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Regular Article

Wettability alteration of oil-wet limestone using surfactant-nanoparticle formulation

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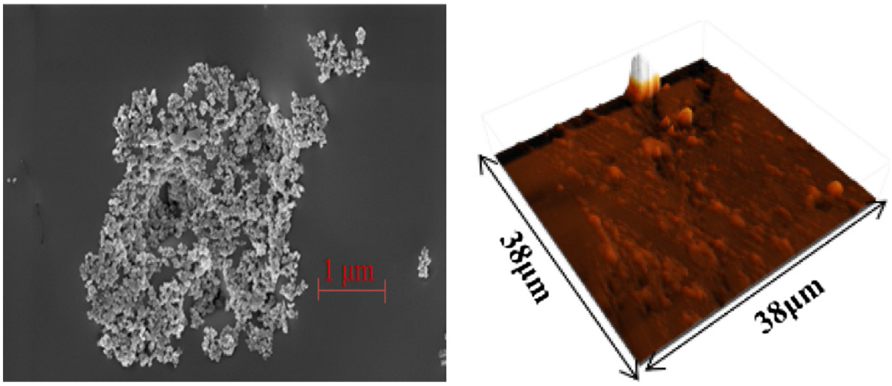
GRAPHICAL ABSTRACT



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ABSTRACT

Wettability remains a prime factor that controls fluid displacement at pore-scale with substantial impact on multi-phase flow in the subsurface. As the rock surface becomes hydrophobic, any oleic phase present is tightly stored in the rock matrix and produced (hydrocarbon recovery) or cleaned up (soil-decontamination) by standard waterflooding methods. Although surface active agents such as surfactants have been used for several decades for changing the wetting states of such rocks, an aspect that has been barely premeditated is the simultaneous blends of surfactants and nanoparticles. This study thus, systematically reports the behaviour of surfactants augmented nanoparticles on wettability alteration. Contact angle, spontaneous imbibition, and mechanistic approaches were adopted to assess the technical feasibility of the newly formulated wetting agents, tested over wide-ranging conditions to ascertain efficient wetting propensities. The contact angle measurement is in good agreement with the morphological and topographical studies and spontaneous imbibition. The wetting trends for the formulated systems indicate advancing and receding water contact angle decreased with increase in nanoparticle concentration and temperature, and the spontaneous water imbibition test also showed faster water-imbibing tendencies for nanoparticle-surfactant exposed cores. Thus, the new formulated nanoparticle-surfactant systems were considered suitable for enhancing oil recovery and soil-decontamination, particularly in fractured hydrophobic reservoirs.

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1. Introduction

Porous rock wetting and imbibition are complex processes which pose a continual challenge in subsurface reservoir practices. Typically, formations exhibit different degrees of wetting tendencies such as water-wet, oil-wet, or intermediate wet (or anything in between). Water-wet formations display a great affinity for water than oil, and oil-wet formations retain the oleic phase much better in the tight pore matrix of the rock. It is, however, a key question how the wetting state of such formations can be rendered more water-wet to facilitate better hydrocarbon recovery [1–4], soil-decontamination, or enhanced carbon geo-sequestration processes [5–8]. Surfactant-flooding has been recognised as an approach that promotes adequate displacement of oil from porous media when used in adequate volumes, especially in depleted formations [9]. Its usage has been widely investigated [10–23] as active agents for reduction of oil–water interfacial tension (IFT) [11,24–26] and residual oil saturation [10]. Surfactants are also good wettability modifiers for solid–liquid interfaces [15,27,28], although, the kinetics, uniformity and wettability alteration efficiency of the surfactants are complex and depend on the properties of the surfactant and the solid surface of the porous medium that the surfactants are in contact with [29,30]. Surfactants can accumulate in three-dimensional nano and micro structures (micelles, vesicles, liquid crystalline phases) when they reach a sufficient concentration in solution [31,32] but their prime characteristic in enhancing oil recovery (EOR) is the capacity to adsorb on surfaces or interfaces [33–36] even at minimal concentrations. This can lead to surfactant loss due to adsorption on the reservoir rock surface; an effect which needs to be minimized as the efficiency of the EOR process is reduced [22,24,36–38].

Recently, nanoparticle - typically, stable metal oxides sized between 1 and 100 nm [4,39–41] have received increased interest as an additive to EOR-surfactant formulations [42,43] as it displays different and better properties in comparison to the bulk material counterparts. Its great chemical stability makes it particularly interesting for formulations of suspensions or emulsions [4,44]. Ahmadi and Shadizadeh [45] assessed the adsorption behaviour of Zyziphus spina-christi surfactant in the presence of silica nanoparticles on sandstone shale and found that adsorption losses on shale sandstone were better inhibited by hydrophobic silica nanoparticle than hydrophilic silica nanoparticle due to more hydrophobic bonds created between hydrophobic tail of surfactant and hydrophobic part of nano silica particles. Lan et al. [46] investigated the synergistic effects of silica nanoparticles and cationic surfactants on the emulsion stability on basis of concentration and dispersion ph. It was found that the interfacial adsorption of the silica nanoparticle increased with increasing cationic surfactant concentration, thus, an indication of a clear synergistic effect on interfacial tension (IFT) reduction, such effect in IFT reduction was attributed to emulsion stability.

Despite the relevance of studies on adsorption behaviour and IFT at the liquid–liquid interface [37,47], the mechanisms and interaction between surfactant augmented nanoparticles on the solid–liquid interface is not fully understood and remains a challenge especially for contact lines moving in nanoscale systems. Such effect has barely been reported in oil wet limestone reservoir, as such an understanding of the wetting propensity in this formation is imperative, as fluid displacement at pore scale is greatly dependent on the reservoir wettability. This rock type is of interest as its naturally fractured and hydrophobic nature makes it difficult for water to imbibe into its matrix owing to negative capillary pressure; capillary pressure is thus defined as the pressure variation between two fluid phases that are in contact. Such contacts between immiscible fluids in the rock pore spaces leads to pressure discontinuity across the interfaces and it is dependent on IFT, pore size, and wetting angle and thus considered [48,49]. The pressure difference between the wetting and non-wetting fluid phase is established as:

$$P_c = P_n - P_w \tag{1}$$

where P_c - capillary pressure; P_n - non-wetting pressure; P_w - wetting pressure.

Typically, oil recoveries from such fractured reservoirs are usually very poor with average recovery factor of about 10–35% [25,36,44], however, if such oil-wet surface can be rendered water-wet, spontaneous imbibition of water into the matrix pores (where most of the oil resides) massively increases recovery factors to 50–70% [50–54]. However, water wet media exhibit increased snap-off actions, which lead to increased residual oil saturations after water breakthrough and subsequent poor oil recovery [55]. The relevance of wetting and its effect on rock-fluid properties cannot be over emphasized, aside its importance in subsurface reservoir evaluation, it is of great relevance for characterization and selection of materials. Hence, we tested the wetting propensity of new nanoparticle-surfactant formulations in strongly hydrophobic limestone, which can enhance the possibilities for significant additional oil recoveries from fractured reservoirs. Two different surfactants (cationic and non-anionic) and nanoparticles (zirconium oxide and nickel oxide) were systematically evaluated as a function of surfactant type and concentrations, nanoparticle-surfactant type and concentrations, temperature, and imbibition.

2. Experimental procedure

2.1. Materials

Triton X-100 (TX-100 Sigma Aldrich - purity 99.0 mol.%; molecular weight - 625 g/mol; critical micelle concentration - 0.2–0.9 mM) and cetyltrimethylammonium bromide (C_{16}TAB Sigma Aldrich - Purity 99.0 mol.%; molecular weight - 364.45 g/mol; critical micelle concentration - 0.92 mM) were used as surfactants (Fig. 1). Dodecyltriethoxysilane ($C_{18}H_{40}O_3Si$; Purity 99.0 mol.%; Molecular weight 332.59 g/mol; 265.25 °C) from Sigma Aldrich (Fig. 1) was used as a wettability modifier, see below; and Zirconium (IV) oxide (ZrO_2) from Sigma Aldrich (purity: 99.5 wt%) and Nickel (II) oxide (NiO) (purity 99.5 wt%) were used as nanoparticles (Table 1). Iceland spar calcite crystal (from Ward Science) was used as a representative of limestone formations. Toluene (from Sigma Aldrich; purity 99.9 mol.%) was used as model oil. Ultrapure deionised water (Purity 99.0 mol.%; David Gray) was used as dispersing agents for all the tests.

2.2. Fluids formulation, surface cleaning, and modification

Surfactant (C_{16}TAB, TX-100: 0.05–0.5 wt%) solutions were prepared with a 220V/50HZ magnetic stirrer and deionised water as a dispersing agent. Nanoparticle-surfactants (ZrO_2/C_{16}TAB; ZrO_2/TX-100, NiO/C_{16}TAB; NiO/TX-100) were formulated by adding fixed surfactant concentration (C_{16}TAB and TX-100–0.5 wt%) to the nanosuspensions of varied concentrations (ZrO_2 and NiO - 0.004–0.05 wt%). The mixture was stirred with a magnetic stirrer (60 min) and sonicated with a 300VT ultrasonic homogenizer (60 min) to create homogeneous fluids.

Calcite crystals were cleaned with acetone, methanol and deionised water to remove surface fragments and inorganic contaminants. The samples were then dried in air plasma for 15 min [56,57] to remove any residual organic contaminants. The cleaned samples were modified to oil-wet by ageing in silane (dodecyltriethoxysilane) for 12 h at 90 °C. Samples were then separated from