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A systematic experimental investigation on the synergistic effects of aqueous nanofluids on interfacial properties and their implications for enhanced oil recovery

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ABSTRACT

Nanofluids have been proposed as potential enhanced oil recovery agents and additives to hydraulic fracturing fluids. The underlying mechanisms responsible for effectiveness of these fluids, however, are not well understood. In this study, we experimentally investigate synergistic effects of aqueous nanofluids on interfacial properties of oil/brine/rock systems and their role in influencing oil displacement from sandstone and carbonate rock samples. The nanofluids were prepared by dispersing three widely-used nanoparticles (i.e., SiO_x, Al_2O_3, and TiO_2) and five different chemical agents (i.e., oleic acid, polyacrylic acid, a cationic, an anionic, and a nonionic surfactant) in base brine solutions. The efficacy of the mixtures was examined using a framework that including a comprehensive stability analysis, IFT and wettability characterizations, and oil recovery tests at ambient as well as high pressure and high temperature conditions (i.e., spontaneous imbibition and core-flooding experiments, respectively). Effects of stable nanofluids, identified from stability analysis, on interfacial tension and dynamic contact angle were carefully investigated. We show that co-adsorption and self-structuring of nanoaggregates and chemical agents at the solid interface leads to wettability alteration. Both spontaneous imbibition and high pressure and high temperature core-flooding results reveal the effectiveness of SiO_x + nonionic surfactant nanofluid in enhancing oil recovery in Berea sandstone due to a synergistic effect between nanoparticles and surfactant molecules. In contrast, the stability of nanofluids was highly compromised in Edwards limestone due to dissolution and interaction of calcium ions with nanoaggregates at high temperature. This was evident in the drastic difference between oil recoveries obtained through ambient-temperature spontaneous imbibition and high-temperature core-flooding experiments conducted on carbonate core samples. Finally, we provide new insights on interfacial interactions in nanofluid/oil/rock systems as they relate to wettability alteration, IFT reduction, and the effect of dissolved ions such as calcium in carbonate rocks. We use this improved understanding to explain the recovery trends observed in our study.

1. Introduction

Nanofluids, here defined as suspensions of nanometer-sized materials in base fluids [1–4], have been studied for applications in various disciplines such as heat transfer [5], biomedicine ([6]), and soil remediation [7] due to their significant impacts on interfacial properties. Nanofluids and nanoparticles also have many potential applications in the oil and gas industry. They have been used as additives to drilling fluids due to their ability to manipulate thermal, rheological, and electrical properties of solutions [8]. Furthermore, nanofluids are considered as potential replacements for traditional Enhanced Oil Recovery (EOR) agents since they have the tendency to reduce interfacial tension (IFT) and alter the wettability of rock surfaces even at high salinity and high temperature conditions [9].

Nanoparticles have high surface area to volume ratio and hence possess high adsorption affinity [10], which grants them the ability to actively interact with fluid-fluid interfaces. Therefore, nanofluids may exhibit smaller interfacial tensions compared to the base fluids [1,11,12]. Murshed et al. [1] conducted IFT measurements using pendent drop method and observed approximately 20 mN/m decrease by introducing hydrophilic TiO_2 nanoparticles into deionized water. In a similar study, Amraei et al. [11] used du Nouy ring method and measured the IFT of SiO_2 nanofluids/n-hexane fluid system at different nanoparticle concentrations. The authors reported a decrease in IFT from 44.13 mN/m to values as low as 1.76 mN/m at 8% SiO_2 nanofluid concentration (solution of distilled water, isopropyl alcohol, and

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ethylene glycol). Binks et al. [13] showed silica nanoparticles and cationic surfactant molecules have synergistic effects on the stability of oleic-aqueous microemulsions. Similar synergistic effects were reported by Eskandar et al. [14] between silica nanoparticles and two conventional surfactants (i.e., lecithin and oleylamine) in stabilizing negatively and positively charged sub-micron paraffin oil-in-water emulsions. To promote the stabilizing effects, Saleh et al. [15] utilized hydrophilic silica nanoparticles modified with polystyrene sulfonate (PSS) as emulsifiers and found better emulsion stability compared to the other emulsifiers reported in the literature.

Furthermore, nanofluids can physically interact with fluid-solid interfaces and consequently alter the wettability of solid surfaces. For instance, nanoparticles have been proposed in oil industry as wettability alteration agents [2,9–11,16–22]. Amraei et al. [11] and Karimi et al. [9] reported a decrease in contact angles on carbonates by introducing different nanofluids (i.e., SiO_2 and ZrO_2, respectively). Additionally, TiO_2 [10], polysilicon [18], and Al_2O_3 [20] were used to conduct similar tests on sandstones, and significant changes in wettability of rock surfaces from oil-wet to intermediate-wet or water-wet conditions were observed. Karimi et al. [9] reported the formation of nanometer-sized ribbons and nanoflower-like morphologies on rock surfaces after aging carbonate plates in nanofluids. They suggested that the wetting properties of the newly-developed surface was changed due to the adsorption of nanoparticles. It is also found that the spreading and wetting of nanofluids on solids are impacted by self-structuring of nanoparticles in the confined three-phase contact region that is located inside the wedge film within aqueous phase between an oil drop and a solid surface [4,23,16].

Owing to their role in reducing brine/oil interfacial tension, stabilization of oil-in-water and water-in-oil microemulsions, and enhancement of wetting behavior, nanofluids potentially have significant applications in enhanced oil recovery processes. Esfandyari Bayat et al. [24] studied the effect of different metal oxide nanoparticles on EOR from limestone samples. Based on their displacement tests, it was found that SiO_2, Al_2O_3, and TiO_2 nanoparticles all have the potential of being used as EOR agents due to their effects on viscosity and interfacial tension as well as wettability. Similarly, ZrO_2 nanofluid was suggested as a candidate EOR agent in carbonate rock systems because of its ability to alter wettability [9]. In another study, SiO_2 nanoparticles were reported to enhance the performance of water-alternating-gas recovery scheme in oil-wet carbonate [25]. The promising performance of nanofluids in enhancing oil recovery is not limited to carbonates [10,19,26–29]. Hendraningrat et al. [19] conducted core-flooding tests in Berea sandstone samples using SiO_2 nanofluids. Although both hydrophobic and hydrophilic SiO_2 nanoparticles were found to lower interfacial tension and contact angle, the authors indicated that nanoparticles may not provide a better recovery due to the impairment of porosity and permeability in the core samples. This may have been caused by instability of their nanofluids at experimental conditions. Similarly, Youssif et al. [30] reported 0.1 wt% as the optimum concentration of silica nanofluids for enhancing oil recovery, and they claimed that any further concentration increment leads to formation damage. In contrary to the previous findings, enhancement of oil production due to deposition of nanoparticles is reported by Li and Torsæter [31]. They observed improvement in the sweep efficiency due to channel plugging effects caused by precipitation of nanoparticles. By comparing the results of core-flooding tests to those of interfacial tension and contact angle measurements, Hendraningrat and Torsæter [26] concluded that wettability alteration is the dominant mechanism responsible for the effectiveness of nanofluids in enhancing oil recovery. Additional recovery in sandstone samples due to both wettability alteration and reduction in interfacial tension using modified SiO_2 and TiO_2 nanoparticles was also reported [10,27].

Moreover, nanoparticles have potential applications in hydraulic fracturing. Although polymer solutions have been used as stimulation fluids for decades, they leave residues behind that can impair permeability of reservoir rock and sandpacks within fractures. This is one of the biggest challenges that limits application of polymer solutions as fracturing fluids. Therefore, breakers (e.g., enzymes) have been used to degrade polymers remaining in the solution and filter cake ([32]). Delayed release or encapsulation of these breakers is critical in successful removal of remaining polymers. Barati et al. [32,33] have proposed that nanoparticles could successfully entrap and delay the release of enzymes in fracturing fluids, which could protect the enzymes against severe conditions such as alkaline brine and high temperature. Additionally, the ultra small size of nanoparticles could help distribute the enzyme more uniformly [32,33]. In another example, researchers have proposed to use viscoelastic surfactant (VES) solutions as fracturing fluids to overcome the drawbacks of polymers solutions. Yet, VES systems have their own limitations due to excessive fluid leak-off and poor thermal stability. Crews et al. [34] demonstrated that the use of pyroelectric nanoparticles not only could increase the low shear rate viscosity of VES solutions by 10-fold, but also could reduce the leak-off rate of these fluids.

In this study, we evaluate nanofluid mixtures as EOR agents or additives to fracturing fluids through a detailed investigation of their interfacial properties and impacts on oil recovery. Nanofluids are prepared by dispersing nanoparticles in brine solutions in the presence of different chemical agents. First, we carefully study the stability of these colloidal solutions by applying different techniques proposed in the literature and critically comparing the results. Once stable nanofluids are identified, interfacial tension between crude oil and aqueous phases as well as wettability of reservoir rock samples are studied in the presence of nanofluids. In the next step, the effect of nanofluids on oil recovery is investigated using spontaneous imbibition experiments at ambient conditions, and core-flooding tests at high pressure and high temperature. The results are then analyzed based on interfacial properties of nanofluids in the brine/oil/rock systems investigated. This study extends our fundamental knowledge on the underlying mechanisms involved in enhanced oil recovery using nanofluids.

In the following sections, we first present materials and methods used in this study. Afterward, stability analysis and effects of nanofluids on IFT and contact angle are discussed in detail. We then present and discuss the results of spontaneous imbibition and core-flooding experiments conducted in sandstone and carbonate rock samples. Finally, we include a section on conclusions and proposed future work.

2. Materials and methods

2.1. Fluids

Materials include n-Decane (99%, Extra Dry, AcroSeal), Silicon Oxide (SiO_x, 99.5 + %, S-type, 15–20 nm spherical particles, amorphous, bulk density < 0.10 g/cm^3, US Research Nanoparticles, Inc.), Aluminum Oxide (< 50 nm, molecular weight = 101.96 g/mol, gamma phase, Aldrich), Titanium Dioxide (99 + wt%, 10–25 nm, Anatase, US Research Nanoparticles, Inc.), Sodium Chloride (100%, ACS-grade, Fisher Scientific), distilled-deionized water (Conducivity 1.48×10^{-4} S/m, produced by Auto distill WG280, Yamato), oleic acid (99 + %, Sigma-Aldrich) (OA), polyacrylic acid (Sigma-Aldrich) (PAA), liquid nonionic surfactant (linear alcohol, C_{9-11}, Ethoxylate, Stepan Co.), liquid anionic surfactant (ammonium alkyl, C_{6-10}, Ether Sulfate, Stepan Co.), liquid cationic surfactant (n-Alkyl dimethyl benzyl ammonium chloride, Stepan Co.), Sodium dodecyl sulfate (BioReagent, Sigma-Aldrich) (SDS), Toluene (99.9%, Certified ACS, Fisher Scientific), Methanol (99.9%, Certified ACS, Fisher Scientific), and Acetone (99.9%, Certified ACS, Fisher Scientific).

Nanofluids were prepared by dispersing 0.1 wt% nanopowders (i.e., SiO_x, Al_2O_3, and TiO_2) in 1 mM NaCl brine solution with or without chemical agents (i.e., OA, PAA, and cationic, anionic, and nonionic surfactants). NaCl brine solution with 1 mM concentration was selected in this study in order to be consistent with slick water composition that