



Evaluation of a surfactant carrier for the effective propagation and target release of surfactants within porous media during enhanced oil recovery. Part I: Dynamic adsorption study

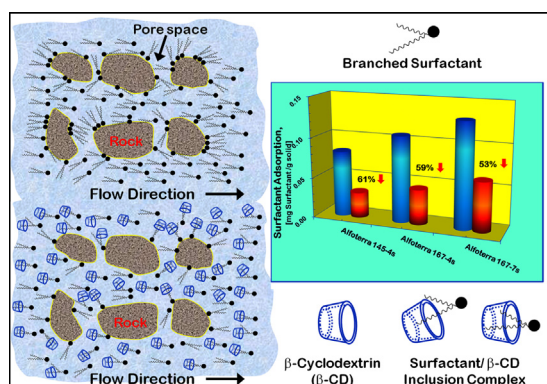
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HIGHLIGHTS

- Complexation between commercial EOR surfactants and β -CD was confirmed.
- The surfactant carrier is effective in inhibiting the adsorption of surfactant.
- Surfactant adsorption was inhibited up to 61% relative to the conventional process.
- The surfactant carrier shows potential for enhanced oil recovery applications.

GRAPHICAL ABSTRACT



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ABSTRACT

This proof of concept research evaluates a new approach to prevent the adsorption of surfactant onto a sand/kaolin blend. This process is based on the formation of inclusion complexes between surfactants and β -cyclodextrin (β -CD). First, the kinetics and formation of surfactant/ β -CD inclusion complexes was determined using several analytical techniques including optical and scanning electron microscopy (SEM) and ^1H NMR and Fourier transform infrared (FTIR) spectroscopy. Next, the effectiveness of this method in preventing surfactant adsorption was evaluated using dynamic adsorption tests and the Quartz Crystal Microbalance Technology (QCM-D). The experimental results demonstrate the formation of equimolar surfactant: β -CD inclusion complexes in soft brine; while the dynamic adsorption evaluation shows significant reductions of surfactant adsorption onto a sand/kaolin blend of up to 61%. This exploratory study showcases the potential of this technique for minimizing the loss of surfactant to adsorption.

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1. Introduction

Surfactant flooding is an enhanced oil recovery approach for improving oil productivity from mature fields. As stated by Pope

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(2011), the primary goal of adding surfactants to the injection water is to lower the interfacial tension (IFT) to ultra-low values (≈ 0.001 mN/m), at which essentially all of the oil trapped by capillary forces can be displaced [1]. Ultra-low IFT takes place when the interactions between surfactant, oil, and water reach an exact equilibrium of affinities, condition at which, the capillary number is high enough to promote the mobilization of residual oil drops trapped at pore level [2,3]; the lower the interfacial tension the

higher the oil solubilization in the microemulsion phase [4]. The lowest IFT values are achieved at the optimum formulation; nevertheless a small variation of the formulation from the optimum causes an increase of IFT from the minimum value. Consequently, during surfactant flooding, an accurate control of the surfactant slug is necessary to ensure a good performance. Furthermore, in field applications the achievement of ultra-low IFT does not guarantee the establishment of miscible displacement as anticipated; therefore the surfactant slug displaces oil and water flowing together ahead of the surfactant front [5]. Surfactant flooding has been extensively studied over the last decades [6–16].

Surfactant retention during chemical flooding is caused by a number of mechanisms, such as surfactant precipitation due to interactions with formation water, surfactant diffusion into dead-end pores, surfactant partition into the oil phase, and surfactant adsorption onto the solid–liquid interface. Surfactant retention is affected by several factors including the surfactant chemical structure, the mineralogical composition of rocks, and the presence of electrolytes in the reservoir brine, among others. The adsorption of branched alcohol propoxylated sulfate anionic surfactants onto rock surfaces has been studied by several researchers [14,17–22].

The formation of noncovalent host–guest inclusion complexes with β -CD is well-known and the complexation between β -CD and various types of guests (i.e. surfactants) have been studied using several analytical approaches. Furthermore, β -CD is the most commonly used cyclodextrin due to its availability and affordability for industrial applications [23–32].

The objective of this exploratory study was to evaluate the functionality of surfactant: β -CD inclusion complexes in preventing surfactant adsorption onto a sand/kaolin solid blend.

2. Materials and experimental methods

2.1. Materials

2.1.1. Brine

A sodium chloride solution of (NaCl 2 wt%) was used as soft brine (pH = 7.43 \pm 0.29). NaCl was purchased from Windsor-The Canadian Salt Company Limited (Pointe-Claire, Quebec); its composition is provided elsewhere [33].

2.1.2. Surfactants

Four monoalkyl branched alcohol propoxy sulfate anionic surfactants-sodium salts (Table 1) were provided by Sasol North America Inc. (Houston, TX, USA). Fig. 1 illustrates the generic structure of the Alfoterra surfactant series [34].

2.1.3. β -Cyclodextrin

β -CD (assay = 98 wt%, molecular weight = 1135 g/mol) was purchased from Cyclodextrins Technology Development Inc. (Gainesville, Florida, USA). Its solubility in water at 25 °C is 1.85 wt% [31].

2.1.4. Solid material

A solid blend of 5 wt% kaolin + 95 wt% sand was used. Kaolinite and sand were acquired from Matheson Coleman & Bell Company (Gardena, CA, USA) and Shaw Resources Company (Milford, Nova

Scotia, Canada) respectively. The pore size distributions of these solid materials were determined by the sieve method (ASTM E 11-04) [43]. The BET technique (Autosorb-1; Quantachrome) was used to determine the surface area and the mineralogical compositions were determined via X-ray diffraction (XRD). Table 2 summarizes these results.

The surface charge of the solid substrate has an important effect on surfactant adsorption. Table 2 shows that sand contains 74.3% of quartz, which carries a positive charge at low pH, while at neutral and higher pH values, quartz surface is negatively charged and at this condition it tends to adsorb simple organic compounds [8,35,36]. Moreover, muscovite displays a negative surface charge at low pH and positive charge at high pH [37,38]. The surface charge of sylvite is negative at pH < 10.5. At neutral pH, kaolinite presents negative charges on the face and positive charges at the edges [39]. Furthermore, the siloxane and hydroxyl structures on the surface of kaolinite interact differently with interfacial water molecules. Thus, siloxane structures show weakly interactions with interfacial water molecules; while hydroxyl groups strongly interact via hydrogen bonding with interfacial water molecules [40].

2.2. Experimental methods

2.2.1. Critical micelle concentration determination

The critical micelle concentration (CMC) of the surfactants in free- and complex-state was determined in soft brine following the conventional surface tension method at 25 \pm 1 °C using a TensioCaD tensiometer manufactured by CAD Instruments (Les Essarts Le Roi, France).

2.2.2. Inclusion complex formation: stoichiometric ratios and binding constant

The stoichiometric ratios and the binding constants of the surfactant/ β -CD inclusion complexes were determined following the approach presented by Lu et al. and Okubo et al. [25,41].

2.2.3. Characterization of the surfactant/ β -CD complexation

Alfoterra 167-4s was used for the characterization of the surfactant/ β -CD inclusion complex following the procedure presented by Yallapu et al. [42]. The detailed experimental procedure can be found in Kittirisawai [43].

2.2.3.1. Optical microscopy: guest/host compatibility determination. A compact inverted metallurgical microscope model Olympus GX41, manufactured by Olympus (Center valley, PA, USA) was used. The images were taken at 200 \times magnification.

2.2.3.2. Scanning electron microscopy (SEM). Scanning electron microscopy (SEM) was used to study the compatibility between surfactant and β -CD as well as the surface morphology of the inclusion complex using a scanning electron microscope, Model SU-70 manufactured by Hitachi (Tokyo, Japan).

2.2.3.3. ^1H Nuclear magnetic resonance (^1H NMR) spectroscopy. ^1H Nuclear magnetic resonance (^1H NMR) spectroscopy was applied to confirm the formation of the inclusion complex Alfoterra

Table 1
General surfactant properties [34].

Surfactant Alfoterra	Appearance at 25 °C	Active content (wt%)	Moles of propoxy (PO) groups	Hydrophobe carbon number range	Molecular weight (g/mol)
123-4s	Yellow, clear liquid	28	4	C ₁₂ –C ₁₃	527
145-4s	Thick slurry	30	4	C ₁₄ –C ₁₅	558
167-4s	Thick slurry	30	4	C ₁₆ –C ₁₇	580
167-7s	Amber, clear liquid	30	7	C ₁₆ –C ₁₇	754

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