



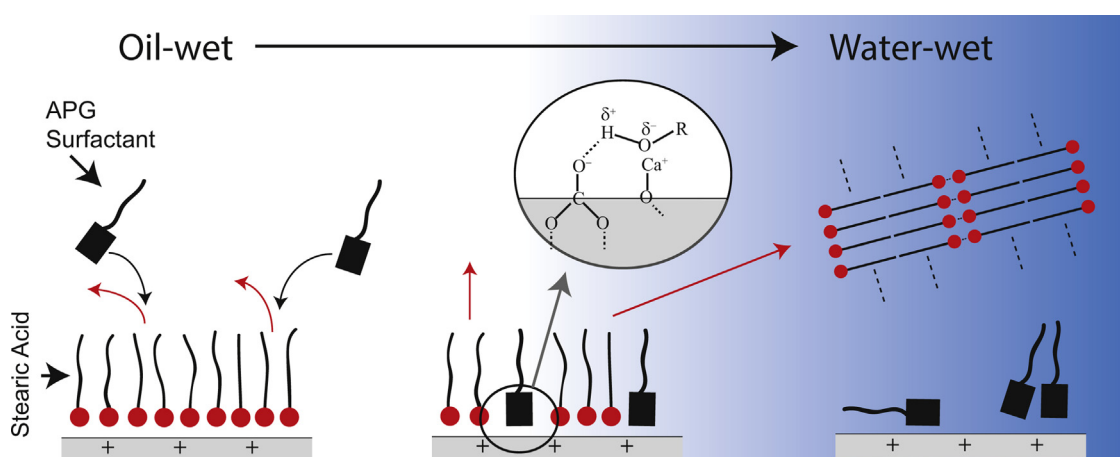
Mechanism of calcite wettability alteration by alkyl polyglucoside



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GRAPHICAL ABSTRACT



HIGHLIGHTS

- We studied the effect of APG and DTAB on calcite impregnated with stearic acid (SA).
- APG and DTAB effectively desorb SA from the calcite surface, above and below CMC.
- DTAB forms ion-pairs with SA which increases DTAB adsorption on calcite markedly.
- APG replaces SA at $-Ca^+$ sites due to interaction with APG $-OH$ groups.
- Different APG surface aggregates forms depending on APG concentration.

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ABSTRACT

Surfactant injection into oil-wet carbonate reservoirs offers a large potential for increased oil recovery due to reservoir wettability alterations. Here, the mechanism of wettability alteration by non-ionic surfactant alkyl polyglucoside (APG) is investigated and compared to that of the cationic surfactant dodecyltrimethylammonium bromide (DTAB). Techniques used include 1H and ^{13}C magic angle spinning NMR, zeta potential, adsorption and contact angle (CA) measurements. APG monomers effectively desorb stearic acid (SA) from an SA treated calcite surface by replacing it at cationic sites on the surface, both above and below the APG critical micelle concentration (CMC). Increased polarization of the APG hydroxyl groups upon interaction with $-Ca^+$ sites is a driving force for APG adsorption. CAs show that APG treatment changes wettability to water-wet both below (CA = 66.9°) and above (CA = 77.2°) CMC. An observed sphere-to-rod transition occurring in APG solution above 1 mM is accompanied by a structural transition from half-micelles to patches of partial bilayers at the calcite surface, which further increases APG adsorption and CA (CA = 88.1°). In the presence of SA, adsorption of APG onto calcite is similar to

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that of DTAB below CMC, while above CMC APG adsorption is 2–3 times higher than DTAB. In absence of SA, DTAB adsorption is negligible. CAs are comparable after APG and DTAB treatment, making APG an interesting candidate for such purposes due to its effectiveness at very low concentrations.

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1. Introduction

Surfactant flooding for enhanced oil recovery (EOR) purposes have been attempted and reviewed frequently over the past 40 years, both in the laboratory and in field tests; however, the complexity of reservoir properties and interactions which occur between surfactants and reservoir components make it difficult to predict the effect of such injections, and surfactant flooding has therefore been used with variable successes and economic feasibility [1,2].

It is generally recognized that the efficiency of oil recovery by water flooding is significantly higher in water-wet reservoirs compared to oil-wet ones [2]. Therefore, an area where surfactants have received attention is their ability to change the wettability of a reservoir [2–4]. A promising reservoir candidate for such surfactant injections is naturally fractured oil-wet carbonate reservoirs. The wettability of these reservoirs can be altered over time from an originally water-wet to an oil-wet surface due to adsorption of polar compounds present in the crude oil onto the cationic carbonate surface [5].

An oil-wet carbonate matrix prevents spontaneous imbibition of water into the rock due to very low capillary pressure; consequently, water injected into the reservoir follows fracture corridors from the injection well to the production well without displacing any significant amount of oil [6]. However, imbibition experiments show that surfactants can improve oil recovery to between 50 and 70% of the oil originally in place (OOIP) for such reservoirs, which is generally attributed to changes in rock wettability [4,7–11]. This is a potential vast improvement, considering that the ultimate recovery of oil-wet fractured reservoirs is less than 25% of the OOIP.

Molecular-level knowledge about the underlying mechanisms will increase the probability of a successful surfactant injection. However, there is still uncertainty regarding the mechanisms of wettability alterations by surfactants despite receiving much attention in recent years. Wettability alterations by anionic surfactants have been proposed to occur by co-adsorption of the surfactant on the surface with the hydrophilic head group oriented toward the bulk [7], although sodium carbonate has proved to reduce the adsorption of some anionic surfactants on carbonate surfaces [9,12].

Cationic surfactants are often considered for carbonate reservoirs due to their same charge with respect to the carbonate surface which reduces depletion of surfactants from the injection fluid. Cationic surfactants are thought to form ion-pairs with the adsorbed acidic components and, hence, desorb them from the surface [4,7,13,14].

Non-ionic surfactants have in general proved to be effective in both reducing IFT and in changing the wettability of an oil-wet surface [15–20]. Ahmadi et al. [19] found that contact angles measured on carbonate plugs were reduced after core flood tests with a cationic (cetyltrimethylammonium bromide), an anionic (sodium dodecyl sulphate) and two non-ionic surfactants (TritonX-100 and saponin). The most effective surfactant was found to be the non-ionic saponin bio-surfactant resulting in a reduction in contact angle from 175° to 135° [19]. Non-ionic surfactants have also proven efficient in carbonate reservoir field tests such as for the Yates field and Cottonwood Creek field (USA), the latter of which

wettability alteration was proposed as the main mechanism for EOR [21].

Despite this, very few publications have proposed mechanisms of wettability alteration by non-ionic surfactants. Jarrahan et al. [22] proposed that wettability alteration by the non-ionic surfactant TritonX-100 occurs when the surfactant displaces acidic components on the surface, after which the acidic components re-adsorb by hydrophobic interactions with the tail of the non-ionic surfactant. However, there are large differences in the interfacial behavior of non-ionic surfactants depending on the headgroup being ethylene oxide based, such as TritonX-100, or polyhydroxyl [23,24]. Polyhydroxyl non-ionic surfactants include a large class of bio-surfactants and a mechanistic approach to such surfactants can therefore be beneficial.

Non-ionic alkyl polyglucosides (APG) are sugar-based polyhydroxyl surfactants, and are of interest because they are easily bio-degradable, are synthesized at low cost from renewable resources and have very low eco-toxicity [25]. These are desired qualities due to the large quantities needed for a full scale injection. Furthermore, APG has unique properties compared to other non-ionic surfactants such as nearly temperature independent interfacial properties, a tendency to form very low IFT with organic phases and foaming properties similar to anionic surfactants [26]. The use of APG surfactants is therefore now widespread in household, cosmetic and agricultural products [25], and is also a promising candidate for EOR purposes [16,17,20,27,28].

In this study we investigate molecular-level details concerning surfactant induced wettability alteration of calcite by a C₁₂–C₁₄ APG formula, as well as the cationic surfactant dodecyltrimethylammonium bromide (DTAB), by using magic angle spinning (MAS) NMR spectroscopy together with adsorption, zeta potential, dynamic light scattering (DLS) and contact angle measurements. Alkyl trimethyl ammonium bromides such as DTAB are perhaps the most commonly considered surfactants for wettability alteration of carbonates [4], and DATB is therefore included in this study as a comparison to APG. Moreover, NMR may shed further light on the previously proposed mechanism of wettability alteration by DTAB through ion-pair formation with SA [13]. The effectiveness of wettability alteration of the calcite to oil-wet by stearic acid (SA) and, conversely, wettability alteration back to water-wet by APG and DTAB is considered. In order to avoid interference of paramagnetic impurities on the NMR measurements, precipitated calcite treated with SA is used as a model oil-wet carbonate reservoir surface under high total acid number conditions. Furthermore, oil-surfactant interactions are disregarded in this study in order to better access the core mechanisms between the acid, surfactant and the calcite.

2. Materials and methods

2.1. Materials

Ultrafine precipitated calcium carbonate SOCAL[®]31 (purity ≥ 98%) was a generous gift from Solvay Chemicals (Brussels, Belgium). These are homogeneous particles (Fig. 1) with an average diameter of 59 nm and specific surface area of 17 m²/g. The

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