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Wettability Alteration in Carbonates using Zirconium Oxide Nanofluids: EOR Implications

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ABSTRACT: Wettability alteration is an important method to increase oil recovery from oil-wet carbonate reservoirs. Chemical agents like surfactants are known as wettability modifiers in carbonate systems. However, the effectiveness of these agents can be increased by the addition of chemicals such as polymers, ionic materials, and nanoparticles. The impacts of nanoparticles on the wettability of carbonate systems have not been reported yet, and it is still in its infancy. In this work, the effect of ZrO₂-based nanofluids on the wettability alteration of a carbonate reservoir rock was experimentally studied. Several nanofluids were made composed of ZrO₂ nanoparticles and mixtures of nonionic surfactants. The effect of nanofluids on the wettability of carbonate samples were investigated by measuring the contact angles, and it was shown that designed nanofluids could significantly change the wettability of the rock from a strongly oil-wet to a strongly water-wet condition. Scanning electron microscopy (SEM) images and X-ray Diffraction (XRD) data verify adsorption of nanoparticles on the rock and formation of nanotextured surfaces. Moreover, this paper reports the quick imbibitions of ZrO₂ nanofluids into oil-wet core plugs saturated with stock tank oil. The results show that a considerable amount of oil can be quickly recovered by free imbibitions of the nanofluids into the core plugs. A theoretical approach is also presented to explain the wettability alteration by formation of composite nanotextured surfaces.

1. INTRODUCTION

Many of the world's largest oil fields are found in carbonate reservoirs characterized by, low-permeability, fractured, and oil-wet rocks.^{1,2} Oil recovery from fractured carbonate reservoirs is limited to exploitation of oil trapped into the low permeable formations.^{3–5} After the primary production period, waterflooding is applied as a relatively cheap⁶ and qualified choice to enhance oil recovery. Most carbonate reservoirs are preferentially oil-wet,^{7–9} and therefore, the recovery of oil from these reservoirs by waterflooding techniques is relatively low. The presence of fractures can reduce the sweep efficiency of the injected fluid, and consequently, it can lower the amount of recovered oil. Considering the significant amount of oil in place in fractured oil-wet carbonate reservoirs, there is a huge interest to improve the oil recovery from these systems.

The efficiency of the waterflooding process can be enhanced using some chemical agents such as surfactants, solvents, and pH controllers. When added to the injecting water, these chemicals can modify the wettability of the rock surface to more water wetting or significantly reduce the interfacial tension between reservoir oil and the injected fluid. Surfactants are mainly employed to increase the capillary number through lowering interfacial tension between oil and water, and polymers are utilized to improve the mobility ratio and sweep efficiency.^{10,11} The polymer solution significantly affects the oil and water flow rates, and consequently, it sweeps a larger fraction of the oil reservoir than water or surfactant solution alone. Introducing inorganic alkaline chemicals such as sodium

hydroxide or sodium carbonate can enhance the oil recovery by reducing interfacial tension and spontaneous emulsification, which results from *in situ* surfactant generation or by wettability alteration.

Numerous experimental works have been published discussing the role of wettability in various aspects of oil recovery.^{12–15} In several investigations, the wettability of porous media was changed by chemical treatment.^{1–4,6,16–24} Wettability alteration by chemical treatment is an ongoing field of research motivated by academic and industrial interests²⁵ and plays an important role in almost all oil recovery techniques.¹⁶ The alteration of reservoir rock wettability by surfactants has been deemed as an important mechanism for the recovery of oil from fractured carbonate reservoirs, and the use of ionic surfactants for changing the wettability of carbonates from oil-wet to water-wet conditions is well documented in the literature.^{17–24} The mechanism is believed to be pair-ion making and desorption of organic compounds from the rock surface by surfactants. The rate of change in wettability process depends, however, on the surface activity of the surfactant. The surface activity can be increased by the addition of other chemicals such as polymers and polyelectrolytes.²⁶ The interaction between surfactant and polymers can increase the surface activity of the surfactants, resulting in

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significant reduction in the interfacial tension between the oil and the injected fluid and also wettability change through multilayer formation.²⁷ The surface activity of the surfactants and the polar components in the oil phase can also be affected by introducing different ions and counterions. It has been shown that ions such as SO_4^{2-} , Ca^{2+} , and Mg^{2+} have the capability to change the reservoir rock wettability.^{28,29} Webb et al.³⁰ investigated the spontaneous imbibitions at reservoir conditions on cores from Valhall and concluded that seawater can change the capillary pressure curve in a way that increases the oil recovery.

The use of nanoparticles for oil recovery from hydrocarbon reservoirs has been suggested by some researchers.^{31–35} However, there is no report about the use of nanoparticles for wettability alteration of carbonate systems. The properties of nanoparticles are mainly governed by their surface energies, and therefore, adsorption of nanoparticles on a solid surface can significantly change the surface energy and wettability of the system. Nanoparticles are very active and energetic materials with a high tendency to form nanotextured surfaces in combination with surfactants, resulting in a significant change in the interfacial properties of the system. The interaction between nanoparticle and surfactants can also make a considerable change in the surface activity of surfactant molecules. Surfactants with higher surface activity show more adsorption into the surface. Thus, they can significantly reduce the interfacial tension and can affect the wettability more strongly. Strong attraction between nanoparticle and surfactant molecules may result in formation of multilayers of surfactant–nanoparticle complexes. Such complex formation can strongly affect the wetting property of the carbonate systems. Most of the metallic oxide nanoparticles are of hydrophilic nature. Therefore, their adsorption onto a surface can change the wettability toward water wetting. However, formation of nanotextures develops a new roughness on the surface that may govern the wettability more than the wettability of adsorbed nanoparticles does.

In this paper, the use of nanoparticles to alter the wettability of the rock is studied. Procedures for synthesis, testing, and application of nanofluids are described in detail. The impact of nanofluids on alteration of wettability and free imbibitions is analyzed comprehensively. As will be discussed in the following sections, this interfacial impact can considerably enhance the oil recovery from hydrocarbon reservoirs. In section 2, we describe the materials and the methods used in our experiments. The method for synthesizing and characterizing nanoparticles is described in detail. The wettability evaluation, as it is mentioned in the next section, is performed by contact angle measurements. The impact of wettability alteration on the amount of recovered oil is investigated using a free imbibitions test, and the results are presented and discussed in section 3. Section 4 is devoted to our concluding remarks.

2. MATERIALS AND METHODS

2.1. Materials. Crude oil from Nowrooz oil field, located in the northern offshore of the Persian Gulf and a member of Bahreng Oil Area, was provided by National Iranian Oil Company (NIOC). The oil contains a considerable amount of asphaltene (10 wt %). Also, it has a viscosity of approximately 64 cSt at 70 °C (425 cSt at ambient temperature). The oil was initially diluted with kerosene in a 50/50 v/v ratio, and the mixture was used as an oil phase in spontaneous imbibition experiments. The diluted mixture had a density of 0.861 g/cm³. n-Heptane with a purity of 99.9% was provided by Merck Company. Distilled water having a conductivity of 0.05–0.08 $\mu\text{s}/\text{cm}$

was used in all experiments. Glycerin was obtained from Merck Company and used as received. Also, all the surfactants listed in Table

Table 1. Molecular Structure and HLB Values of the Used Surfactants

name	formula	molecular wt	HLB value
ethoxylated nonylphenol-4 mol (NON-EO4)	$\text{C}_{15}\text{H}_{23}(\text{OCH}_2\text{CH}_2)_4\text{OH}$	396.56	8.9
lauryl alcohol-2 mol (LA2)	$\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_2\text{OH}$	274.43	6.3
Lauryl alcohol-7 mol (LA7)	$\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_7\text{OH}$	494.7	12.4
Tween 80	$\text{C}_{64}\text{H}_{124}\text{O}_{26}$	1310	15
Span 20	$\text{C}_{18}\text{H}_{34}\text{O}_6$	346.46	8.6
Span 80	$\text{C}_{24}\text{H}_{44}\text{O}_6$	428.61	4.3
Span 85	$\text{C}_{60}\text{H}_{108}\text{O}_8$	957.49	1.8

1 and ethoxylated nonylphenol 20 mol were obtained from Kimyagaran Emrooz Company. The molecular weight of the surfactants and their hydrophilic–lipophilic balance (HLB) values are also shown in Table 1. The spherical ZrO_2 nanoparticles, with an average particle size of about 24 nm (estimated from scanning electron microscopy (SEM) images), were prepared using the sol–gel method, as described in the next section. $\text{ZrO}_2\cdot 8\text{H}_2\text{O}$, citric acid, orthophosphoric acid (85%), succinic acid, potassium hydroxide, ethanol, and dodecytrimethylammonium bromide (CTAB) were obtained from Merck Company. The synthesized ZrO_2 nanoparticle was mixed with different chemicals to make different nanofluids, as shown in Table 2. The potential of different nanofluids to alter the wettability of

Table 2. Nanofluid and Fluid Systems Used in This Work^a

fluid	formula	nano particle concn (gr/cc)	pH
1	Tween 80 + Span 85 + glycerin + LA2	0	2–3
2	Tween 80 + Span 85 + glycerin + LA2 + nanoparticle	0.05	2–3
3	Tween 80 + Span 85 + glycerin + LA2 + nanoparticle	0.10	2–3
4	Tween 80 + Span 85 + glycerin + LA7 + nanoparticle	0.05	2–3
5	Tween 80 + Span 85 + glycerin + span80 + nanoparticle	0.05	2–3
6	Tween 80 + Span 85 + glycerin + Span 20 + nanoparticle	0.05	2–3
7	Tween 80 + Span 85 + glycerin + NON-EO4 + nanoparticle	0.05	2–3

^aA mixture of these fluids (5 wt %) with distilled water was used in free imbibition and wettability alteration tests.

oil-wet carbonate rocks was tested using outcrops from a reservoir nearby the Nowrooz oil field (i.e. Aghajery in the south of Iran). Carbonate core plugs had a diameter of 3.80 cm and the lengths ranging from 7.50 to 8.50 cm, with porosity and average permeability equal to 20% and 30 md, respectively.

2.2. Nanoparticle Synthesis. ZrO_2 nanoparticles were prepared using the sol–gel method.³⁶ Zirconium oxychloride ($\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$) was used as a source of Zr. The starting solution was prepared by mixing 3.22 g of zirconium oxychloride with 2.10 g of citric acid, 1.18 g of succinic acid, 0.50 g of CTAB as surfactant, and 10 mL of ethoxylated nonylphenol, 20 mol EO. The solution was then kept in 80 °C for about 5 h. The solid product was washed and filtered with ethanol and distilled water. The sample was then dried in an oven at 110 °C for 4 h, and finally, it was calcined at 800 °C for 8 h.

2.3. Characterization Tests. SEM (Philips XL-30W model) and XRD (3003 PTS Seifert with $\text{Cu K}\alpha$ radiation, $\lambda = 1.54 \text{\AA}$) devices were used to investigate the morphology and mineralogy of zirconium

oxide nanoparticles and also the surfaces of aged carbonate plates in nanofluid solutions.

2.4. Contact Angle Measurement. Side images of drops on the carbonate plates were taken using a microscopic camera and contact angles were measured. The volume of drops was manually tuned with a precision syringe in order to obtain the smallest possible drops.

2.5. Preparation of Carbonate Substrates and Core Plugs. To perform contact angle measurements, carbonate core plugs were first cut in small plates ($3 \times 2 \times 0.2$ cm) using a trimming machine and burnished with an endface grinder to achieve a flat and relatively smooth surface. The plates and core plugs were cleaned in a Dean–Stark apparatus for 7 days in contact with toluene vapor at ambient pressure. The above equipment was provided by VINCI Company. The plates were then aged for a week in the crude oil at 80°C . After cooling, the samples were washed with *n*-heptane and distilled water and dried at 40°C for 24 h. The dried samples were submerged in different prepared nanofluids at 40°C for two days. Two plates were used for each sample. The final samples, then, were dried at 40°C for about 24 h and the dried plates were used for contact angle measurements. For imbibition tests, the core plugs were put in a core flooding apparatus. The cores were initially evacuated and then saturated by oil at a constant injection rate of 2 cc/h. The oil-saturated cores were then aged in the oil at 80°C for 2 weeks.

2.6. Spontaneous Imbibition Test. Oil recovery during free imbibition tests was measured using Amott–Harvey cells.³⁷ The saturated core plugs were placed into Amott–Harvey cells containing different nanofluids at a 5 wt % concentration in distilled water. As the nanofluids imbibe into the core plugs, oil is expelled from them and floats into the volumetric buret. The cells were maintained at 70°C , and oil recovery was measured versus time.

3. RESULTS AND DISCUSSION

3.1. Wettability of Calcite Surfaces Treated with Different Nanofluids. Wettability conditions were estimated for several systems, by measuring water phase contact angle in presence of air and *n*-heptane. As mentioned earlier, we used two plates to measure the impact of each nanofluid on the contact angle. The maximum deviation between the contact angle data of each sample is found to be 15° . Therefore, the reported contact angle data in our experiments contain a maximum error of $\pm 7.5^{\circ}$. The air/water contact angle of a cleaned calcite plate was about 32° and the contact angle between water and *n*-heptane was measured equal to 35° , as shown in Figure 1 (A, B), implying a strong water-wet condition. On the other hand, air/water and *n*-heptane/water

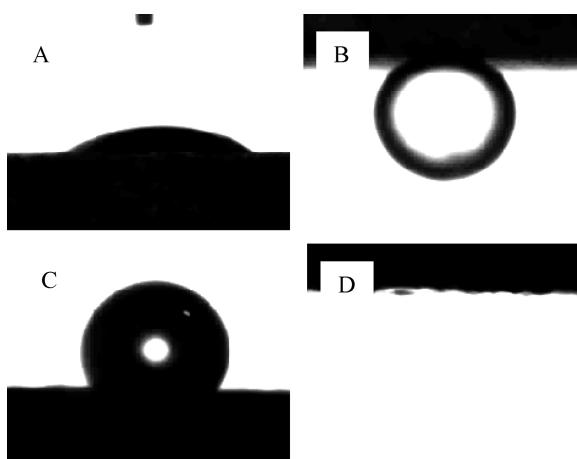


Figure 1. Wetting condition of a clean carbonate rock ((A) air/water, (B) water/*n*-heptane) and a carbonate rock aged in the oil ((C) air/water, (D) water/*n*-heptane).

contact angles on the plates aged in the oil, as shown in Figure 1 (C, D), were 118° and 180° , respectively, indicating a strong oil-wet condition. The change of wettability from water-wet to strong oil-wet condition, as verified by SEM images (Figure 2), was due to the presence of an oil film on the solid surfaces of samples aged in the crude oil. Images in Figure 2 show the morphology of a carbonate plate before and after aging in the oil. It can be observed that cleaned substrates have a surface containing carbonate particles with sharp edges, while the plates aged in the oil have a relatively smooth surface, covered with oil.

The results of contact angle measurements for samples aged in nanofluids are shown in Figures 3 and 4. Fluid 1 contains no nanoparticle at acidic pH. As shown in Figures 3 and 4, the wettability of samples aged in fluid 1 has changed from strongly oil-wet to neutral condition. The change of wettability, however, has been considerably improved by the addition of different concentrations of ZrO_2 nanoparticles (fluids 2 and 3). According to Figure 3, it can be seen that the solution without nanoparticles alters the wetting property from oil-wet to an intermediate state and introducing nanoparticles into the solution results in wetting alteration from oil-wet to strongly water-wet condition. The results of air/water contact angle measurements (Figure 4) also show that the use of fluid 1 for aging the oil-wet carbonate plates results in neutral wetting for air/water contact angle, while water spreads completely on the other samples aged in fluids 2 and 3. The change of wettability to a more water-wetting condition may be due to the adsorption of nanoparticles onto the solid surface and a consequent change of surface free energy. Energy dispersive X-ray, EDX, analysis of the samples aged in the fluids 2 and 3 are shown in Figure 5(A, B). As it is evident from this figure, the surfaces are composed of Ca and Zr as constituent materials. The original rock was mainly composed of Ca with no Zr element. Therefore, presence of Zr on the aged rock surface proves that zirconium was adsorbed onto the surface.

Figure 6A shows an SEM image for the surface of the sample aged in fluid 1. As it is obvious from this image, the morphology is somehow the same as that of clean surface (Figure 2A). In marked contrast to fluid 1 (Figure 6A), parts B and C of Figure 6 reveal the formation of nanostructures on the surfaces of carbonate plates when aged in fluids 2 and 3. Aging the oil-wet plates in fluids 2 and 3 results in the construction of some nanosized ribbons (Figure 6B) and nanoflowerlike morphologies (Figure 6C) on the rock surfaces. These nanostructured surfaces can be responsible for alteration of wettability of an oil-wet rock to a strongly water-wet surface.

The only difference between fluid 2 and 3 is the nanoparticle concentration. The concentration of nanoparticles in fluid 3 is twice as much as that in fluid 2. The contact angle measurements (Figure 3) show that fluid 2 has been more capable of changing the wettability to a water-wet condition than fluid 3. This fact suggests the impact of nanostructured type on the wettability of solid surfaces. It is well-known that a solid surface can show different contact angle values considering the roughness of the solid surface. Therefore, according to the above results, there must be an optimum value for the nanoparticle concentration for wettability modification.

Fluids 4–7 are prepared similar to fluid 2, with the exception of using different surfactants instead of lauryl alcohol-2 mol (LA2). The pH values and the concentration of all the other components in these fluids are the same as those in fluid 2. As it is obvious from Figure 4, replacing LA2 with the surfactants

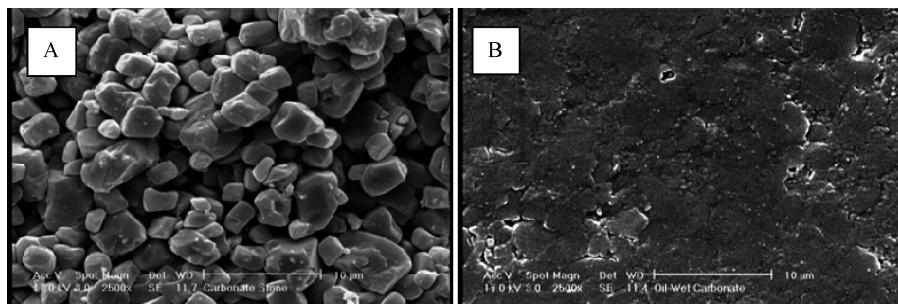


Figure 2. SEM images of a clean carbonate rock (A) and a carbonate rock aged in oil (B).

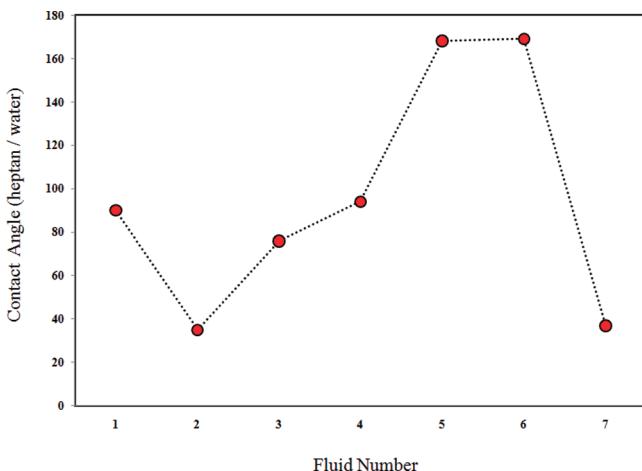


Figure 3. Measured *n*-heptane/water contact angle of the oil-wet carbonate rocks aged in different nanofluids.

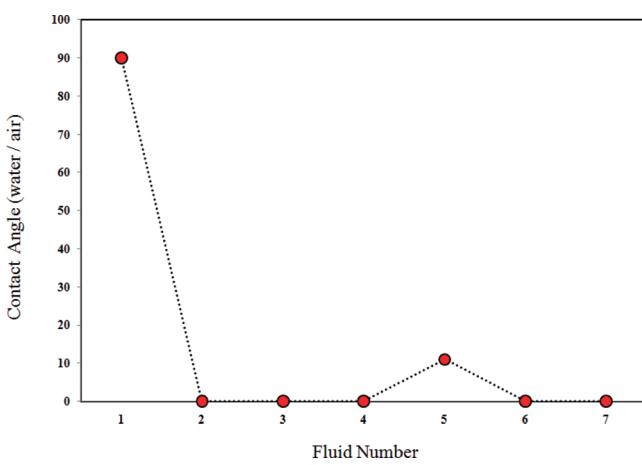


Figure 4. Measured air/water contact angle of the oil-wet carbonate rocks aged in different nanofluids.

mentioned in fluids 4–7 makes little or no effect on the air/water contact angle, which is expected. Metal oxide nanoparticles have high surface energies, and therefore, their adsorption enhances the wettability of any liquids with low surface tensions in the presence of air. However, the tendencies of nanostructured surfaces toward water and hydrocarbon are different for each sample, as shown by contact angle measurements.

Fluid 7, with ethoxylated nonylphenol-4 mol (NON-EO4) instead of LA2, shows contact angle values similar to the those obtained with fluid 2. Both NON-EO4 and LA2 are nonionic surfactants with very similar head groups. NON-EO4 has

higher HLB values than LA2, and hence, it is more hydrophilic. However, although there is a general belief of the existence of a correlation between HLB and wetting properties, we cannot correlate the wettability changes observed in the investigated systems with the related HLB values. For instance, HLB for Span 20 (used in fluid 6) is close to the HLB value of NON-EO4, while the contact angle data are quite dissimilar. Moreover, lauryl alcohol 7 mol (LA7, used in fluid 4), with a much higher HLB than those of Span 20 and LA2, shows a contact angle between those of fluid 2 and fluid 6. Interestingly, Span 80 (used in fluid 5) has a much lower HLB than Span 20 and shows a similar impact on the contact angle between water and *n*-heptane on the aged surfaces to that in fluid 6.

Dynamics of wetting is also investigated by virtue of contact angle measurement on carbonate surfaces being aged in fluid 2 for various periods of time. Figure 7 shows the contact angle values between water and *n*-heptane on samples aged in fluid 2. The horizontal axis of this figure shows the aging time. According to results shown in this figure, a minimum of 48 h is required for the aging time for alteration of wettability from oil-wet to water-wet condition. A similar conclusion can be drawn from measured air/water contact angle values, as reported in Figure 8. These results are very important when investigating the capability of nanofluids to modify the wettability of mineral surfaces in practical time scales.

3.2. Spontaneous Imbibition Test. Figure 9 shows the results of spontaneous imbibitions of fluids 2 and 3 into the core plugs saturated with oil. This figure also reveals the result of similar test using distilled water as the imbibing fluid. As it is evident from this figure, very small amount of oil has been produced by distilled water, shortly after the initiation of the experiment. This small amount of oil cannot be considered as recovered oil, for it is just oil removed from the core surface as a result of gravity. Fluids 2 and 3, however, imbibe rapidly into the core plugs, resulting in a considerable oil recovery of about 40% in just half a day. The ultimate recovery by fluid 2 is about 10% higher than the recovery obtained by imbibitions of fluid 3 into the core, which is in accordance with measured contact angle data. However, the quick response of the system to the presence of nanofluids may not be related to the wettability and its alteration. As mentioned before, considering the data presented in Figures 7 and 8, a minimum aging time of 48 h is required for alteration of wettability by selected nanofluids. On the other hand, Figure 9 shows maximum recovery rate in early stage of the experiment, shortly after contact between nanofluids and core plugs. The mechanistic reason for this quick and strong response is unknown to us, though it is certainly related to the interactions between rock–nanofluid, rock–oil, and oil–nanofluid. Formation of nanoparticle–surfactant complexes and the consequent interaction between

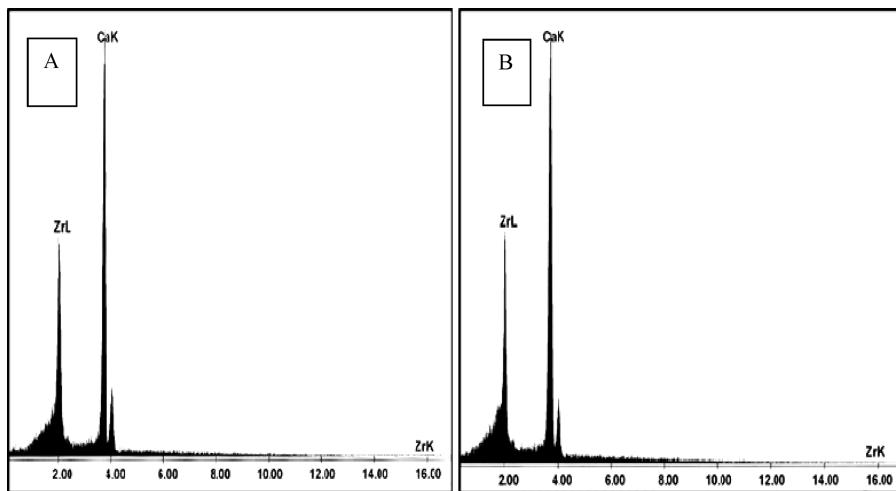


Figure 5. EDX analysis of carbonate rocks aged in fluid 2 (A) and fluid 3 (B).

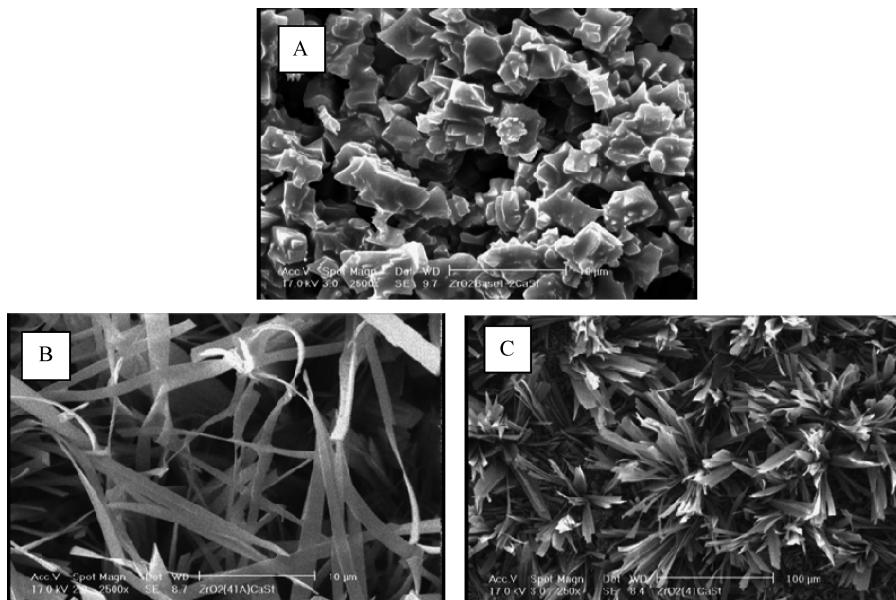


Figure 6. SEM images of an oil-wet carbonate rock aged in fluid 1 (A), fluid 2 (B), and fluid 3 (C).

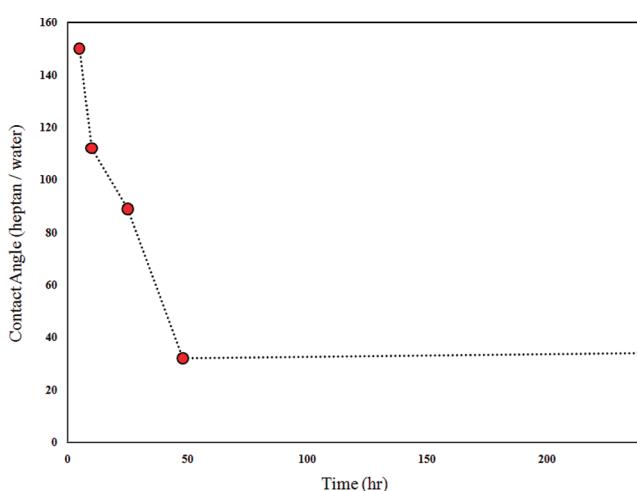


Figure 7. Effect of the aging time on the wettability of carbonate plates aged in fluid 2 as measured by *n*-heptane/water contact angle.

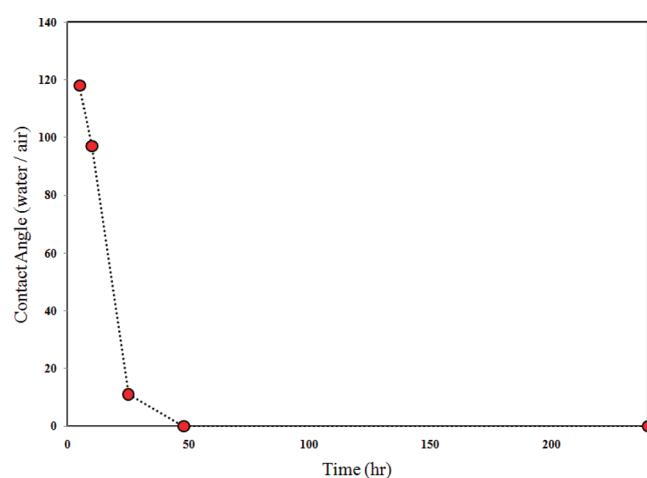


Figure 8. Effect of the aging time on the wettability of carbonate plates aged in fluid 2 as measured by air/water contact angle.

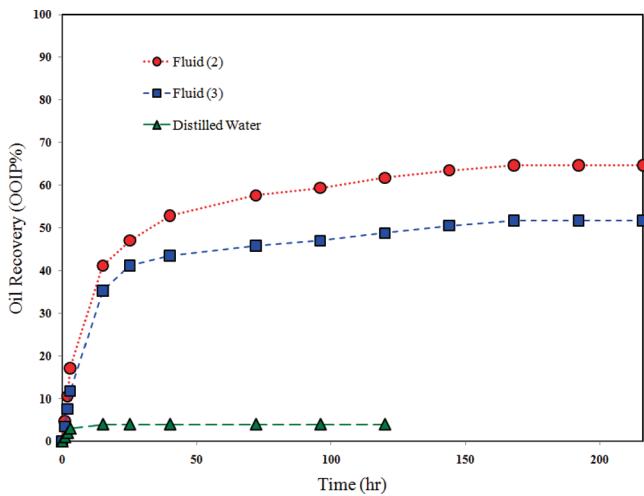


Figure 9. Spontaneous imbibitions of nanofluids 2 and 3 into oil-wet oil saturated core plugs at 70 °C.

oil and rock can be a possible explanation for the observed phenomena. Also, formation of emulsions stabilized with nanoparticles, known as Pickering emulsions, can be another reason for such a quick fluid imbibitions. Detailed experiments such as monitoring the phase behavior of nanofluid–oil systems, measuring ζ potentials and interfacial tensions, and atomic force microscopy (AFM) analysis of the rock surfaces can help to prove/disprove the above ideas.

The next section is comprised of our attempts to theoretically explain the impact of adsorbed nanoparticles on the wettability.

3.3. Theoretical Explanation. Wettability of a solid surface relates directly to the solid–fluids and fluid–fluid interactions. The interaction between two immiscible phases directs the interfacial energy. Attraction causes lower interfacial energy, and repulsion forces result in higher energy surface. The interfacial forces in a three-phase system relate to one another in a famous form known as Young's law,

$$\cos \theta = \frac{\sigma_{\text{sw}}^{\text{sw}} - \sigma_{\text{so}}^{\text{so}}}{\sigma_{\text{wo}}^{\text{wo}}} \quad (1)$$

where θ is contact angle and σ denotes interfacial tension. Superscripts sw, so, and wo represent the solid–water, solid–oil, and water–oil interfaces, respectively. Young's law describes the equilibrium condition for ideal state, where the surface is perfectly smooth and homogeneous. The impact of heterogeneity on the contact angle was first considered by Cassie.^{38,39} According to Cassie, the contact angle on a heterogeneous surface consisting of two different materials is an average value of contact angles on homogeneous materials, weighted by the area fractions. In mathematical form

$$\cos \theta = f \cos \theta_1 + (1-f) \cos \theta_2 \quad (2)$$

where θ_i is the contact angle on the homogeneous surface of pure i th component and f is the area fraction of first material on the heterogeneous surface. The effect of roughness on the contact angle is investigated by Wenzel⁴⁰ and stated in a simple equation as

$$\cos \theta^* = r \cos \theta \quad (3)$$

In this equation, θ^* is contact angle on the rough surface and r is the roughness ratio. All the investigated systems in this work

are rough and composite. The roughness of surfaces, as obvious from SEM images in Figure 6, is related to the nanostructure forms of the aged surfaces. The aging time and nanoparticle concentration affect the surface roughness through the formation of different nanostructures, hence resulting in surfaces with different wettability. To check the impact of adsorbed nanoparticles on the surface wettability, we assume that the surface is first covered by an oil film. This assumption, as evident from Figure 2B, is a reasonable assumption. Adsorption of nanoparticles and formation of nanostructures on the surface change the surface from a pure and almost smooth oil film to a composite and rough surface. The final surface is composed partly of oil film and partly of a structure made of nanoparticles. The oil film can be assumed to be composed of heavy oil, mainly asphaltene components. Considering the nanoparticle as material 1 and asphaltene as material 2, combining eqs 1 and 2 gives the following:

$$\cos \theta = f \frac{\sigma_{\text{nw}}^{\text{nw}} - \sigma_{\text{wo}}^{\text{no}}}{\sigma_{\text{wo}}^{\text{wo}}} + (1-f) \frac{\sigma_{\text{aw}}^{\text{aw}} - \sigma_{\text{wo}}^{\text{ao}}}{\sigma_{\text{wo}}^{\text{wo}}} \quad (4)$$

where superscript n denotes nanostructure and a represents asphaltene. The difference between nanostructure–water and nanostructure–oil interfacial energy determines wettability of nanostructure. Similarly, the difference between asphaltene–water and asphaltene–oil interfacial energy determines the wettability of samples before aging in nanofluids. It has been shown by Bahramian and Danesh⁴¹ and Bahramian⁴² that interfacial tension between any two condensed phases can be related to the mutual solubility as

$$\sigma^{\alpha\beta} = - \frac{RT}{a} \ln \left[\sum_{i=1}^c \sqrt{(X_i^\alpha X_i^\beta)} \right] \quad (5)$$

where T is temperature, a is molar surface area, and X is mole fraction. Considering no solubility of water and oil in solid phases, eqs 4 and 5 yield

$$\begin{aligned} \sigma_{\text{wo}}^{\text{wo}} \cos \theta = & -f \frac{RT}{2a_n} \ln \left(\frac{X_{\text{ZrO}_2}^{\text{w}}}{X_{\text{ZrO}_2}^{\text{o}}} \right) - (1-f) \frac{RT}{2a_o} \\ & \ln \left(\frac{X_a^{\text{w}}}{X_a^{\text{o}}} \right) \end{aligned} \quad (6)$$

In the above equation, a_n is the molar surface area of the nanostructure–fluid interface and a_o is the molar surface area of oil-film-covered surface–fluid interface. Subscript a in the equation represents asphaltene component. ZrO_2 has negligible solubility in oil and water. However, because water has a high dielectric constant, it is much more soluble in water than in oil. Therefore, the first term in the right-hand side of the above equation is negative. On the other hand, the second term is positive, for the solubility of asphaltene in oil is much higher than that in water. In regular solutions, we can plausibly assume that $a_n = a_o = a$. Thus, a wettability dimensionless function (wdf) can be defined for our composite systems, as follows:

$$\begin{aligned}
 wdf &= \frac{2a\sigma^{wo}}{RT} \cos \theta \\
 &= f \ln \left(\frac{X_a^w X_{ZrO_2}^o}{X_a^o X_{ZrO_2}^w} \right) - \ln \left(\frac{X_a^w}{X_a^o} \right) \\
 &= f \ln \left(\frac{k_a}{k_n} \right) - \ln k_a
 \end{aligned} \tag{7}$$

where k_a and k_n are partition coefficients of the asphaltene and the nanoparticle forming material (here, ZrO_2), respectively. According to the above equation, wdf changes linearly with area fraction of the nanostructures on the composite surface. Moreover, the partition coefficient of materials forming nanoparticles governs the way that wettability changes after the f -fraction of the surface area is covered by nanostructures. Figure 10 shows the variation of the wettability dimensionless

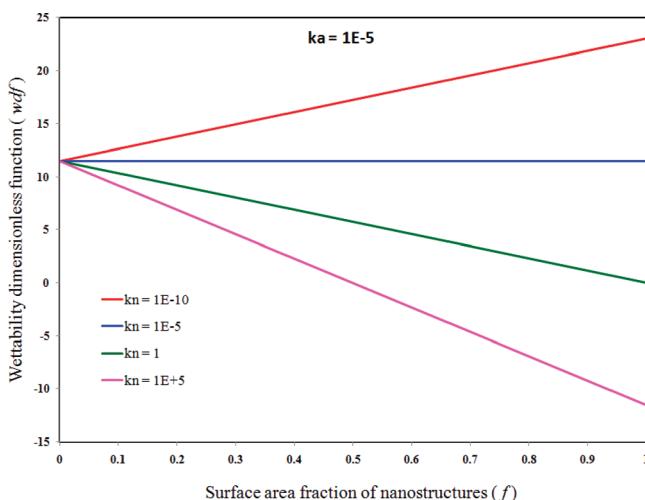


Figure 10. Variation of wettability dimensionless function with respect to the surface area fraction of nanostructures. The partition coefficient of asphaltene (as the material covered the oil-wet surface) is assumed constant and equal to 1×10^{-5} .

function with respect to the surface area fraction of the nanostructures, considering different partition coefficients for k_n at constant k_a . In this figure, positive wdf corresponds to oil-wet surfaces, while negative wdf denotes water-wetness. According to this figure, if k_n is lower than k_a , then the formation of nanostructures improves the hydrophobic nature of the surface. Functionalizing the nanoparticles with insoluble polymers can therefore reduce k_n and, thus, can pave the way for making hydrophobic surfaces. On the other hand, if materials forming nanoparticles partition in water more than asphaltene does, then the formation of nanostructures can improve the hydrophilic nature of the surface. Figure 10 shows that particles with high enough k_n can change the wettability to complete water wetting in even small area fractions. It is worth noting that particles with $k_n = 1$, at best, can change the wettability to neutral wetting state. This information can be used when designing nanoparticles for wettability alteration of gas reservoirs. The above equations, however, cannot see the effect of surface roughness. The roughness ratio, defined in eq 3, must be used to modify the wdf on the rough surfaces.

Based on the above discussions, the contact angle data reported in Figure 3 can be interpreted mainly by variation of

surface area fractions and roughness ratios. Assuming that all the nanostructures in all samples are made just of ZrO_2 , k_n and k_a are constant in all cases. Therefore, different wettabilities can be attributed to different surface area fractions and roughness ratios. However, the presence of surfactants in the nanofluids also can influence the surface structure. They can remove the asphaltene phase from the surface, or can contribute to the building blocks of the nanostructures. Such contribution can result in different k_n for each sample, thus different surface wettabilities.

4. CONCLUSION

Wettability alteration on a carbonate rock is studied using ZrO_2 nanofluids, composed of ZrO_2 nanoparticles and mixed nonionic surfactants. The following conclusions can be drawn from this study:

- ZrO_2 nanofluids are wettability modifiers for carbonate systems, and they can change the wettability of carbonate rocks from strongly oil-wet to strongly water-wet condition.
- SEM images confirm adsorption of ZrO_2 nanoparticles on the surface and the consequent formation of nanostructured ribbons. The formation of composite surfaces with adsorbed nanoparticles and original oil-wet surface is responsible for the wetting properties of the new developed surface.
- Wettability change by adsorption and growth of ZrO_2 nanoparticles on the rock surface is a slow process, requiring a period of at least 2 days.
- A theoretical model presented was based on the regular solution theory and the Cassie's model of composite surfaces. According to the model, the hydrophilic or hydrophobic nature of nanoparticles is mainly governed by the partition coefficient of materials forming nanoparticles. It is shown that adsorption of hydrophilic nanoparticles to form a smooth composite surface can improve the water-wetting nature. Nanoparticles that equally partition in oil and water can produce smooth composite surfaces with neutral wettability. Thus, the main factors affecting the wettability of composite nanotextured surfaces are area fractions of nanostructures, partition coefficient of the materials forming nanostructures, and surface roughness.
- Use of the nanofluids in free imbibitions tests revealed the strong capability of these new agents for oil recovery from hydrocarbon reservoirs. The mechanism of oil recovery by selected nanofluids, however, may not be attributed solely to the alteration of wettability, drawing the conclusion that this needs more research and experiments.

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NOMENCLATURE

a = molar surface area (m^2/mol).

c = number of component in a mixture.

f = area fraction.

k = partition coefficient.

r = roughness ratio.

R = gas constant.

T = temperature (K).

wdf = wettability dimensionless function (eq 7).

X = mole fraction.

Greek Letters

σ

interfacial tension.

θ

contact angle.

Superscripts

ao

attributed to asphaltene–oil interface.

aw

attributed to asphaltene–water interface.

no

attributed to nanoparticle–oil interface.

nw

attributed to nanoparticle–water interface.

o

attributed to oil phase.

so

attributed to solid–oil interface.

sw

attributed to solid–water interface.

w

attributed to water phase.

wo

attributed to water–oil interface.

α

attributed to phase α .

β

attributed to phase β .

Subscript

1

first compound.

2

second compound.

a

asphaltene.

n

nanoparticle.

i

i th compound.

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