

The effect of concentration of silica nanoparticles surface-modified by zwitterionic surfactants for enhanced oil recovery (EOR)

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Abstract—We investigated the effects of silica nanoparticle (NP) on nanofluid flooding for enhanced oil recovery. All NPs used in experiments were identically surface modified with PSS-co-MA and a zwitterionic surfactant. In core flooding experiments, the oil production from Berea Sandstone showed an increasing trend as the NP concentration increased within the range of 0.1 to 2.0 wt%. This result was closely associated with variance of interfacial tension (IFT) and contact angle (CA). IFT continued to decrease as the NP concentration increased until 2.0 wt%. However, IFT cannot further decrease with an increase in the NP concentration beyond 2.0 wt%, because total interaction energy may be reduced due to the decrease of electrostatic repulsion force by the closer spacing between NPs. When combined with silica nanofluid soaking, the CA of the rock/oil/nanofluids increased with increasing NP concentration; this indicated wettability alteration to a more water-wet condition caused by an enhanced fluid ability to spread silica NPs along the rock surfaces. Because of this effect, the capillary pressure is expected to be sufficiently reduced by nanofluid flooding, compared with brine flooding. However, at higher NP concentration, the NPs caused permeability reduction and an increased pressure drop attributable to the residual NPs in rock pores. This result implies additional oil recovery attributable to improved sweep efficiency related to the log jamming phenomenon caused by the residual NPs, as well as the IFT reduction and wettability alteration, thus leading to enhanced oil recovery.

Keywords: Enhanced Oil Recovery (EOR), Nanoparticle Concentration, Silica Nanofluid, Capillary Pressure

INTRODUCTION

Nanoparticles (NPs) have attracted considerable attention as a promising means of increasing oil recovery, resulting in the term “NP-based enhanced oil recovery” (Nano-EOR) [1]. Nano-EOR has a few advantages, compared with conventional EOR techniques. Particles smaller than 100 nm can move readily through pore throats of porous rock and distribute to pore network locations where they can provide efficient and noticeable differences in various manners [2]. The NPs can alter the fluid properties of the displacement fluid, including its viscosity [3-5], interfacial tension (IFT) [6-9] or rock surface wettability [10]. For example, Hu et al. [11] reported a remarkable maximum 31.4% increase in oil recovery at breakthrough points using TiO₂ NPs. Many potential mechanisms for nanofluid EOR have been proposed [12-15]. The concentrations of NPs are directly related to flow through the porous reservoir rock.

From the perspective of nanofluid flow, log jamming theory provides a potential mechanism for EOR [11,16-18]. The mechanism is as follows: NPs can remain at more-permeable channel entrances during nanofluid flooding, which forces the displacing fluid to flow through unswept regions; this increases the overall sweep and displacement efficiency, leading to increased oil recovery. During this

process, NP accumulation in porous media can cause permeability reduction [15,19-21]. In this process, the NP concentration can be important. The jamming effect may be insufficient if the NP concentration is particularly low, resulting in a minimal increase in oil recovery. However, the permeability reduction phenomenon may be predominant if the NP concentration is adequate. Accordingly, an optimal NP concentration should exist [20]. Because the optimal NP concentration differs depending on the properties of the reservoir rock and the nanofluid (e.g., particle size or additive type), there is a need to clarify the relationships of NP concentration and oil recovery with various types of NPs.

Wettability alteration also can occur because of residual NP existence on the surfaces of rock; the NP concentration has an effect on the level of wettability alteration. Theoretical and experimental investigations have shown that nanofluids reduce oil adsorption on rock surfaces by contributing to a structural disjoining force (film) between the oil and the rock surfaces, then creating a wedge film structure on the rock surfaces [22-25]. The degree of aqueous nanofluid film spreading on rock surfaces is a function of NP concentration. At higher NP concentration, the wedge film energy amplitudes increase because of increasing particle confinement in the oil-nanofluids-rock contact regions [25]. This wettability also reflects the characteristics of both the nanofluid and the reservoir rock; thus, changes according to NP concentration differ depending on the conditions of the rock and nanofluid. Yuan et al. [26] tested the efficiency of wettability alterations by nanofluids at different NP con-

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centrations (from 1 to 7 wt%). They observed that a greater potential energy barrier leads to greater nanofluid film stability on the rock, thus producing more water-wet conditions. Their experimental results showed that a concentration beyond 1 wt% does not contribute to additional wettability alteration because the potential energy barrier for a system with 7 wt% NP is less than the barrier for a system with 1 wt% NP. This result indicates that there is an optimal NP concentration for wettability alteration. Moreover, NP retention on rock surfaces may affect the wettability alteration. Therefore, further experimental studies (e.g., concerning the relationship between the amount of NP retention and rock wettability, as well as the relationship between potential energy barrier variation and NP retention density on rock surfaces) are needed to determine the optimal NP concentration for rock wettability.

Thus far, few studies have examined the effects of NP concentration on IFT [27]. For example, Radiom et al. [28] found that the IFT of TiO_2 nanofluids depends weakly on the particle concentration and exhibits a decreasing trend at higher concentrations. They demonstrated that the nanofluid IFT reduction is attributable to the reduction in cohesive energy at the liquid-air interface. This is related to the Brownian motion of NPs within the liquid. This Brownian motion can disperse NPs located at the interface to new orientations, resulting in lower total interface free energy. Consequently, this reduces the IFT [28]. Correspondingly, Zhu et al. [29] observed that the IFT of Al_2O_3 nanofluids decreases with increasing NP concentration from 0.1 vol% to 0.5 vol%. They showed that variations of IFT are attributable to a reduction of the liquid surface layer interaction force when Al_2O_3 NPs are incorporated into the base fluid. In contrast, Tanvir et al. [30] demonstrated that the nanofluid IFT increases linearly with increasing concentration because the van der Waals force between NPs at the liquid-gas interface increases the surface free energy, thus increasing the IFT. These dissimilar results among previous studies have shown that the influence of particle adsorption on oil-nanofluids IFT is not well understood. In addition, for research on IFT variation, the NP spatial density at the oil-nanofluids interface is important [31]. The NP concentration can affect the spatial density at the oil-nanofluids interface; this effect may change the IFT at the interface. From this perspective, additional studies are needed regarding the effects of NP concentration on IFT at the oil-nanofluids interface. Thus far, a limited number of transport experiments have been performed to investigate NP retention during transport in porous media [13, 14, 32, 33]. Accurate assessments of the potential for NP flooding as an agent of EOR require detailed analyses of several aspects, such as the relationship between NP concentration and capillary pressure, the effects of NP retention on flooding injectivity in porous media, and the recovery efficiency and flow pressure differences during nanofluid injection. The objective of the present work was to investigate the effects of NP concentration on EOR applications. This study is novel in several respects. First, we examined the capillary pressure (P_c) to discover how NP-induced changes in IFT and rock wettability affect the flow in porous rock. We measured the contact angle (CA) in the three-phase (oil/nanofluid/rock) contact area to determine the extent to which the NP concentration affects the rock wettability alteration. The variation of IFT at the oil-nanofluid interface was also measured using variation of pendant drop

shape analysis with different concentrations of silica NPs. Then, capillary pressure was calculated using the measured IFT and CA data in the NP concentration range of 1.0–2.0 wt%. Second, we analyzed how the mass of NPs adsorbed per bulk volume of rock affects the relative permeability and change in oil recovery. We determined the variations of endpoint relative permeability and reduction of oil saturation as functions of retention density. Third, we evaluated changes in apparent viscosity according to NP retention using the pressure drop during nanofluid flooding. The oil recovery and flow mechanism were analyzed using our experimental results.

MATERIALS AND METHODS

1. Materials

A hydrophilic silica NP, Ludox CL-X colloidal silica (45 wt% suspension in H_2O and particle diameter of 22 nm), was purchased from Sigma-Aldrich (St. Louis, MO, USA). An anionic polymer, poly (4-styrenesulfonic acid-co-maleic acid) sodium salt (PSS-co-MA), and a zwitterionic surfactant, 3-(N,N-dimethylmyristylammonio) propanesulfonate (TPS), both of 99% purity, were both purchased from Sigma-Aldrich. The oil used was KF-96-10 (Shinetsu, Tokyo, Japan), which is a distillate of petroleum having a viscosity of approximately 10 cP. Brine (3 wt% NaCl) was used as an aqueous phase. For the flow experiments, Berea Sandstone cylinders with a diameter of 3.8 cm and length of 5.7 cm were used. Their measured properties were porosity of 20–22% and permeability of 141–145 md.

2. Preparation of Silica NP Dispersions (Silica Nanofluids)

First, the nanofluids were prepared by adding silica NP dispersions with various concentrations (0.1, 0.5, 1.0, 1.5, 2.0, 3.0 wt% silica content, diameter of 22 nm) to a 3 wt% NaCl brine. Then, to surface modify the NPs, a 0.5 wt% concentration of PSS-co-MA (an anionic polymer) was added to each nanofluid; each mixture was stirred for 5 min at 800 rpm with a magnetic stirrer [12]. Next, a 0.1 wt% concentration of TPS (a zwitterionic surfactant) was added to each nanofluid; the nanofluids were mixed again for approximately 1 h. Finally, the NP dispersions were mixed to homogeneity for 2 min in 2-s/1-s bursts (on/off time) at 3,000 rpm with an ultrasonic homogenizer (Digital Sonifier, Branson, Brookfield, CT, USA).

3. Characterization of Silica Nanofluids

Transmission electron microscopy (TEM) was used to observe the shapes and sizes of NPs in the static condition. The measurements were performed with a JEN 2100F electron microscope (Jeol, Peabody, MA, USA). The hydrodynamic sizes and size distributions of particles in the nanofluids were analyzed by dynamic light scattering (Zetasizer Nano ZS-90, Malvern Pananalytical, Malvern, UK). The zeta (ζ) potential was measured using the same instrument. The suspension concentration was 10.0 mg/mL, and measurement was performed over a period of 3 min for each sample at 25 °C. The steady state viscosity of the colloidal dispersion was measured over a shear rate range using a viscometer (DV3, Brookfield Engineering Laboratories, Inc., Middleboro, MA, USA). Each measurement was conducted at 25 °C. IFT and CA measurements were performed to analyze the stabilized nanofluids with NPs and surfactant. The change in CA was measured at oil side that had

been initially equilibrated on the brine-soaked rock surface during diffusion of the introduced NPs. The measurements were made using a tensiometer (Theta, Biolin Scientific, Sweden), and the data were analyzed using OneAttension imaging software (Dyne Testing, Staffordshire, UK). Each measurement was at 25 °C.

4. Core Flooding Experiments

Berea Sandstone was packed into a core holder. To prepare the initial state of the Berea Sandstone, brine was injected into it. Next, oil was injected into the brine-saturated sandstone until no additional brine was produced. The initial brine and oil volume fractions in the sandstone were calculated from the amount of brine produced. Ageing time was two days under room temperature. Theoretically, as the ageing time and temperature increase, the rock surface tends to change to more oil-wet, but this study was conducted at room temperature to examine the effect of the concentration of silica nanoparticles under same conditions with minimal rock-surface change. For core flooding experiments, the NP dispersions (i.e., silica NPs/PSS-co-MA/TPS mixtures) were injected into the core holder at a constant flow rate of $1 \text{ cm}^3 \text{ min}^{-1}$. The fluid that flowed through the sandstone was collected in a measuring cylinder; oil recovery was calculated by the amount of oil extracted from the oil contained in the sandstone (original oil in place). Pressure transducers (DXD, Heise, USA) were installed at the inlet and outlet of the core holder to monitor the pressure change. To avoid any effect from the NP thermal motion, all experiments were carried out at 25 °C.

5. NP Retention Density Measurement

To measure the NP retention density (A_{NP}) on the rock surface, we collected the injected and effluent nanofluids following a brine flush with a glass vial at the inlet and outlet of the Berea Sandstone, respectively. Nanofluid was collected when oil no longer flowed out during the EOR experiment. The collected nanofluid was sufficiently dried for 24 h at 80 °C using a forced convection oven. The masses of the dried inlet nanofluid ($M_{NP,in}$) and the dried effluent nanofluid ($M_{NP,eff}$) were measured using an ultra-precise electronic balance. The retained mass of NPs ($M_{ret,NP}$) was determined by the material balance method ($M_{ret,NP} = M_{NP,in} - M_{NP,eff}$). To calculate the NP retention density (i.e., mass of NPs adsorbed per bulk volume of Berea Sandstone), the $M_{ret,NP}$ was divided by the calculated bulk volume (V_{bulk}) of the sandstone ($A_{NP} = M_{ret,NP}/V_{bulk}$ [mg/cm³]).

RESULTS AND DISCUSSION

1. Dispersion of Silica NPs in Nanofluids

For characterization of silica NPs in the nanofluids, we performed TEM analysis. The results revealed spherically shaped particles of uniform size with a mean diameter of approximately 22 nm in the dried condition (Fig. 1). When NPs were suspended in brine, the silica suspension indicated that the dispersion was thermodynamically stable and homogeneous. This status originated from the negatively charged surfaces of the silica NPs [34,35]. In our previous study, after incorporation of TPS (zwitterionic surfactant) and PSS-co-MA (anionic polymer), the sizes in the dispersions were similar to the sizes of the isolated NPs (22–27 nm) [31]. Thus, aggregation did not occur. The dispersions were also stable in the presence of the surfactant and polymer because of the nega-

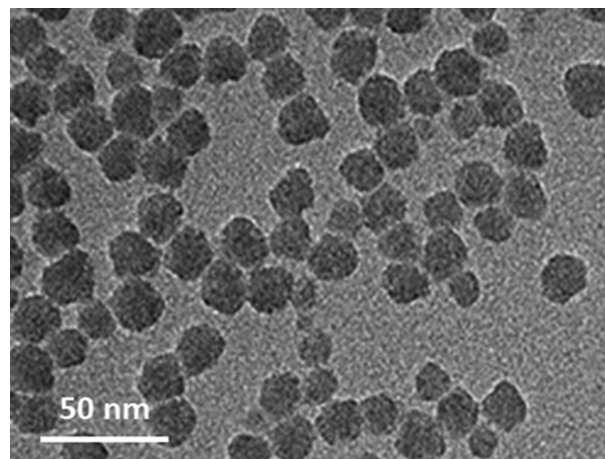


Fig. 1. TEM Image of silica nanoparticles.

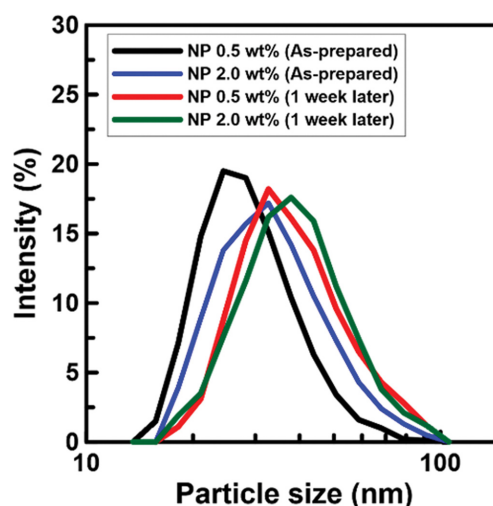
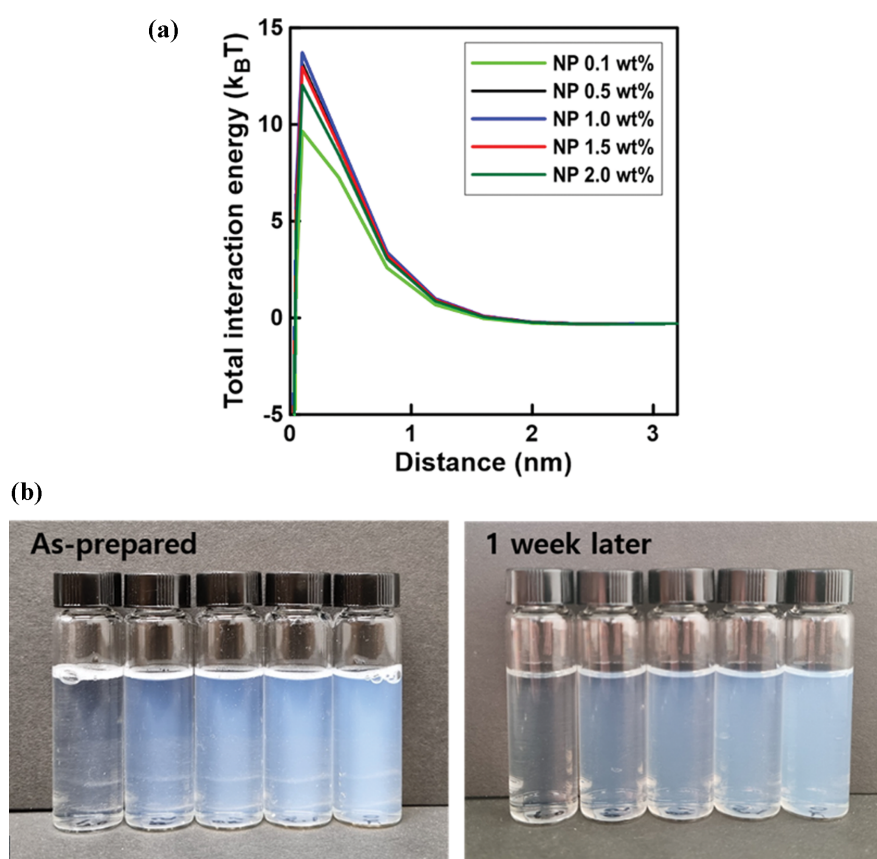


Fig. 2. Hydrodynamic radius of NPs immediately after preparation and after storage for one week.

tively charged surfaces of silica NPs [35]. Furthermore, the formation of a sufficient polymer steric layer on NP surfaces is necessary to stabilize NPs in the nanofluids. Adsorption of the zwitterionic surfactant onto NPs is mediated by the dipole-charge interaction between trimethylammonium groups of the zwitterionic surfactant and the negatively charged particles with PSS-co-MA under the brine condition [12]. Thus, the hydrodynamic radius of NP did not change significantly after one week of silica nanofluids from DLS measurement (Fig. 2). In our previous studies, the ζ potentials were less than approximately -40 mV after incorporation of TPS and PSS-co-MA onto the surfaces of the silica NPs (Table 1). This showed that the stability was attributable to the stable distance between NPs; particle-particle repulsion was effective [12]. The DLVO theory is useful for demonstrating the force balance of charge-stabilized dispersions. In this approach, we calculated the total interaction energy between two particles is obtained by summation of attractive VdW (van der Waals) and the repulsive electrostatic interaction ($V_{tot} = V_{vdw} + V_{elec}$) and plotted as a function of the interparticle distance (Fig. 3(a)). The energy barrier was in the range of approx-

Table 1. Zeta potential measurement of silica nanofluids

Concentration (wt%)				Mean value (mV)	Standard deviation (mV)
Silica nanoparticle (Ludox CL-X)	Anionic polymer (PSS-co-MA)	Zwitterionic surfactant (TPS)	NaCl		
0.1	0.5	0.1	3.0	-45.7	±3.2
0.5	0	0		-41.2	±2.9
	0	0.1		-36.6	±3.7
	0.5	0		-51.1	±3.1
	0.5	0.1		-49.6	±3.8
1.0	0.5	0.1	3.0	-50.2	±2.7
1.5	0.5	0.1		-49.4	±3.1
2.0	0.5	0.1		-48.4	±2.6

**Fig. 3. (a) Total DLVO interaction energy between silica NPs as a function of NP concentration, (b) Phase behavior of NPs immediately after preparation and after storage for 1 week.**

imately 10–15 $k_B T$ in all this experimental cases (silica NP with concentration range of 0.1–2.0 wt%). According to previous research, this sufficiently large energy barrier ($>10 k_B T$) remained in a stable state for a long time [36]. From long-term phase stability test, silica dispersions with concentration range of 0.1–2.0 wt% retained stable phase behavior after storage for one week (Fig. 3(b)).

2. Variation of IFT and Wettability Alteration According to NP Concentration

NP adsorption at the oil–fluid interface affects the IFT. To fully

understand how the NP concentration in the nanofluids affects the IFT, we measured changes in IFT between the oil and nanofluids directly under various NP concentrations. When PSS-co-MA chains and TPS surfactant are effectively adsorbed onto silica NPs, these electrostatically charged NPs reach the interface via interfacial energy reduction because of the TPS surfactant, so they are likely to remain as a trapped monolayer at the interface [37]. Thus, when zwitterionic surfactant is adsorbed on the NP surface, NP has amphiphilic properties [38,39]. Therefore, it can be readily located even at the

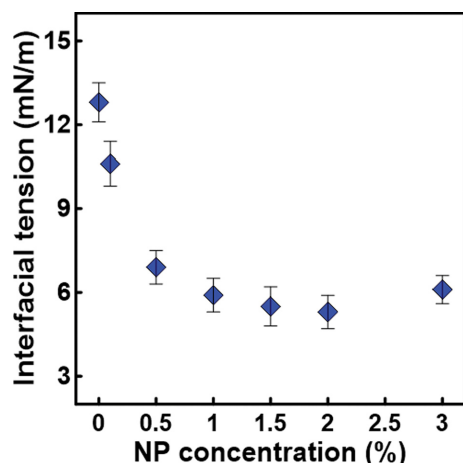


Fig. 4. Variation of interfacial tension (IFT) as a function of NP concentration at oil-NP fluid interface (0 wt% of NP concentration means that zwitterionic surfactant and PSS-co-MA were present in the brine without NP).

oil-water interface. In our experiment, the IFT continued to decrease in the silica NP concentration range of 0.1–2.0 wt% as the concentration of silica NPs in the nanofluids increased (Fig. 4). This phenomenon occurred because more NPs were driven into the oil/nanofluids. The NP number density in the nanofluids influences the IFT reduction. A previous study confirmed that NP spatial density at the oil-nanofluids interface is important for interfacial stability [31]. At higher NP concentration, NPs adsorb readily to the oil-nanofluids interface; thus NP spatial density is increasing with the reduction of the interfacial area covered by each particle. However, when the NP concentration exceeds 2 wt%, the IFT cannot further decrease with increasing NP concentration and a weak opposite trend begins to develop. This phenomenon can be explained by van der Waals and repulsive interactions. When NPs are added into the aqueous phase, the molecules of the NPs and brine interact with each other. The NPs become closer to each other when the silica NP concentration becomes sufficiently high. Accordingly, the forces of adjacent NPs and the forces of the liquid molecules interfered in the liquid surfaces [27]. Thus, total interaction energy may

reduce with decreasing electrostatic repulsion force, thereby increasing interfacial energy and IFT. This result is consistent with the findings in a previous study [40]. Because of these effects, we concluded that the optimal NP concentration in this study, in terms of IFT, was 1.5–2.0 wt%.

To evaluate how the addition of NPs in suspension affects the rock surface wettability, the effects of NP adsorption on wettability alteration were investigated in a concentration-dependent manner. Soaking in silica nanofluids changed the CA of the sandstone rock. The CA is a quantitative measure of Berea Sandstone wetting by nanofluids. In the brine condition (3 wt% NaCl) without NPs, the rock/oil/-nanofluids CA was 120.5°. However, the silica nanofluid increased the CA in a concentration-dependent manner, from 128° for 0.1 wt% nanofluid to 151.5° for 2.0 wt% nanofluid; this indicated alteration of rock surface wettability to a more water-wet condition. The reason for this change may be the disjoining pressure. The structural disjoining pressure is correlated with the fluid ability to spread along a rock surface because of the interfacial force imbalance among rock, the oil phase, and the nanofluids [41]. The presence of NPs in the three-phase contact region tends to create a wedge-film structure comprising nanofluid film (disjoining pressure) between rock surface and oil drop. As the particle concentration increases, more NPs diffuse into the wedge film. Thus, the disjoining pressure substantially increases at a particular wedge thickness with increasing NP concentration. Because of this pressure increase, the oil-nanofluids interface advances; the nanofluids then spreads on the rock surface, thus detaching the oil drop. Accordingly, a higher hydrophilic silica NP concentration increases water-wetness, as shown in Fig. 5.

3. Variations of Capillary Pressure (P_c) According to NP Concentration

To determine how nanofluid-induced changes in IFT and rock wettability affect the flow in porous rock, we measured the pore size distribution and mercury capillary pressure (P_c) of Berea Sandstone using the mercury injection method. The maximum value of the probability density of the pore size distribution was in the range of 5 to 20 μm (Fig. 6(a)). This pore size range is reasonable for Berea Sandstone [42]. Then, the capillary pressure for the oil-nanofluid phase was calculated using the equation $P_c = P_{c, \text{Fig. 6}} (\gamma_{\text{oil/nanofluids}}$

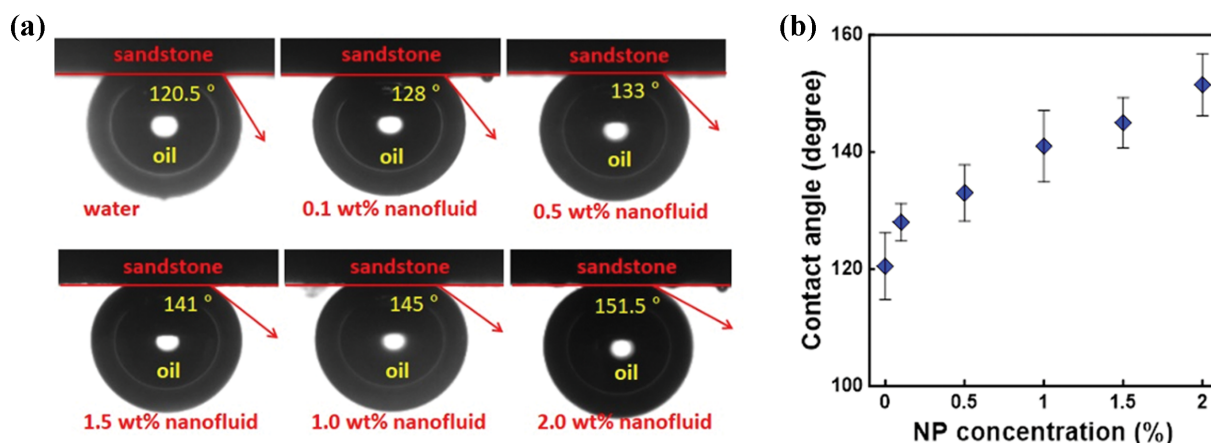


Fig. 5. (a) Images and (b) values of contact angle as a function of NP concentration. (a) Images of contact angle, (b) Values of contact angle.

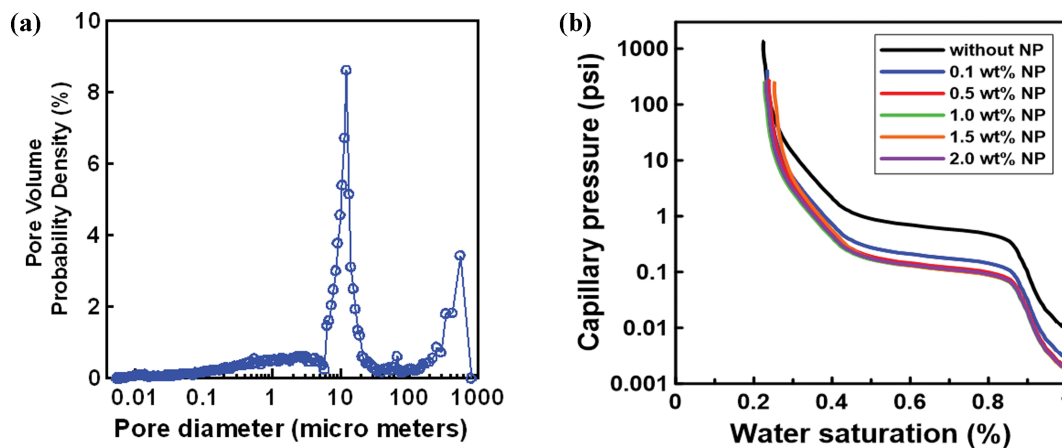


Fig. 6. Variation of capillary pressure (P_c) with NP concentration (a) Pore size distribution of Berea Sandstone, (b) Capillary pressure as a function of NP concentration.

$\cos \theta_{oil/nanofluids/rock} / \gamma_{air/Hg} \cos \theta_{air/Hg/rock}$), where $P_{c\ Hg}$ is the capillary pressure measured by the mercury injection method [43]; $\gamma_{oil/nanofluids}$ and $\gamma_{air/Hg}$ are the IFT values at the oil/nanofluid interface (10.6-5.3 mN/m) and the air/Hg interface (385 mN/m); and $\theta_{oil/nanofluids/rock}$ and $\theta_{air/Hg/rock}$ are the CA values at the oil/nanofluid/rock interface (128-151.5°) and the air/Hg/rock interface (130°), respectively. In addition, the minimum nanofluid saturation in the experiment was obtained through core flooding until no more nanofluid was discharged from porous rock. The results showed that the minimum nanofluid saturation was in the range of 22.4-25.2%. The calculation results confirmed that P_c was substantially reduced during nanofluid flooding, compared with brine flooding. In particular, the P_c decreased rapidly through the 0.1-1.0 wt% NP range, although there was no substantial difference in P_c within the NP concentration range of 1.0-2.0 wt% (Fig. 6(b)). In terms of changes in IFT and rock wettability, these results imply that residual oil in the rock can flow easily with nanofluid injection at the NP concentration of 1.0 wt%. Thus, the nanofluids used in this study can reduce the P_c in the matrix by reducing the ST and/or by changing the wettability of the rock surface when adsorbed onto surfaces. However, this P_c calculation does not consider NP retention in the rock pores.

4. Variations of Pressure Drop and Relative Permeability with NP Concentration

The main objective of this study was to quantitatively characterize the transport and retention of particles under different NP concentrations. To determine the qualitative relationship between transport and NP concentration, we observed the pressure drop (Δp) across the sandstone during the core flooding process as function of NP concentration. Our experimental results showed that Δp increased with increasing NP concentration (Fig. 7(a)). This phenomenon may be attributable to NP retention on rock grain surfaces. Because NPs were retained in pores during injection, incoming NPs accumulated on top of the previously captured NPs. These NPs could also become lodged in pore throats if the applied shear force was less than the capillary force. In this scenario, the injection pressure built up gradually as more pores became occupied. Additionally, to characterize multiphase flow in porous media according to NP concentration, we calculated the relative permeability of the

oil-nanofluid phase using both the Corey correlation and experimental permeability values. The relative permeabilities were calculated as follows [44]: $k_{rw} = k_{rw}^0 \left(\frac{S_w - S_{wir}}{1 - S_{wir} - S_{or}} \right)^n$, $k_{ro} = k_{ro}^0 \left(\frac{S_o - S_{or}}{1 - S_{wir} - S_{or}} \right)^m$,

where k_{rw} and k_{ro} are the relative permeabilities of nanofluid and oil for each saturation, respectively (when two fluids flow simultaneously in a rock); S_{wir} is the irreducible nanofluid saturation (minimum nanofluid saturation in rock); S_{or} is the residual oil saturation (it is ratio of the volume of residual oil to the total pore volume in the rock); and m and n are adjusted parameters (we used the value of 2 for both). k_{rw}^0 and k_{ro}^0 are the relative permeabilities of nanofluid and oil at S_{wir} and S_{or} respectively [12]. As the NP concentration increased, the S_{or} decreased, from 0.246 at 0.1 wt% NP to 0.165 at 2.0 wt%; the relative nanofluid permeability at the endpoint (k_{rw}^0) also increased, from 0.178 at 0.1 wt% NP to 0.027 at 2.0 wt% (Fig. 7(b)), which indicated that oil recovery increases as the NP concentration increases in the porous media. Such a result is presumably because a higher injected NP concentration causes an increased pressure drop with higher NP retention at the rock surface; this can supply a force for flow through unswept regions, thereby increasing displacement efficiency and oil recovery. To confirm this conclusion, we measured the retention density (mg/cm^3), which was the mass of NPs adsorbed per bulk volume of Berea Sandstone. As shown in Fig. 7(c), greater NP adsorption (retention density) on sandstone pore surfaces can be achieved by increasing the injected NP concentration. Moreover, the retention density affected the endpoint nanofluid relative permeability and changed the oil saturation ($S_o - S_{or}$) in the sandstone core. With increasing retention, the endpoint nanofluid relative permeability decreases because of the increased Δp , thus changing the oil saturation via S_{or} reduction. These results imply that the log jamming phenomenon may be important in oil recovery, along with changes in IFT and rock wettability.

5. Suspension Rheology According to NP Concentration

The rheological viscosity of a fluid can differ between a heterogeneous state flow through a complex pore network and a homogeneous bulk state flow measured by a rheometer. We compared

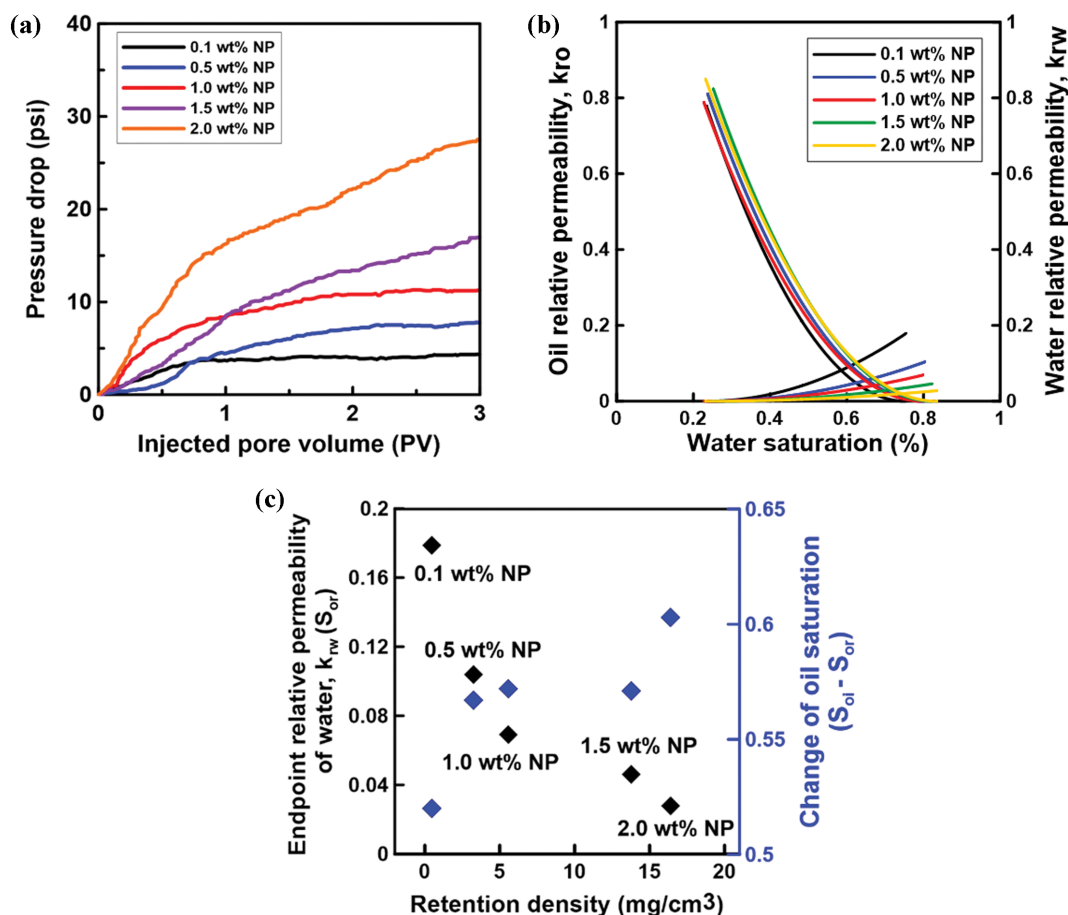


Fig. 7. Transport characteristics of nanofluids at various NP concentrations during core flooding. (a) Pressure drop at different NP concentration, (b) Relative permeability at different NP concentration, (c) Retention density according to NP concentration.

the viscosity of NP suspensions in the conditions of bulk state (bulk viscosity) and porous (apparent viscosity) flow. First, in the bulk state, we measured the bulk viscosity of NP suspensions to characterize flow properties according to NP concentration. The NP suspensions displayed a non-Newtonian shear thinning in which the viscosity decreased with increasing shear rate (Fig. 8). At low shear rate, there was remarkable resistance between NPs during fluid flow; therefore, this phenomenon presumably had considerable influence on the NP suspension viscosity. In particular, when the NP concentration was higher, a greater effect was observed because of resistance between particles in the low shear rate region. This may be related to greater potential for agglomeration between particles at low shear rates. However, in the high shear rate section, the viscosity difference according to NP concentration was generally low. Thus, friction between particles had a smaller influence on viscosity at higher shear rates; the influence of NP concentration was generally low because of low aggregation between particles in relation to high shear stress. These results were similar in other studies. This can also explain that the non-Newtonian characteristics of nanofluids are more obvious at a higher volume fraction and a longer holding time since the chance of aggregation is higher [45]. Once agglomeration is formed, a larger stress is necessary to break the ligand structure among particles when shearing takes place; there-

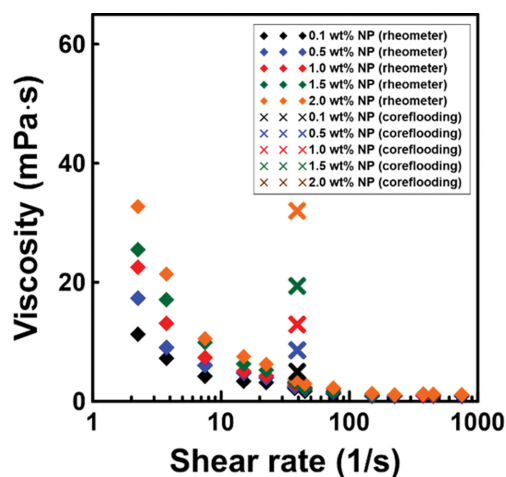


Fig. 8. Apparent viscosity according to NP concentration.

fore, a high relative viscosity would be observed in the fluids [45].

We also calculated the apparent viscosity (μ_{app}) of the porous medium using the equation $\mu_{app} = k\Delta p A / (qL)$ with the Δp observed during the core flooding experiment [45]. In this formula, A is the cross-sectional area of Berea Sandstone (11.4 cm^2), k is the abso-

lute permeability (142 mD), L is the length of the sandstone (5.7 cm), and q is the flow rate (1 cm³/min). Our experimental results show that the NP retention on rock surfaces could influence fluid rheology. In particular, the apparent viscosity of the porous medium with a mixture of residual oil and NP fluids was higher than the bulk viscosity. To calculate the bulk viscosity, the shear rate within the pores in Berea Sandstone can be estimated from the formula $\gamma = 4v/(8k\phi)^{-0.5}$, where ϕ is the porosity (0.213), v is the [46,47]. This formula is useful for correlating and predicting the rheological properties of non-Newtonian fluids under permeable media flow [34]. In this experiment, the estimated shear rate within the pores was approximately 40 s⁻¹. From this value, the bulk viscosity by rheometer measurement was in the range of 0.8–2.3 mPa·s. However, the range of apparent viscosity at the shear rate of 40 s⁻¹ was between 4.9 and 31.9 mPa·s during core flooding. As the NP concentration increased, the apparent viscosity also increased; it was 4.9 mPa·s for 0.1 wt% NP and 31.9 mPa·s for 2.0 wt% NP. This showed that the behavior of the NP injection fluid cannot be explained by the bulk viscosity of the nanofluid because of NP retention in the porous medium. Therefore, NP retention influenced the viscosity and injectivity of the fluid flowing in the porous medium.

6. Variations of Oil Recovery According to NP Concentration

To determine the impact of NP concentration on oil recovery, we conducted core flooding experiments using brine and different NP concentrations (0.1–2.0 wt%). All NPs used for these experiments were identically surface modified with PSS-*co*-MA and a zwitterionic surfactant. The experiments showed that, as the NP concentration increased from 0.1 to 2.0 wt%, oil production increased from 67.8% to 76.2% of original oil-in-place (Fig. 9). These results are explained by several factors. First, the dependence of additional oil recovery on NP concentration is consistent with the IFT and CA. The changes in IFT and CA are also a function of NP concentration, such that the IFT decreases and CA increases with increasing NP concentration, as shown in Figs. 4 and 5. These findings reflect the increase in total NP surface area with increasing particle concentration, such that the NP area in contact with surfactant increases. Second, the log jamming phenomenon may affect

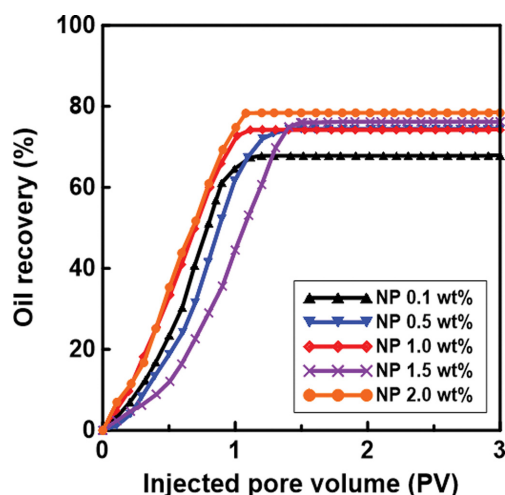


Fig. 9. Oil recovery as a function of NP concentration during core flooding experiments.

the oil recovery. As shown in Fig. 7(a), the Δp increased as the NP concentration increased, although the P_c was predicted to decrease through variations of IFT and rock surface wetting because of residual NPs in the rock pores. When the nanofluid injection volume was less than 1 pore volume, the pressure increased more steeply as the NP concentration increased (Fig. 7(b)). This implies that pressure drop built up gradually as residual NPs became lodged in the pore throats. Accordingly, residual NPs can cause the displacing fluid to flow through unswept regions with as the pressure drop builds up; this may produce increased overall sweep and displacement efficiency. Thus, we confirmed that the retention density eventually influenced oil recovery, as shown in Fig. 7(c). These results indicate that the log jamming phenomenon may be important in oil recovery, along with changes in IFT and wettability.

CONCLUSIONS

We explored the effect of concentration of silica NP surface-modified by zwitterionic surfactants and PSS-*co*-MA on oil recovery. The following conclusions were drawn from the results of the study.

- (1) The oil production showed an increasing trend as the silica NP concentration increased from 0.1 to 2.0 wt%. The oil recovery was strongly dependent on changes in IFT and CA. IFT continued to decrease as the concentration of silica NPs increased from 0.1 to 2.0 wt%. However, IFT could not decrease further with increasing NP concentration because total interaction energy may be reduced due to the decrease of electrostatic repulsion force by the closer spacing between NPs.
- (2) As the NP concentration increased to 2.0 wt%, the silica NPs also changed the CA of the sandstone rock to a more water-wet condition. This is presumably because the aqueous nanofluid film exhibits greater ability to spread along rock surfaces at higher NP concentration. In relation to variation of IFT and wettability, the calculated apparent capillary pressure (P_c) was expected to be sufficiently reduced by the NP flooding method. However, this P_c calculation did not consider the NP retention remaining in the rock pores.
- (3) Although a decrease in P_c was expected, the experimental results showed that the Δp of core flooding increased as the NP concentration increased because of residual NPs in the rock pores. Thus, the behavior of the injected NP fluid cannot be explained solely by the IFT and rock surface wettability. Residual NPs influence the viscosity and injectivity of a fluid flowing in a porous medium.
- (4) In addition to changes in the IFT and wettability, the log jamming phenomenon may influence oil recovery. This can cause the displacing fluid to flow through unswept regions, which increases the overall sweep and displacement efficiency, thus leading to enhanced oil recovery.

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REFERENCES

1. M. Y. Rezk and N. K. Allam, *Ind. Eng. Chem. Res.*, **58**, 16287 (2019).
2. S. Li, L. Hendraningrat and O. Torsaeter, *The international petroleum technology conference*, Beijing, China, March 26-28 (2013).
3. V. Y. Rudyak and S. L. Krasnolutsii, *Phys. Lett. A*, **378**, 1845 (2014).
4. P. C. Mishra, S. Mukherjee, S. K. Nayak and A. Panda, *Int. Nano Lett.*, **4**, 109 (2014).
5. C. Metin, R. T. Bonnecaze and Q. P. Nguyen, *SPE Res. Eval. Eng.*, **16**, 327 (2013).
6. H. Fan and A. Striolo, *Phys. Rev. E*, **86**, 051610 (2011).
7. S. Betancur, L. J. Giraldo, F. Carrasco-Marín, M. Riazi, E. J. Manrique, H. Quintero, H. A. García, C. A. Franco-Ariza and F. B. Cortés, *ACS Omega*, **4**, 16171 (2019).
8. L. S. de Lara, M. F. Michelon, C. O. Metin, Q. P. Nguyen and C. R. Miranda, *J. Chem. Phys.*, **136**, 164702 (2012).
9. A. Bila and O. Torsaeter, *Energies*, **13**, 5720 (2020).
10. X. Sun, Y. Zhang, G. Chen and Z. Gai, *Energies*, **10**, 345 (2017).
11. Z. Hu, S. M. Azmi, G. Raza, P. W. J. Glover and D. Wen, *Energy Fuels*, **30**, 2791 (2016).
12. H. A. Son and T. Ahn, *Appl. Sci.*, **11**, 524 (2021).
13. B. Peng, L. Zhang, J. Luo, P. Wang, B. Ding, M. Zeng and Z. Cheng, *RSC Adv.*, **7**, 32246 (2017).
14. B. Yuan, W. Wang, R. G. Moghanloo, Y. Su, K. Wang and M. Jiang, *Energy Fuels*, **31**, 795 (2017).
15. B. Ju and T. Fan, *Powder Technol.*, **192**, 195 (2009).
16. L. Hendraningrat, S. Li and O. Torsaeter, *The SPE russian oil and gas exploration and production technical conference and exhibition*, Moscow, Russia, 16-18 October (2012).
17. B. Ju, T. Fan and Z. Li, *J. Pet. Sci. Eng.*, **86**, 206 (2012).
18. K. Li, D. Wang and S. Jiang, *Oil Gas Sci. Technol.*, **73**, 37 (2018).
19. S. Lim and D. Wasan, *J. Colloid Interface Sci.*, **500**, 96 (2017).
20. H. Eltoum, Y. L. Yang and J. R. Hou, *Pet. Sci.*, **18**, 136 (2021).
21. S. K. Choi, H. A. Son, H. T. Kim and J. W. Kim, *Energy Fuels*, **31**, 7777 (2017).
22. H. Zhang, A. Nikolov and D. Wasan, *Energy Fuels*, **28**, 3002 (2014).
23. D. T. Wasan and A. D. Nikolov, *Nature*, **423**, 156 (2003).
24. A. Nikolov, P. Wu and D. Wasan, *Adv. Colloid Interface Sci.*, **264**, 1 (2019).
25. J. Zhou, Y. Wang, J. Geng and D. Jing, *Phys. Fluids*, **30**, 072107 (2018).
26. L. Yuan, Y. Zhang and H. Dehghanpour, *Energy Fuels*, **35**, 7787 (2021).
27. M. H. U. Bhuiyan, R. Saidur, M. A. Amalina, R. M. Mostafizur and A. K. M. S. Islam, *Procedia Eng.*, **105**, 431 (2015).
28. M. Radiom, C. Yang and W. K. Chan, *The international society for optical engineering*, Singapore, 18-20 April (2010).
29. B. J. Zhu, W. L. Zhao, J. K. Li, Y. X. Guan and D. D. Li, *Mater. Sci. Forum*, **688**, 266 (2011).
30. S. Tanvir and L. Qiao, *Nanoscale Res. Lett.*, **7**, 1 (2012).
31. H. A. Son and T. H. Lee, *Appl. Sci.*, **11**, 7184 (2021).
32. T. Zhang, M. J. Murphy, H. Yu, H. G. Bagaria, K. Y. Yoon, B. M. Nielson, C. W. Bielawski, K. P. Johnston, C. Huh and S. L. Bryant, *SPE J.*, **20**, 667 (2015).
33. H. Yu, Y. He, P. Li, S. Li, T. Zhang, E. Rodriguez-Pin, S. Du, C. Wang, S. Cheng and C. W. Bielawski, *Sci. Rep.*, **5**, 8702 (2015).
34. H. A. Son, K. Y. Yoon, G. J. Lee, J. W. Cho, S. K. Choi, J. W. Kim, K. C. Im, H. T. Kim, K. S. Lee and W. M. Sung, *J. Pet. Sci. Eng.*, **126**, 152 (2015).
35. K. Y. Yoon, H. A. Son, S. K. Choi, J. W. Kim, W. M. Sung and H. T. Kim, *Energy Fuels*, **30**, 2628 (2016).
36. F. Matter, A. L. L. Barron and M. Niederberger, *Nano Today*, **30**, 100827 (2020).
37. F. Reincke, S. G. Hickey, W. K. Kegel and D. Vanmaekelbergh, *Angew. Chem.*, **43**, 458 (2004).
38. L. Qi, C. Song, T. Wang, Q. Li, G. J. Hiraski and R. Verduzco, *Langmuir*, **34**, 652 (2018).
39. L. Qi, H. Shamsijazeyi, G. Ruan, J. A. Mann, Y. H. Lin, C. Song, Y. Ma, L. Yang, J. M. Tour, G. J. Hirasaki and R. Verduzco, *Energy Fuels*, **31**, 1339 (2017).
40. M. Moosavi, E. K. Goharshadi and A. Youssefi, *J. Heat Mass Transf.*, **31**, 599 (2010).
41. A. Chengara, A. Nikolov, D. T. Wasan and A. Trokhymchuk, *J. Colloid Interface Sci.*, **280**, 192 (2005).
42. J. Q. Shi, Z. Xue and S. Durucan, *Energy Procedia*, **4**, 5001 (2011).
43. H. W. Brown, *Petroleum Trans. AIME*, **192**, 67 (1951).
44. T. Ahmed, *Reservoir engineering handbook (10th ed.)*, Gulf Professional Publishing, Elsevier (2010).
45. F. Duan, D. Kwek and A. Crivoi, *Nanoscale Res. Lett.*, **6**, 1 (2011).
46. L. W. Lake, *Enhanced oil recovery*, United States, Prentice Hall (1989).
47. T. Zhang, M. Roberts, S. L. Bryant and C. Huh, *The SPE International Symposium Oilfield Chemistry*, Woodlands, TX, April 20-22 (2009).