1**  
Physico-chemical properties of nanoparticles used in this study.

Property	Unit	Typical value for AEROSIL 300	Typical value for AEROSIL R816
Behavior in the presence of water	–	Hydrophilic	Slightly hydrophobic
Appearance	–	Fluffy white powder	Fluffy white powder
BET surface area	m <sup>2</sup> /g	300 ± 30	190 ± 20
Average primary particle size	nm	7	12
Tamped density	gr/l	50	60
PH value	–	3.7–4.7	4.0–5.5
C-content	wt%	–	0.9–1.8
SiO <sub>2</sub>	wt%	≥ 99.8	≥ 99.8
Al <sub>2</sub> O <sub>3</sub>	wt%	≤ 0.050	≤ 0.050
Fe <sub>2</sub> O <sub>3</sub>	wt%	≤ 0.003	≤ 0.010
TiO <sub>2</sub>	wt%	≤ 0.030	≤ 0.030
HCl	wt%	≤ 0.025	≤ 0.025



**Fig. 1.** TEM images of nanoparticles used; (left) hydrophilic nanoparticle, (right) slightly hydrophobic nanoparticles.

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