Wettability Alteration of Sandstone Cores by Alumina-Based Nanofluids

ARTICLE *in* ENERGY & FUELS · JUNE 2013

Impact Factor: 2.79 · DOI: 10.1021/ef4002956

5 AUTHORS, INCLUDING:

Pedro Benjumea
National University of Colombia

Farid B. Cortés
National University of Colombia

Marco A. Ruiz
National University Colombia

energy&fuels Article
pubs.acs.org/EF

Wettability Alteration of Sandstone Cores by Alumina-Based Nanofluids

Juliana Giraldo, Pedro Benjumea,* Sergio Lopera, Farid B. Cortés, and Marco A. Ruiz

Grupo de Investigación en Yacimientos de Hidrocarburos, Facultad de Minas, Universidad Nacional de Colombia Sede Medellín, Calle 59A No. 63-20 Medellín, Colombia

ABSTRACT: Wettability alteration can occur at different stages during the producing life of a reservoir. Oil recovery from oil-wet reservoirs can significantly be increased by altering its wettability from an oil-wet to a strongly water-wet condition. Chemical agents such as surfactants are known as wettability modifiers in oil-wet systems. More recently, nanofluids prepared by dispersing nanoparticles in several liquid agents have been considered as potential wettability modifiers. In this work, the effectiveness of alumina-based nanofluids in altering the wettability of sandstone cores with an induced oil-wet wettability was experimentally studied. Eight nanofluids with different nanoparticles concentration, ranging from 100 ppm to 10000 ppm, were prepared by dispersing alumina nanoparticles in an anionic commercial surfactant. The effect of nanofluids on wettability alteration was investigated by contact angle and imbibition tests, and it was shown that designed nanofluids could significantly change the wettability of the sandstone cores from a strongly oil-wet to a strongly water-wet condition. Imbibition tests also allowed identifying the effect of nanoparticles concentration on the suitability of the treatment for enhancing the imbibition process and restoring the original core wettability. Results showed that the effectiveness of the anionic surfactant as wettability modifier could be improved by adding nanoparticles in concentrations lower or equal than 500 ppm. The best performance was achieved when a concentration of 100 ppm was used. Additionally, a core displacement test was carried out by injecting in a sand pack a nanofluid prepared by dispersing alumina nanoparticles in distilled water. The treatment was effective in altering the sand pack wettability from an oil-wet to a strongly water-wet condition as indicated by a significant reduction in the residual water saturation and a displacement to the right of the oil relative permeability curve and the crossover point.

1. INTRODUCTION

Wettability plays an important role in oil recovery processes and reservoir productivity. It is a major factor controlling the flow and spatial distribution of fluids in porous media. Regardless of their origin and mineralogical composition, most reservoir rocks are believed to be in a mixed-wet state, that is, neither completely water-wet nor completely oil-wet. The concept of mixed wettability was first introduced by Salathiel[1] and studied in detail by Kovscek et al.[2]

Wettability alteration can occur at different phases during the producing life of a reservoir.[3] Oil-based drilling fluids can alter rock minerals from water-wet to an oil-wet or mixed-wet state.[4] Emulsifiers and surfactants included in these fluids, even at low concentrations, have been shown to be responsible for the change in wettability.[5,6] The potential for asphaltenes to adsorb onto mineral surfaces and thus to alter reservoir wettability has long been recognized.[7] Wettability may be altered in reservoirs when the onset of asphaltenes precipitation is approached by pressure depletion.[7] Favorable conditions for wettability alteration by asphaltenes precipitation may also occur in gas-injection processes.[8] Ionic interactions and surface precipitation have been identified as the main mechanisms contributing to wettability alteration of mineral surfaces exposed to asphaltenes precipitation in presence of water.[7]

Improved oil recovery by surfactant induced wettability alteration has been the focus of several experimental and theoretical studies.[3] Recovery efficiency by waterflooding in natural fractured reservoirs, specially mixed- and oil-wet carbonates, can be improved by dissolving low concentrations of surfactants in the injected water to alter the wettability of the reservoir rock to a more water-wet state. This wettability alteration accelerates the spontaneous imbibition of water into matrix blocks, thereby increasing the oil recovery during waterflooding.[9,10] The permanent alteration of wettability from liquid-wet to preferentially gas-wet using an alcohol-based-surfactant/polymer solution has been proposed as an alternative to mitigate well deliverability loss by water or condensate blocking in retrograde gas condensate reservoirs.[11]

Different mechanisms have been proposed to explain the wettability alteration by surfactants. According to Hammond and Unsal,[12] most probable mechanisms include (1) surfactant adsorption onto the oil-wet solid surface (coating mechanism) and (2) surfactant molecules complexing with contaminant molecules from the crude oil which are adsorbed on the rock surface so as to strip them off (cleaning mechanism). Based on experimental results, Salehi et al.[9] argued that ion-pair formation between the charged head groups of surfactant molecules and the adsorbed crude oil components on rock surface was more effective in changing the rock wettability toward a more water-wet state than the adsorption of surfactant molecules as a monolayer on the rock surface through hydrophobic interaction with the adsorbed crude oil components.

More recently, some researchers have suggested that the mobility and effectiveness of wettability modifiers such as

Received: February 19, 2013
Revised: May 28, 2013
Published: June 12, 2013

surfactants can be increased by the addition of nanoparticles.[13−18] The two characteristics of nanoparticles that make them particularly attractive for assisting enhanced oil recovery processes are (1) their size and (2) the ability to manipulate their behavior.[19] Due to their size (diameter ranging from 1 to 100 nm), nanoparticles have large specific surface areas and can flow through typical reservoir pore spaces with sizes at or below 1 μm. A large surface area leads to an increase in the proportion of atoms on the surface of the particle, which results in an increase in surface energy. The adsorption of a very active and energetic material on a solid surface can significantly alter the surface energy and wettability of the system. By tuning nanoparticle properties, it is possible to design nanofluids or "smart fluids", which are prepared by adding small volumetric fractions of nanosized solid particles to a liquid phase in order to enhance or improve some of the fluid properties.[20,21]

Ju et al.[13−15] conducted experimental and theoretical studies on wettability and absolute permeability alteration caused by adsorption of lipophobic-hydrophilic polysilicon nanoparticles (LHP) on the surface of sandstone core samples. From core displacement experiments, they concluded that oil recovery by waterflooding was enhanced by injecting slugs of suspensions of LHP (ranging from 10 to 500 nm) in diesel fuel. According to them, since the hydrophobic pore wall was changed into hydrophilic due to LHP adsorption, the relative permeability of the oil phase (K_{ro}) increased, decreasing the resistance to oil flow, while at the same time, the relative permeability of the water phase (K_{rw}) decreased significantly. From results of numerical simulation, the authors also concluded that porosity and permeability declined due to retention of LHP during its transport in porous media.

Onyekonwu and Ogolo[16] also studied the ability of polysilicon nanoparticles to enhance oil recovery. They conducted core displacement experiments on water-wet rocks using dispersed lipophobic-hydrophilic (LHPN), hydrophobic-lipophilic (HLPN), and neutrally wet polysilicon nanoparticles (NWPN). Ethanol and water were used as dispersing agents for HLPN and NWPN, and LHPN, respectively. According to the authors, NWPN and HPLN, used in a concentration of 3000 ppm, could enhance oil recovery in water-wet cores by wettability alteration and reduction of the interfacial tension. On the other hand, LHPN, used in a concentration of 2000 ppm, made already water wet rocks strongly water wet yielding poor recovery factors and indicating that its use for enhanced oil recovery processes should be restricted to oil wet formations.

Karimi et al.[18] performed an experimental study on the effect of zirconium oxide (ZrO_2)-based nanofluids on wettability alteration of a carbonate reservoir rock. Several nanofluids were made composed of ZrO_2 nanoparticles and mixtures of nonionic surfactants with hydrophilic−lipophilic balance (HLB) ranging from 15 to 1.8. Two different nanoparticles concentrations were tested (50000 and 100000 ppm). The effect of nanofluids on wettability alteration was investigated by measuring the contact angles before and after treatment. Additionally, the impact of wettability alteration on oil recovery was evaluated by free imbibition tests. The authors concluded that designed ZrO_2-based nanofluids were effective wettability modifiers for carbonate systems since they could significantly change the wettability of the rock from a strongly oil-wet to a strongly water-wet condition. The wettability alteration by adsorption and growth of ZrO_2 nanoparticles on the rock surface was a slow process, requiring a period of at least 2 days. Results also showed that a considerable amount of oil could be quickly recovered by free imbibition of the nanofluids into the core plugs.

The use of alumina-based nanofluids as wettability modifiers have not been reported yet. This study is aiming at evaluating the effectiveness of alumina-based nanofluids to alter the wettability of sandstone cores from oil-wet to water-wet. Special attention was put on the effect of nanoparticles concentration on the treatment effectiveness. Eight nanofluids with nanoparticles concentration ranging from 100 ppm to 10000 ppm were prepared by dispersing alumina nanoparticles in an anionic commercial surfactant. The effect of nanofluids on wettability alteration was investigated by contact angle and imbibition tests. Additionally, a core displacement test was carried out by injecting in a sand pack a nanofluid prepared by dispersing alumina nanoparticles in distilled water.

2. MATERIALS AND METHODS

2.1. Preparation and Characterization of Nanofluids. Alumina (aluminum oxide, Al_2O_3) nanoparticles synthetized by the sol−gel method and an anionic surfactant commercially called as PRNS were supplied by Petroraza SAS (Colombia). Nanoparticles were characterized by N_2 adsorption at −196 °C and X-ray diffraction (XRD). The BET surface area (S_{BET} = 123.2 m^2/g) was calculated using the model of Brunauer, Emmet and Teller (BET) presented by Rouquerol et al.[22,23] X-ray diffraction patterns were recorded with a Philips PW1710 diffractometer using Cu Kα radiation. Mean crystallite size of the particles (dp = 35 ± 4 nm) was obtained by applying the Scherrer's equation to the main diffraction peak.[24] Nanofluids were prepared by dispersing alumina nanoparticles in the anionic surfactant at five concentrations ranging from 100 ppm (PRNS-100) to 10000 ppm (PRNS-10000). Key surfactant properties such as interfacial tension (31.4 mN/m) and pH (9.3) were not affected by nanoparticles addition.

2.2. Establishment of an Oil-Wet State in Core Plugs. An oil-wet state in laboratory cores was established by inducing asphaltene precipitation from a dead crude oil on used core plugs. Sandstone core plugs with a diameter of 1.27 cm (0.5 in.), length of 5.4 cm (2.1 in.), and an average porosity of 20% were used in contact angle and imbibition tests.

A heavy crude oil (19.2°API, 64 mPas at 25°, and 11% by weight of asphaltenes) produced from a field located in the Upper Magdalena Valley of Colombia (La Hocha field) was used in inducing asphaltene precipitation.

The following 3-step procedure was carried out to establish an oil-wet state: (1) Remove any contaminant from core plugs by solvent cleaning. Core plugs were washed with toluene and then dried at 40 °C during one day. (2) Induce asphaltene precipitation and adsorption on rock surfaces. Core plugs were completely submerged in a 5% V/V solution of *n*-heptane (99% Sigma Aldrich) in crude oil. The solution containing the rock samples was heated at 60 °C and stirred at 500 rpm during 2 days. (3) Prepare core plugs for wettability assessment and alteration. Core plugs were washed with *n*-heptane and distillated water and then dried at 60 °C during 3 h.

2.3. Wettability Alteration under Static Conditions. In order to alter its wettability under static conditions, each core plug with induced oil-wet wettability was submerged in a previously prepared nanofluid with a given nanoparticle concentration (PRNS-100, PRNS-500, PRNS-1000, PRNS-2000, PRNS-10000). Then, each system was heated at 40 °C for 48 h. Finally, each core plug was removed from the corresponding nanofluid and dried at 40 °C for 24 h. This procedure was also performed using a core plug submerged in pure surfactant (PRNS-0).

2.4. Contact Angle and Imbibition Tests. A qualitative assessment of the wettability of the core plugs, before and after the treatment with nanofluids, was performed by estimating the contact angle. This was carried out by placing a droplet of liquid (water or crude oil) onto the surface of the dried cores and then estimating visually the contact angle for the liquid/air/rock systems at room temperature.

Wettability alteration of the core plugs due to the treatment with nanofluids was also evaluated by spontaneous water imbibition into the dried cores at room temperature. Imbibition tests were performed by placing the dried cores inside water while hanging under an electronic balance (see Figure 1). Once water started to imbibe, the cumulated weigh was recorded as a function of time. The imbibition test ended at that time when the recorded weigh remained constant (equilibrium time). The ratio between the weight of water imbibed at a given time (m_w) and the weight of water imbibed at the equilibrium time (m_{wT}) was plotted as a function of time for each treated core plug. Imbibition tests were also carried out in a dried core plug without induced asphaltene deposition (base sample) and in a dried core plug with induced asphaltene deposition but without nanofluids treatment (nontreated sample).

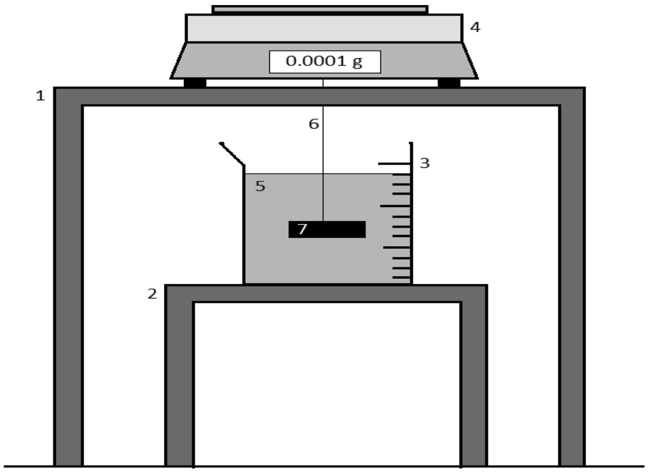

Figure 1. Schematic of the imbibition test assembly: (1) the table, (2) the support table, (3) the beaker, (4) the analytical balance, (5) water, (6) the hook, and (7) the sample.

2.5. Core Displacement Tests. Figure 2 shows a schematic representation of the experimental setup. The setup consists mainly of a tank containing the nanofluid, a commercial pump (Cole-Parmer Instrument Co., Canada), a positive displacement pump (DB Robinson Group, Canada), fraction collectors, and a stainless steel column reactor. Fluids were injected into the porous media from the injection point by positive displacement pump.

A sand pack was selected to carry out displacement tests. The packing material was clean silica sand (Ottawa sand, U.S. Sieves 30−40 mesh). Before packing, the sand was washed with deionized water to remove any dust or surface impurities and then was placed in a vacuum oven at 60 °C for 12 h to evaporate any remaining water. Then, approximately 150 g of the sand was transferred to a stainless steel column (inside diameter of 8 cm and length of 3.81 cm) for packing. The measured absolute permeability and porosity of the porous media were 2.19 Darcy and 33%, respectively. Core displacement tests were conducted using a nanofluid prepared by dispersing alumina nanoparticles in distilled water with a nanoparticle concentration of 500 ppm. Tests were performed at 50 °C and 19.3 MPa (2800 psia) of confining pressure.

The following five-step procedure was performed for evaluating the effectiveness of injecting the alumina-based nanofluid to alter the wettability of sandstone systems: (1) Measure the sand pack absolute permeability. Water (10 pore volumes (PV)) was injected to the sand

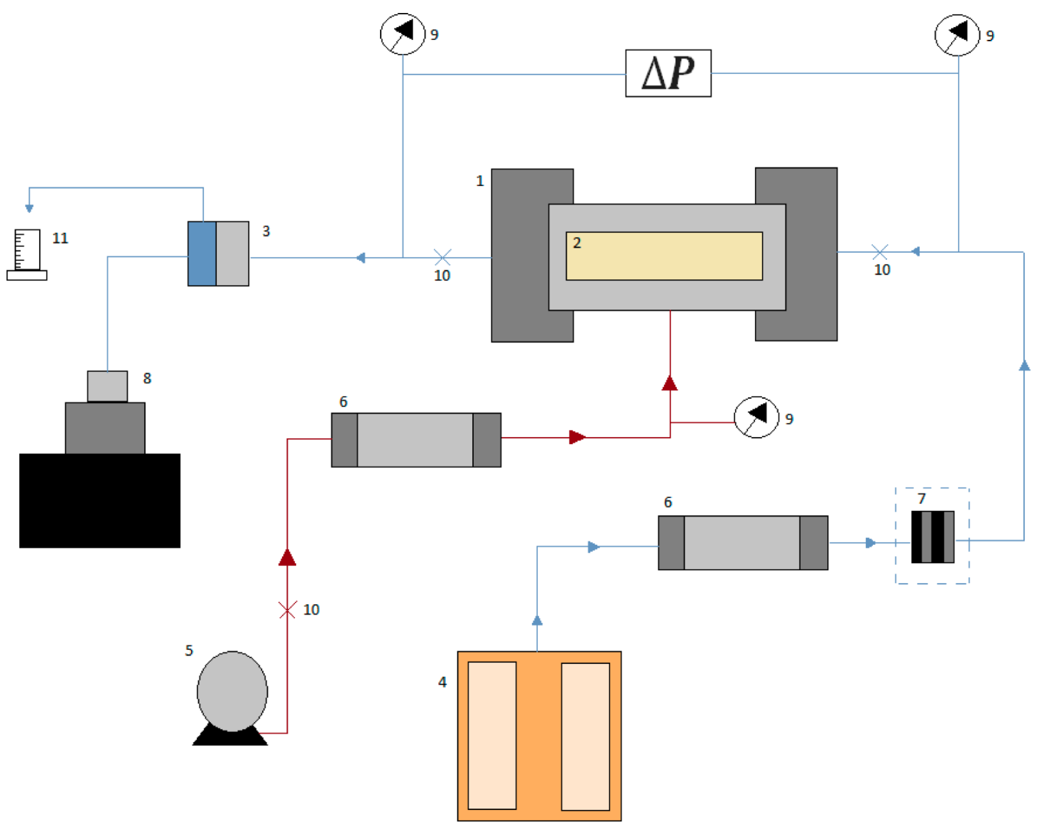

Figure 2. Diagram of the displacement test: (1) the core holder, (2) the core (Ottawa sand Packing), (3) the pore pressure diaphragm, (4) pump one (the positive displacement pump), (5) pump two, (6) the displacement cylinder, (7) the filter, (8) the pressure multiplier, (9) the manometer, (10) a valve, and (11) the test tube.

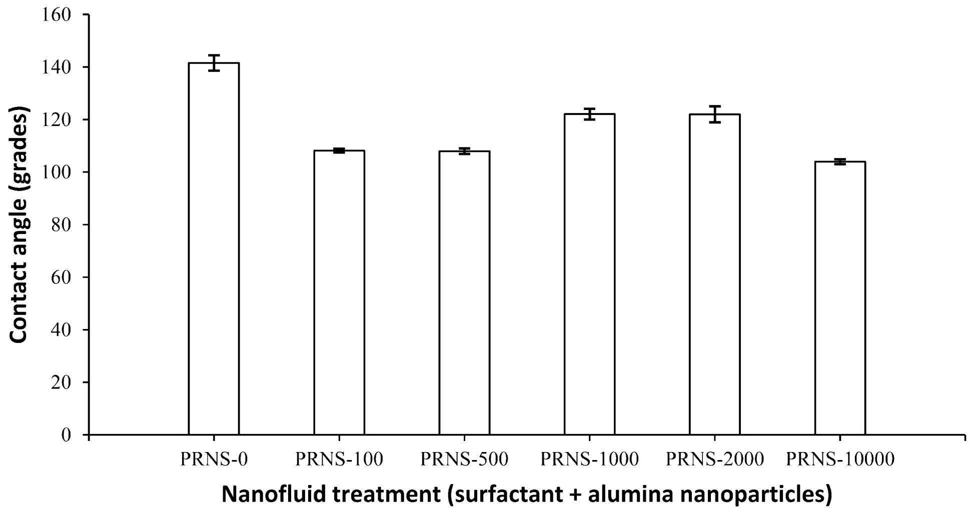

Figure 3. Contact angles for the water/air/rock systems before the treatment with nanofluids. Measurements were carried out by triplicate. The notation PRNS-X indicates the commercial name of the surfactant and the nanoparticle concentration used in ppm (mg/L).

pack under controlled flow rate (0.5 cm^3/min), and two pressure transducers were used to record the pressure values at the injection and production points. Accordingly, the porous media permeability was estimated following Darcy's law. (2) Alter the sand pack wettability by inducing asphaltene precipitation and adsorption. Initially, 50 PV of crude oil were injected to the water-saturated core and the effective permeability to oil at residual or irreducible water saturation (K_{ro} at S_{wr}) was measured. Then, 0.5 PV of *n*-heptane were injected in order to alter the sand pack initial wettability. (3) Construction of the relative permeability curve before nanofluid treatment (base curve). Water (12 PV) was injected, and the oil and water effective permeabilities were measured as water replaced oil within the core. Then, the effective permeability to water at residual oil saturation (K_{rw} at S_{or}) was measured. (4) Inject the nanofluid treatment. Before treatment, 2 PV of crude oil was injected to the sand pack, and the displaced volume of water in the porous media was measured. The main treatment consisted of 0.5 PV of the alumina based-nanofluid (alumina nanoparticles dispersed in water), which was injected simultaneously with crude oil (a coreholder head with two inlet ports was used). Looking for improving the dispersion of nanoparticles in the porous media, an additional quantity of nanofluid of 0.3 PV was injected. (5) Construct the relative permeability curve after nanofluid treatment. Water (20 PV) was injected, and the oil and water effective permeabilities were measured as functions of water saturation.

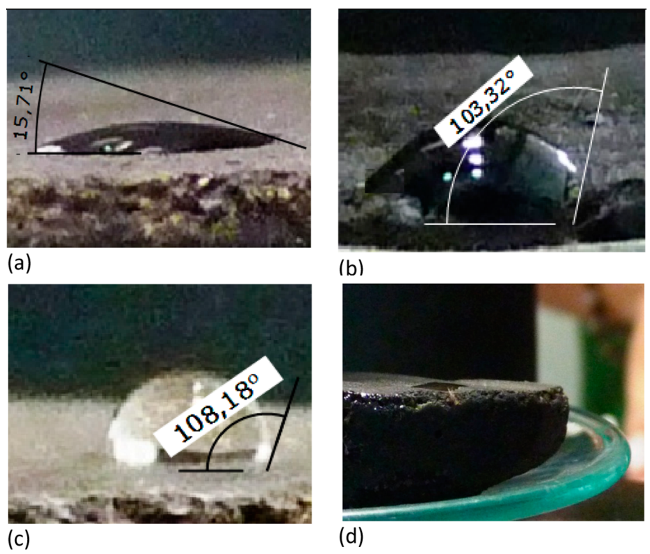

Figure 4. Contact angles for the treatment with a nanoparticle concentration of 100 ppm: (a) oil/air/rock system before treatment, (b) oil/air/system after treatment, (c) water/air/system before treatment, (d) water/air/system after treatment.

3. RESULTS AND DISCUSSION

3.1. Contact Angle and Imbibition Tests.

Figure 3 shows the estimated contact angles before nanofluid treatment for the water/air/rock systems as functions of nanoparticle concentration in the alumina-based nanofluids. Contact angles after nanofluid treatment were practically zero for all systems. Figure 4 shows the drops of water and oil placed onto the rock surface, before and after treatment, when the PNRS-100 treatment was used.

As can be seen in Figure 3, the water-drops placed on the untreated sandstone cores show estimated contact angles varying between 104° and 142°. This indicates the suitability of the procedure followed for inducing an oil-wet condition. Variation in initial contact angles among core samples can be explained by differences in surface roughness and heterogeneities. The change in the contact angle of the water/air/rock systems due to the treatment with nanofluids (from 104°−142° to practically 0°) indicates that the rock wettability was altered from an oil-wetting to a strongly water-wetting condition, but little difference with respect to the nanoparticles concentration could be identified.

As mentioned in section 2, in addition to the contact angle test, all core samples were subject to an imbibition test. A key difference between both tests is the amount of rock surface that comes into contact with water during the experiment. While in the former test only a water drop makes contact with the external surface of the core sample, in the latter test a given volume of water comes into the interconnected porous space of the rock and makes contact with its internal surface area.

Figure 5 compares the results of the spontaneous imbibition tests for the eight samples tested. As explained in section 2.4, the *y*-axis indicates the dimensionless weight gained by a core sample during the imbibition process. Results show a very fast spontaneous imbibition process for the base sample, which is in agreement with its strongly water-wet nature. It is well-known that capillary pressure, which is the main driving force in

dx.doi.org/10.1021/ef4002956 | Energy Fuels 2013, 27, 3659−3665

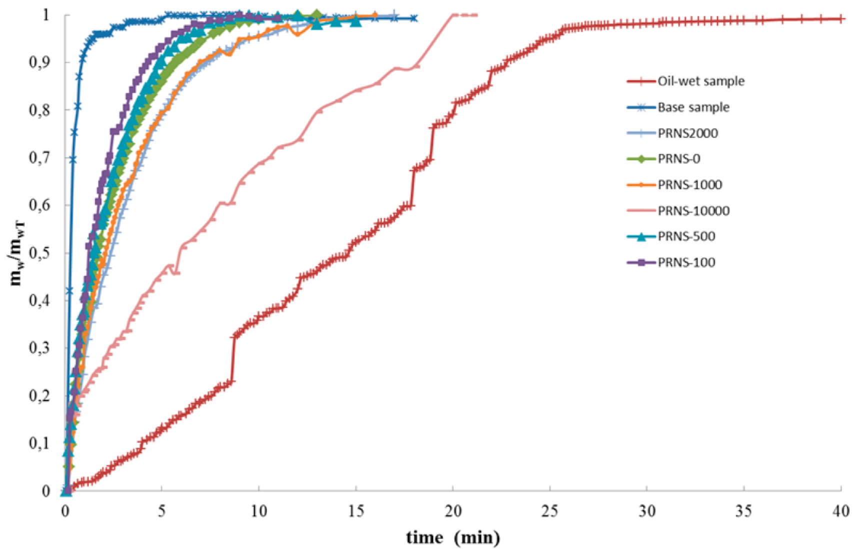

Figure 5. Spontaneous imbibition curves for sandstone cores. The symbols are experimental data. The notation PRNS-X indicates the commercial name of the surfactant and the nanoparticle concentration used in ppm (mg/L).

spontaneous imbibition, increases as the wetting phase is more strongly wetting. Consequently, the nontreated sample (oil-wet sample) exhibits the slowest imbibition process. From Figure 5, it can also be inferred that all treatments, in a different extent, were suitable for restoring the original wettability and enhancing the imbibition process by altering the samples wettability toward more water wetness. Regarding to the effect of nanoparticles concentration on the effectiveness of the treatment to alter rock wettability, different trends can be identified. Although the use of the PRNS-0 treatment (neat surfactant) allowed achieving a significant restoration of rock wettability, its effectiveness as wettability modifier could be improved by adding alumina nanoparticles with concentrations lower or equal than 500 ppm. The best performance was achieved when the PRNS-100 treatment was used. Results indicate that the synergy effect of the treatment with nanofluids (surfactant and nanoparticles) on wettability restoration was lost, as nanoparticles concentration increased above certain level. Treatments with nanoparticles concentration above or equal than 1000 ppm showed performances worse than the PRNS-0 treatment. Among the treatments, the PRNS-10000 exhibited the worst performance.

As mentioned in section 1, it has been argued that surfactant induced wettability alteration is governed by two main mechanisms: cleaning and coating. From a phenomenological point of view, it can be argued that once some oil molecules are removed by the surfactant from the rock surface, some surfactant molecules could be adsorbed onto that cleaned surface. If nanoparticles with high affinity for the oil phase are mixed with the surfactant, the performance of the treatment as wettability modifier could be improved. This kind of nano-particle will be more easily adsorbed onto surfaces covered by an oil phase and can contribute to the treatment durability. This means that adding nanoparticles could be a way to enhance the coating mechanism of the treatment. Additionally, nanoparticles can avoid a posterior aggregation of the removed oil molecules by maintaining them in suspension.

An increase, above a certain limit, in nanoparticle concentration could lead to phenomena-like particle coales-cence and aggregation, which, in turn, might result in particle sizes in the range of micrometers. This kind of greater particles might negatively affect both the coating and cleaning mechanisms of the nanofluid treatment. In addition, particles with sizes in the order of micrometers, sizes in the same order of the pore space openings, could cause formation damage for fine migration and pore plugging.

3.2. Core Displacement Test.

Table 1 presents the results of the effective permeabilities at residual fluid saturations obtained in the displacement tests. Figure 6 shows the relative permeability curves before and after the treatment with the alumina-based nanofluid. Both curves were normalized with the effective oil permeability at residual water saturation before treatment (521.6 mD).

Table 1. Effective Permeabilities at Residual Fluid Saturations before and after Nanofluid Treatment

	moment	
property	before treatment	after treatment
K_o at S_{wr} (mD)	521.6	696.2
K_w at S_{or} (mD)	473.1	329.4
S_{or} (%)	25	21
S_{rw} (%)	7	23

Comparing the results before and after treatment, it can be noticed that there were appreciable changes in the residual water saturation (S_{wr}), the relative oil permeability curve and the point where the water and oil relative permeabilities are equal (crossover point).

The values of the residual water saturation, before (0.07) and after treatment (0.23), indicate that, according to the Craig's rules of thumb,[25] the sand pack changed its wettability from a strongly oil-wet condition (S_{wr} < 0.1) to a strongly water-wet condition (S_{wr} > 0.2). The most probably mechanism explaining this strong change in wettability is the adsorption of alumina nanoparticles on most of the sand grains surface (coating mechanism). Since the sand pack can be considered as an uniform porous media with respect to its mineralogical composition, it is expected that the wettability of the entire surface was varied from oil-wet to water-wet, and consequently, the sand pack behaved as an uniformly wetted system.

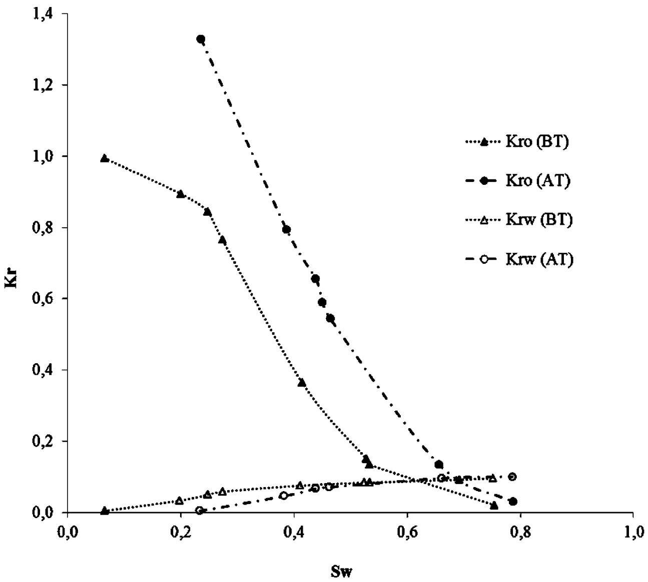

Figure 6. Relative permeability curves before and after nanofluid treatment. The symbols are experimental data. The notation AT and BT indicates that measurements were carried out after treatment or before treatment, respectively.

According to Figure 6, the oil relative permeability curve was displaced to the right due to the nanofluid treatment. This implies that the oil effective permeability at a given water saturation increased as the wettability was varied from an oil-wet to a water-wet condition. In particular, the maximum oil effective permeability (K_o at S_{wr}) underwent an increase from 521.6 mD to 696.2 mD (an increase of 33%). At S_{wr}, the water phase has very little effect on the flow of oil. Because the water does not significantly block the oil flow, the oil effective permeability is relatively high.

Similar to the oil relative curve, the crossover point was also displaced to the right. After the nanofluid treatment the water saturation at which the water and oil relative permeabilities become equal was close to 0.7. According to the Craig's rules of thumb,[25] this value is typical of strongly water-wet cores. A high saturation of the wetting phase is required at the crossover point to compensate for its lower mobility.

4. CONCLUSIONS

Wettability alteration of sandstone cores by nanofluids prepared by dispersing alumina nanoparticles in a commercial anionic surfactant or in water was studied. The following conclusions can be drawn from this experimental study:

- Alumina-based nanofluids can alter the wettability of sandstone cores with induced oil-wet wettability from strongly oil-wet to strongly water-wet condition.
- The effectiveness of anionic surfactants as wettability modifiers can be improved by adding alumina nanoparticles at relatively low concentrations. In this particular study, significant wettability restorations were achieved by using nanofluids with a nanoparticle concentration of 100 ppm. Imbibition tests seem to be a valuable tool for evaluating the effect of nanoparticles concentration on the treatment performance.
- Oil recovery efficiency by waterflooding in oil-wet rocks can be enhanced by dispersing relatively low concentrations of alumina nanoparticles in the injected water to alter the wettability of the reservoir rock to a strongly water-wet state.

■ AUTHOR INFORMATION

Corresponding Author

*Telephone: +57 4 42555319 E-mail: pbenjume@unal.edu.co.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are grateful to Petroraza SAS, COLCIENCIAS, and Universidad Nacional de Colombia for logistical and financial support.

■ REFERENCES

(1) Salathiel, R. Oil recovery by surface film drainage in mixed-wettability rocks. *J. Pet. Technol.* **1973**, *25* (10), 1216−1224.

(2) Kovscek, A. R.; Wong, H.; Radke, C. J. A pore-level scenario for the development of mixed wettability in oil reservoirs. *AIChE J.* **1993**, *39* (6), 1072−1085.

(3) Yefei, W.; Huaimin, X.; Weizhao, Y.; Baojun, B.; Xinwang, S.; Jichao, Z. Surfactant induced reservoir wettability alteration: Recent theoretical and experimental advances in enhanced oil recovery. *Pet. Sci.* **2011**, *8*, 463−476.

(4) Menezes, J. L.; Yan, J. N.; Sharma, M. M. Wettability alteration caused by oil-based muds and mud components. *SPE Drill. Completion* **1993**, *8* (1), 35−44.

(5) Anderson, W. G. Wettability literature survey—Part 1: Rock/oil/brine interactions and the effects of core handling on wettability. *J. Pet. Technol.* **1986**, *38* (10), 1125−1144.

(6) Tong, Z.; Morrow, N. R. Variations in wetting behavior of mixed-wet cores resulting from probe oil solvency and exposure to synthetic oil-based mud emulsifiers. *J. Pet. Sci. Eng.* **2006**, *52*, 149−160.

(7) Al-Maamari, R. S. H; Qaboos, S.; Buckley, J. S. Asphaltene precipitation and alteration of wetting. The potential for wettability changes during oil production. *SPE Reservoir Eval. Eng.* **2003**, *6* (4), 210−214.

(8) Yeh, S. W.; Ehrllch, R.; Emanuel, A. S. Miscible-gasflood-induced wettability alteration: Experimental observations and oil recovery implications. *SPE Form. Eval.* **1992**, *7* (2), 167−172.

(9) Salehi, M.; Johnson, S. J.; Liang, J. T. Mechanistic study of wettability alteration using surfactants with applications in naturally fractured reservoirs. *Langmuir* **2008**, *24*, 14099−14107.

(10) Zhang, J.; Nguyen, Q. P.; Flaaten, A. K.; Pope, G. A. Mechanisms of enhanced natural imbibition with novel chemical. *SPE Reservoir Eval. Eng.* **2009**, *12* (6), 912−920.

(11) Noh, M.; Firoozabadi, A. Wettability alteration in gas-condensate reservoirs to mitigate well deliverability loss by water blocking. *SPE Reservoir Eval. Eng.* **2008**, *11* (4), 676−685.

(12) Hammond, P. S.; Unsal, E. Spontaneous imbibition of surfactant solution into an oil-wet capillary: Wettability restoration by surfactant-contaminant complexation. *Langmuir* **2011**, *27* (8), 4412−29.

(13) Ju, B.; Dai, S.; Luan, Z.; Zhu, T.; Su, X.; Qiu, X. Study of wettability and permeability change caused by adsorption of nanometer structured polysilicon on the surface of porous media. *SPE* **2002**, http://dx.doi.org/10.2118/77938-MS.

(14) Ju, B.; Fan, T.; Ma, M. Enhanced oil recovery by flooding with hydrophilic nanoparticles. *China Particuol.* **2006**, *4*, 41−46.

(15) Ju, B.; Fan, T. Experimental study and mathematical model of nanoparticle transport in porous media. *Powder Technol.* **2009**, *192*, 195−202.

(16) Maghzi, A.; Mohebbi, A.; Kharrat, R. Pore-scale monitoring of wettability alteration by silica nanoparticles during polymer flooding to heavy oil in a five-spot glass micromodel. *Transp. Porous Media* **2011**, *3*, 653−664.

(17) Onyekonwu, M.; Ogolo, N. A. Investigating the use of nanoparticles in enhancing oil recovery. *SPE* **2010**, http://dx.doi.org/10.2118/140744-MS.
(18) Karimi, A.; Fakhroueian, Z.; Bahramian, A.; Khiabani, N. P.; Darabad, J. B.; Azin, R.; Arya, S. Wettability alteration in carbonates using zirconium oxide nanofluids: EOR implications. *Energy Fuels* **2012**, *26* (2), 1028−1036.
(19) Kapusta, S.; Balzano, L. Nanotechnology applications in oil and gas exploration and production. *IPCT* **2011**, http://dx.doi.org/10.2523/15152-MS.
(20) Mokhatab, S.; Araujo, M.; Islam, M. R. Applications of nanotechnology in oil and gas E&P. *J. Pet. Technol.* **2006**, *58* (4), 48−51.
(21) Zitha, P. L. J. Smart Fluids in the Oilfield. *Explor. Prod.: Oil Gas Rev.* **2005**, No. Issue 1, 66−68.
(22) Rouquerol, F.; Rouquerol, J.; Sing, K. S.W. *Adsorption by Powders and Porous Solids: Principles, Methodology, and Applications*; Academic Press: London, U.K., 1999.
(23) Brunauer, S.; Emmett, P. H.; Teller, E. Adsorption of gases in multi-molecular layers. *J. Am. Chem. Soc.* **1938**, *60*, 309−319.
(24) Patterson, A. L. The Scherrer formula for X-ray particle size determination. *Phys. Rev.* **1939**, *56*, 978−982.
(25) Anderson, G. W. Wettability literature survey. Part 5: The effects of wettability on relative permeability. *J. Pet. Technol.* **1987**, *39* (11), 1453−1468.