

Hydrophilic Nanoparticle-Based Enhanced Oil Recovery: Microfluidic Investigations on Mechanisms

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S Supporting Information

ABSTRACT: We discovered a novel nanoparticle (NP)–crude oil interaction and propose a mechanism of NP-based enhanced oil recovery. This NP–crude oil interaction and its effects on oil recovery are systematically investigated by conducting microfluidic experiments in both single-pore scale and “reservoir-on-a-chip” scale. It is confirmed that hydrophilic silica NPs in an aqueous phase could lead to dramatic swelling, dewetting, and disjoining of crude oil. The swelling ratio increased with decreased aqueous phase salinity and with increased concentrations of negative charging of NPs. Natural polar components in crude oil is shown to play a very important role. From a pore-scale perspective, this oil swelling and dewetting increased the flow resistance in the swept region and redirected flooding liquid toward the unswept region. From a reservoir perspective, the mobility ratio was reduced because oil swelling and dewetting modified the relative permeabilities. This improvement in sweep efficiency resulted in approximately 11% incremental oil recovery in a completely homogeneous porous micromodel, with 2000 ppm of NPs suspended in seawater.

1. INTRODUCTION

Nanoparticles (NPs) have been receiving general attention and discussion for their applications in enhanced oil recovery (EOR)^{1–3} due to NPs' many promising interfacial and rheological properties. The mechanisms of NPs in EOR are still in debate, but it has been generally accepted that NPs suspended in an aqueous phase could, under certain conditions, adsorb on the liquid–liquid, liquid–solid or liquid–gas interfaces, reducing total interfacial energy.^{4–7} These adsorptions may help to recover more oil by generation/stabilization of emulsion/foam,^{8,9} reduction of interfacial tension (IFT),^{5,10,11} change of emulsion rheology,^{12–14} modification of disjoining pressure,^{15,16} alteration of wettability,^{17–20} enhancement of ultralow IFT chemical compositions,²¹ etc. Many displacement experiments with reservoir cores or sand packs have been reported that applied NPs directly as an aqueous suspension,^{22–24} emulsion stabilizer or foam stabilizer.²⁵ NP's effect on fluid rheology has also been investigated. Low concentrations (<5 wt %) of NPs do not significantly impact the aqueous viscosity,²⁶ but core flood experiments show that NPs can be used as foam/emulsion stabilizing agents, thereby substantially increasing the apparent viscosity of the displacing phase.^{27,28} Although those coreflood experiments clearly show that NPs, if applied appropriately, can be efficient EOR agents, the fundamental mechanisms for the enhancing oil recovery using NP-based fluids are still not fully understood, partially due to the difficulty of directly visualizing the mobilization phenomena¹ in pore-scale.

Microfluidics^{18,29,30} provide direct visualization of micron-scale flow phenomena and are a powerful tool to investigate pore-scale flow mechanics and other physics that are not easy to study directly on coreflood or sandpack experiments. In

addition, direct observations on microfluidics platforms can also be easily compared with numerical modeling works.^{31–33} Specifically, porous micromodels, with names matching their applications as “rock-on-a-chip”,³⁴ “soil-on-a-chip”,³⁵ “reservoir-on-a-chip”,³⁶ “aquifer on a chip”,³⁷ etc., have been applied to visualize the displacement flow process in porous media,^{38–46} including some works on EOR with direct injection of nanofluids.^{47–53} NPs-based secondary oil recovery was studied by Ryles et al.⁵⁴ They showed that the steady-state IFT between the nanofluid and oil decreases with an increase in the NP concentration, and that increased NP concentration is positively related to final oil recovery. The NP deposition on the solid surface and its positive effect on surface wettability were also visualized.^{47,49} Bazazi et al.⁵⁵ compared water-flooding, surfactant flooding, and NP flooding in a glass micromodel saturated with heavy oil and concluded that emulsion formation during heavy oil displacement with chemicals is a major factor in incremental recovery. Those above research studies directly using micromodels with thousands of pores as “2-D coreflood” experiments and flow conditions in specific pores are not controlled. Thus, although they all gave very strong support of NP flooding's efficiency, they did not give equally strong support of fundamental pore-scale mechanisms. Xu et al.⁵⁶ fabricated a pore-throat microchannel structure and found that hydrophilic NPs function in a similar way to weak surfactants when nonpolar model oil (*n*-decane) was applied. This work has given researchers a better understanding of the rich physics of flow behaviors in a pore-scale, but still is limited by a lack of

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connections from pore-scale observations to porous media-scale models, as well as in using model oil rather than real crude oil. Only by building a bridge between pore-scale and porous media and taking the chemical properties of crude oil into consideration can the new knowledge achieved from microfluidic platforms finally benefit the practice and industry.

In this document, we introduce a two-scale microfluidic framework to investigate the underlying mechanism of NP-based EOR. We first conduct quantitative observations on single dead-end pore microchannels and investigate the NP suspensions' interactions with crude oil. After understanding the pore-scale behaviors, we upscale the experiment to a "reservoir-on-a-chip", which is a porous micromodel with $\sim 10^4$ pores. On the basis of both the pore-scale observations and "reservoir-on-a-chip" scale displacement performance, we propose a theory that transfers the pore-scale physics to a reservoir scale model that can explain the experimental results well.

2. EXPERIMENTAL METHODS

2.1. Materials. Light sweet crude oil (API: 28; viscosity: 37.8 cP @ 25 °C; asphaltenes concentration: 2 wt %; TAN: 0.4 mg of KOH/g, which indicates that it is not active oil) was used for the study. Seawater was prepared in the laboratory by mixing salts in deionized water to obtain the composition as shown in Table 1. Two different

Table 1. Composition of Seawater

component	concentration (mg/kg)
Na	10764
Ca	406
Mg	1297
K	387
Cl	19353
SO ₄	2701
HCO ₃	142
TDS	35050.0

hydrophilic silica nanoparticles containing overall negative (coated with hydroxyl groups) and positive (coated with amine terminated) surface charges were used to study the influence of the electrostatic interactions on the oil swelling. The particle sizes and charges were measured on a Malvern Zetasizer Nano instrument using dynamic light scattering and zeta-potential measurements (Table 2).

Table 2. Particle Size and Zeta-Potential of the Nanoparticle Dispersions

nanoparticle dispersion	particle size (nm)	zeta-potential (mV)
("−") charged NP	15	−32
("+") charged NP	110	+37

2.2. Dead-End Pore Microchannel Design and Experimental Procedure. To quantitatively investigate the interaction between NP suspensions and crude oil, we fabricated a glass dead-end pore micromodel that contained a pair of dead-end pores connected to a main channel through a three-dimensional (3-D) throat (narrower and shallower than the pore body). The depth of the main channel and the pore-body was 22 μm , the width of the main channel was 300 μm , the pore diameter was 230 μm , the width of throat was 33 μm , and the minimum depth of throat was 6 μm .

One experiment was conducted in three steps, as shown in Figure 2:

- (1) Saturate the entire channel with crude oil.

- (2) Inject seawater at 0.1 mL/h to displace the crude oil in the main channel and to trap crude oil in dead-end pores.
- (3) Inject the target fluid (DI water, brine, NP suspensions) at 0.1 mL/h into the main channel, which can keep a constant chemical environment. The trapped oil's evolution during the target fluid injection was captured by microscope.

2.3. Porous Micromodel Design and Experimental Procedure. The porous micromodel (reservoir-on-a-chip) was fabricated similarly to that reported by Xu et al.^{57,58} and provided by the University of Texas of Austin. This micromodel was made of glass. The total pore volume was 4.4 μL , the depth of pore bodies was 22 μm , every pore was connected with four other pores by throats that had a width of 33 μm and minimum depth of 6 μm . The grain diameter was 167 μm . The distance between the center of neighboring pores was 200 μm . The permeability was measured as 1.1 Darcy.

The experiment in porous micromodel was conducted in four steps:

- (1) Saturate the micromodel with seawater.
- (2) Displace seawater in the micromodel with crude oil at a flow rate of 9 $\mu\text{L}/\text{h}$ (4 ft/day) until no mobilization of seawater is observed. In this way, connate water is formed.
- (3) Use seawater to displace crude oil at a flow rate of 9 $\mu\text{L}/\text{h}$ (4 ft/day).
- (4) Continue injecting seawater after the breakthrough of seawater to ensure the system is in steady state.
- (5) Change injection liquid to NPs suspension and keep the injection rate unchanged until reaching steady state.

3. RESULTS AND DISCUSSION

3.1. Single-Pore Scale Observations of Oil–NP Interaction: Oil Swelling and Dewetting. A 5 wt % negatively charged NP suspension in DI water was first injected (left to right) in dead-end pore microchannel as the target fluid. A video showing the evolution of trapped oil is shown in Supporting Information, and some snapshots are shown in Figure 3.

During the injection, an unexpected phenomenon was observed: crude oil gradually swelled considerably, snapped-off into the main channel and finally recovered. This swelling was so significant that even the small oil droplets initially trapped at main channel surface expanded thousands of times, as shown in Figure 3. Simultaneous with the swelling, the oil changed from the wetting phase to the nonwetting phase, and the three-phase region (oil–glass–aqueous) progressed inward with increasing time. The possible explanation for the three phase interface inward movement could be the formation of a nanoparticle layer, much like a wedge, which was also observed by Wasan et al. with their famous theory of disjoining pressure.^{15,16,59}

We tested the oil-swelling behavior under different target fluids, including negatively and positively charged NP suspensions in different concentrations and in seawater/DI water. We quantified the swelling by measuring the swell ratio, which is defined as the ratio of apparent oil volume after 16 h of contacting to target fluids over the initial trapped oil volume, as shown in Figure 4. The swell ratio quantification shows that (1) NP suspensions in DI water could lead to more swelling of crude oil than NP suspensions in seawater; (2) NPs with negative charging could lead to more swelling than NPs with positive charging; (3) for negatively charged NP suspensions, the swell ratio was positively related to the NP concentration. In addition, we also found that even using DI water without NPs, moderate crude oil swelling could still be observed, but using seawater alone cannot show this effect, which matched

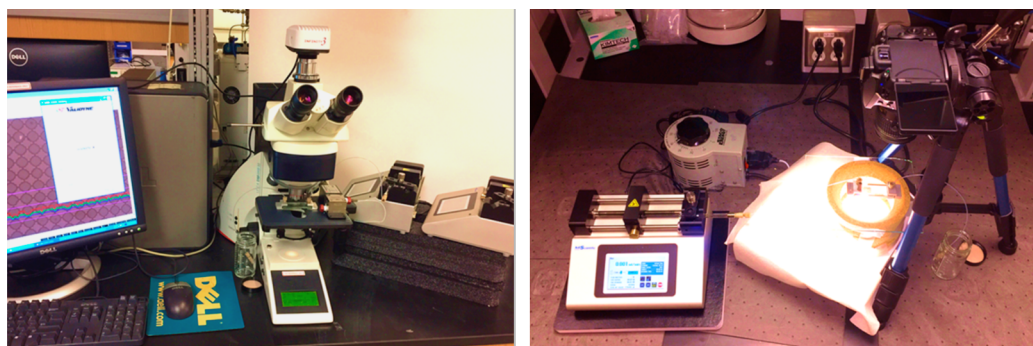


Figure 1. Images of the microscopic visualization setup (left) and macroscopic visualization setup (right) that were applied in this research.

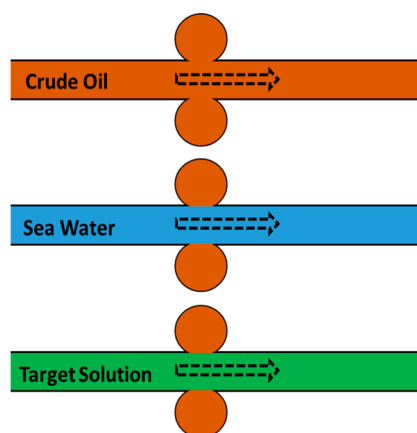


Figure 2. Scheme of dead-end pore microchannel experiment procedure. (Top) Saturate the channel with crude oil. (Middle) Use seawater to displace the crude oil in the main channel and then trap the crude oil in dead-end pores. (Bottom) Inject the target liquid (DI water, seawater, and different NPs' suspension in them) into the main channel for a long time to observe the liquids' interaction with trapped oil.

well with some microscopic observations of low-salinity, water-based enhanced oil recovery.^{60–62,41}

Under microscopic observations with higher magnitude, we found that the swelling was due to spontaneous generation of many tiny droplets inside the oil bulk, initially around the oil–

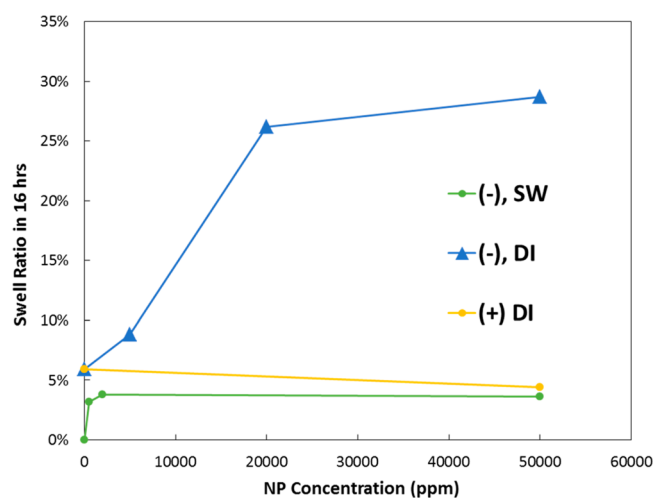


Figure 4. Plot of oil swell ratio in 16 h vs NP concentrations, when using negatively charged NPs in seawater (green), negatively charged NPs in DI water (blue), and positively charged NPs in DI water.

water interface, as shown in Figure 5. Because the crude oil bulk was also dewetting, we defined this new system as a water-in-oil-in-water double emulsion. During contacting with the target fluid, the number and size of those tiny droplets both grew significantly.

3.2. Oil Swelling Dynamics and Mechanisms. In order to clarify why such spontaneous emulsification (generation and

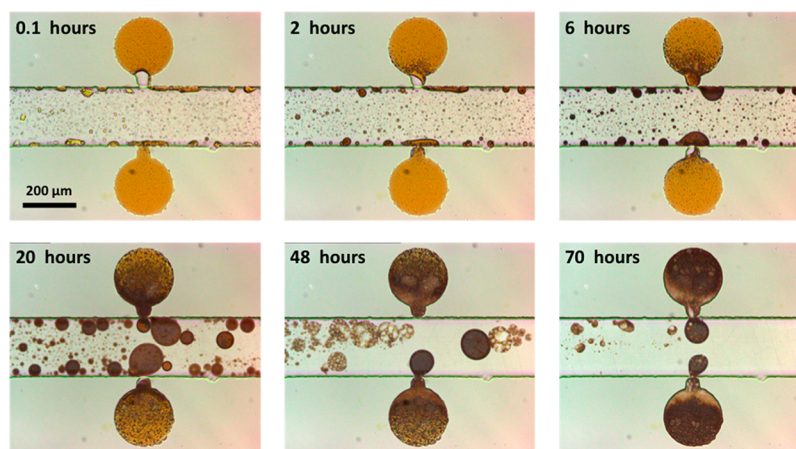


Figure 3. Snapshot of trapped crude oil in microchannel in contact with 5 wt % negatively charged NPs suspension in DI water, at 0.1 h, 2 h, 6 h, 20 h, 48 h, 70 h, respectively. It can be clearly observed that trapped crude oil is swelling. Flow is from left to right. The scale bar represents 200 μm .

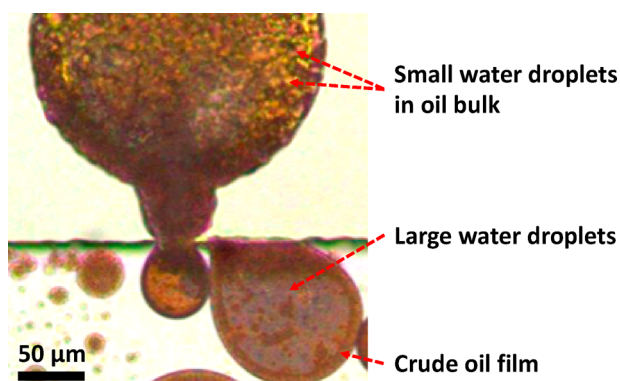


Figure 5. Zoom-in observation of swelled crude oil under 5 wt % negatively charged NP DI water suspension flood after 23 h. We can see small water droplets in the oil bulk and very large water droplets close to the oil–water bulk interface. The scale bar represents 50 μm .

growth of small droplets in oil bulk) happens under NP flooding, we conducted several supplementary experiments.

3.2.1. Strong Attractive Interactions between Tiny Aqueous Droplets. First, as shown in Figure 6, we resaturated the micromodel with crude oil again after generation of some droplets (5000 ppm negatively charged NPs was used to make the droplet generation slower and more controllable). The bulk water phase was thus removed. We observed that the generated droplets in crude oil remained trapped in pores without diffusing out into the main channel and closely packed with each other. Droplets were shown to be (1) very stable without coalescence observed and (2) strongly attracting each other and self-assembled. These observations showed that the droplets were not simple water droplets, but water droplets covered by some surface-active ingredients. Because DI water without NPs can still induce a moderate generation of those droplets, and because NP are hydrophilic, we hypothesized that the surface-active ingredients should be natural polar components in crude oil rather than NPs.

3.2.2. Necessity of Natural Polar Components: Crude Oil vs Pure Hydrocarbon. In addition, we made a bottle test to further confirm the essential role of natural polar components in crude oil. We mixed the 5000 ppm negatively charged NPs suspension in dyed DI water with crude oil (bottle A) and *n*-decane (bottle B) and then slowly stirred the two mixtures at 100 rpm. After 5 h, we observed the emulsion system under a

microscope. As shown in Figure 7, we found that the water-in-oil-in-water double emulsion was only observed in bottle A

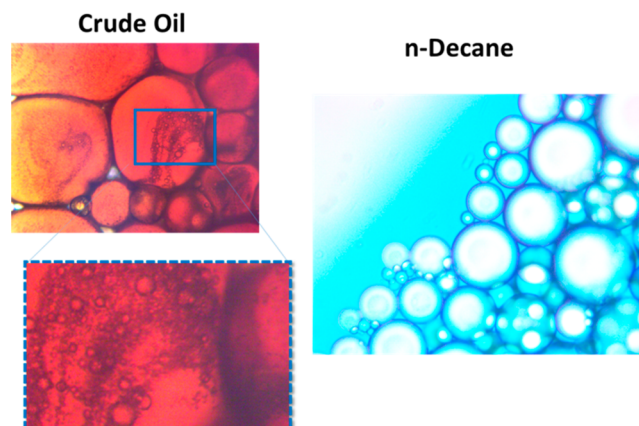


Figure 7. (Left) Microscopic image of the generation of small droplets in crude oil bulk after mixing with NPs suspension in DI water. (Right) Microscopic image of clear decane-in-water macro-emulsion, without small water droplets observed in the oil phase.

(crude oil system), while very clear oil droplets were observed in bottle B (*n*-decane system) without tiny water droplets formed. This observation further supported that the polar components in crude oil played a very important role in spontaneous emulsification and oil swelling. Some previous papers about low-salinity or DI water flood also showed very similar but much weaker and slower spontaneous emulsification, and they also showed that polar components in the oil phase were essential.^{41,60–62}

3.2.3. Interplay between Oleic Polar Components and Water Chemical Potential. Natural oleic polar components in crude oil distribute mainly on water–oil interfaces, oil bulk, and oil–solid interfaces. Those in an oil bulk phase are either in the form of free molecules or in the form of micelles, and the free polar molecule is constant when its total amount is above CMC. In summary, the total amount of polar components in trapped crude oil is constant, and the polar components adsorbed on interfaces and in oil bulk are in competition.

Crude oil before recovery is in equilibrium with the formation brine, which is always of high or moderate salinity. However, DI water has a much higher chemical potential than

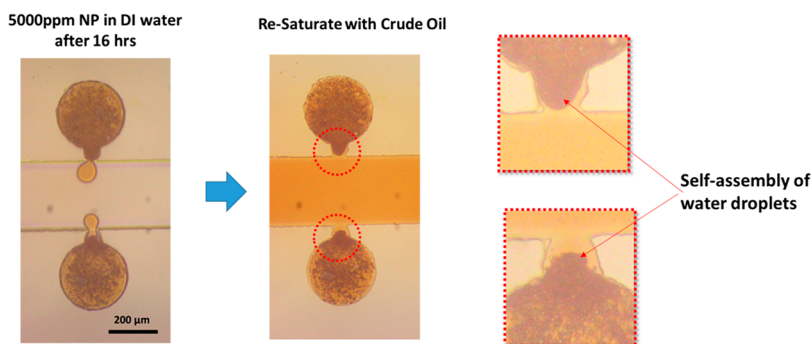


Figure 6. (Left) Microscopic image of trapped and swelled crude oil under injection of 5000 ppm negatively charged NPs for 16 h. Many water droplets (dark dots) were generated in the trapped oil phase. (Middle) Microscopic image of the dead-end pore after resaturating the channel with crude oil. In this case, water bulk was removed, and the small water droplets were not confined anymore by the oil–water bulk interface. (Right) Zoom-in images focusing on small water droplets cut from the middle image. Although no oil–water bulk boundary existed, the small water droplets did not release from the dead-end pore. Rather, they attracted each other without coalescence.

water in brine with high salinity.⁶³ Thus, when DI water is in contact with crude oil, the higher water chemical potential in DI water than in crude oil provides motivation to the system to fill the gap.

Under this differential water chemical potential, water diffuses into the oil phase and becomes trapped by micelles, which consist of polar components and form small water droplets. Growing small water droplets provides increased interface area for polar components to adsorb on, decreasing the concentration of polar components in oil bulk. This decreasing of polar components' concentration in oil bulk increases the water chemical potential in the oil phase^{64,65} and decreases difference between oil bulk and water bulk. Swelling finally stops when the water chemical potential in oil bulk finally becomes equal to that in DI water.

This process is illustrated in Figure 8. In addition, along with the mobilization of polar components toward emulsion

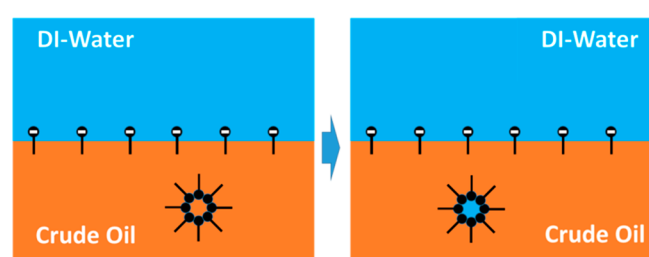


Figure 8. Illustration of DI water-induced spontaneous emulsification in crude oil. The black tadpole-like objects are polar components in the oil phase; the blue phase is the aqueous phase and the brown phase is the crude oil. Polar components distribute on the oil–water interphase and in oil bulk.

droplets' newly generated surfaces, the polar components' concentration on oil–solid interface also decreases, which leads to the dewetting of crude oil from the pore surface.

3.2.4. Hypothesis: NPs Break Polar Component Distribution Balance by Adsorption. In addition, it has been reported that polar components adsorbed on the oil–water bulk interface are mostly negatively charged in neutral or higher pH,⁶⁶ which is the pH range of most applicable NPs suspension; NPs, even very hydrophilic, can adsorb on the crude oil–water bulk interface.^{56,67,68} Consequently, when negatively charged NPs are added to the water phase, they compete against oleic polar components to adsorb on the bulk interface. Due to the much larger adsorption energy of NPs than molecular polar components^{69,70} and the repulsive force between negatively charged NPs and polar components, NPs

will finally occupy most of the bulk interface and repel polar components to oil bulk. Consequently, the concentration of polar components in oil bulk increases, which further decreases the water chemical potential in the oil phase^{64,65} and increases the chemical potential difference between bulk oil and bulk water. Consequently, more water trapping and droplets generation in oil bulk results, as shown in Figure 9.

Similarly, when positively charged NPs were added into oil phase, they can also adsorb on the bulk interface between oil and water. However, in contrast to the repulsive interactions between negatively charged NPs and oleic polar components, positively charged NPs can attract more polar components from the oil bulk to adsorb the NPs' surface. This attraction between NPs and surfactants with opposite charges has been proven as a classic NP–surfactant synergy.⁷¹ This synergistic effect reduced considerably the polar components' concentration in the bulk, which further increased the water chemical potential in oil and decreased the chemical potential difference between the bulk oil and bulk water, thus leading to less water trapping and droplets generation in oil bulk, as shown in Figure 10.

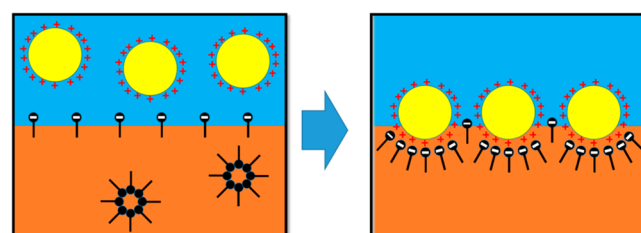


Figure 10. Illustration of positively charged NPs' effect in suppressing spontaneous emulsification in crude oil. The black tadpole-like objects are polar components in the oil phase; the bigger yellow particles with "+" surrounded are positively charged NPs; the blue phase is aqueous phase and the brown phase is the crude oil.

In summary, we proposed a polar component-induced swelling hypothesis and successfully explained all observations in single-pore experiments qualitatively. Effects that can drive more polar components into oil bulk are hypothesized to enhance crude oil swelling, and effects that can remove polar components from oil bulk are hypothesized to compress crude oil swelling. Water chemical potential difference between the aqueous phase and the oil bulk phase was the driving force of this swelling. This hypothesis can be seen as a generalization of some theories proposed for the low-salinity effect.

3.3. NPs Flooding in Reservoir-on-a-Chip. Single-pore experiments clearly showed that oil could swell under NP

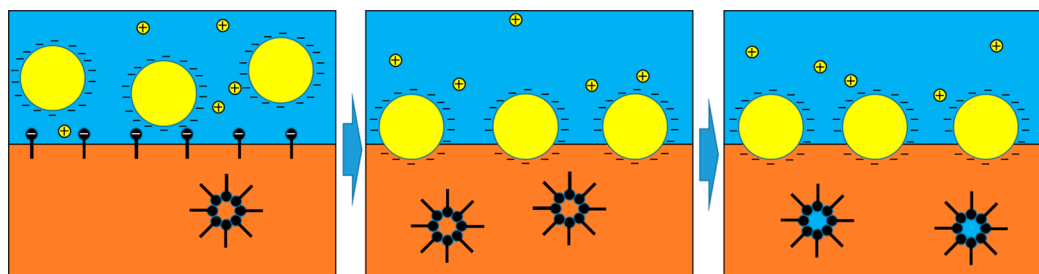


Figure 9. Illustration of negatively charged NPs' effect in inducing spontaneous emulsification in crude oil. The black tadpole-like objects are polar components in the oil phase; the bigger yellow particles surrounded by "-" are negatively charged NPs; the smaller yellow dots with "+" are ions, the blue phase is the aqueous phase and the brown phase is the crude oil.

suspension flooding. However, such pore-scale observation cannot be directly related to the performance of NPs suspension in porous media scale. In practice, seawater or high-moderate salinity brine is always used to prevent the clay swelling, under which salinity the swelling ratio is less than 5% as shown in Figure 4. To confirm whether this minor swelling can help oil recovery at a larger scale, we conducted reservoir-on-a-chip tertiary flooding experiments on a 2.5-D micro-model, which is a regular 2-D array of 104 interconnected 3-D pores. To mimic practical salinity and NP concentrations, 2000 ppm negatively charged NP suspension in seawater was used for this experiment as the tertiary injection fluid.

By visualization and local quantification of saturations, the mechanisms of oil recovery can be clearly revealed. Figure 11

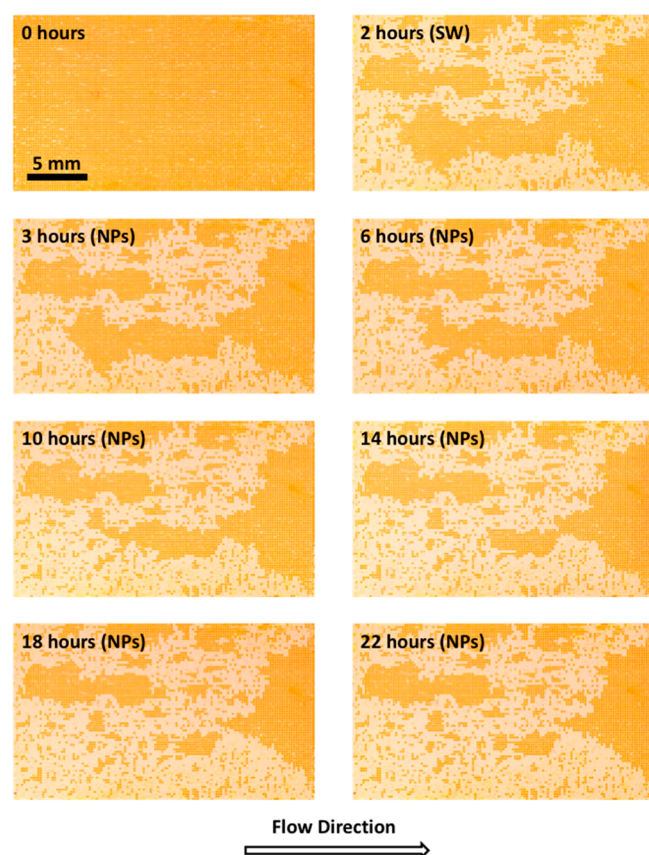


Figure 11. Original Images of micromodel flooding at different times. Note that (1) at time 0, there were irreducible brine droplets trapped in the matrix, and the brine was nonwetting; (2) seawater flooding reached steady state after 2 h; (3) all images after 3 h were captured during the NP seawater suspension flooding. The scale bar is similar for all images, representing 5 mm. The dark yellow phase is the crude oil phase. The flow direction is from left to right.

shows the image of this reservoir-on-a-chip at different times after flooding. Initially, irreducible brine droplets were distributed evenly in the porous media, and those brine droplets were nonwetting (similar to the observation in single dead-end pore microchannel). Because of the Saffman-Taylor instability (viscous fingering),^{72–74} a considerable region was not swept after seawater flooding, as shown in the image captured after 2 h. However, during the NP suspension flooding, the sweep efficiency slowly but considerably increased.

However, when we compared the local oil recovery distribution before and after the NP suspension flood as shown in Figure 12, we found that the well-swept cross sections (between 0% and 15% of normalized distance from injection) had little change, which indicated that the NP suspension flood cannot reduce the residual oil saturation. This observation matched with our pore-scale measurements that only less than 4% swelling of oil can be observed with the 2000 ppm of NP seawater suspension, and the dewetting was also clearly observed after the NP flooding. The slight swelling (generation of tiny droplets in oil phase) and dewetting of oil are shown in Figure 12b.

Figure 13 shows the recovery curve of this experiment. After the secondary seawater flood, 33% oil was recovered. In the first several hours of tertiary NPs suspension flooding, very little incremental oil recovery was achieved. However, after 22 h of NPs suspension injection, the 11.8% incremental oil slowly but definitely recovered. The 22 h corresponded to 40 PV, but the absolute time scale (about 20 h) matched very well with the swelling dynamics measured in the single-pore microchannel. This indicated that NP suspension flooding was not a dimensionless time-dependent process, but an absolute time-dependent process.

We conclude that 2000 ppm negatively charged NPs' seawater suspension flood can improve oil recovery by about 12% in a homogeneous porous micromodel, and the incremental oil recovery is mainly from improving sweep efficiency rather than reducing residual oil saturation.

The classic reservoir model claims that sweep efficiency improvement should be a result of mobility ratio reduction. Mobility ratio (M) is defined as

$$M = \frac{\mu_o/k_{ro}}{\mu_w/k_{rw}}$$

where μ_o and μ_w are the viscosity of oil phase and water phase, respectively; k_{ro} and k_{rw} are the relative permeabilities of oil phase and water phase, respectively. The viscosity of 2000-ppm of NPs suspension in seawater is almost same as seawater without NPs. Thus, the reduction of M should be caused by increasing of k_{ro} or decreasing of k_{rw} .

From a reservoir-scale perspective, the swelling of residual oil increases apparent oil saturation (real oil saturation + water saturation inside residual oil bulk due to the spontaneous emulsification), and the dewetting of oil appears to make the system more water-wet. According to classic relative permeability theory as shown in Figure 14, when oil become less wetting and when oil swells, k_{ro} will increase, and k_{rw} will decrease by increasing apparent oil saturation.

The pore-scale observations can also match the reservoir scale conclusion. As shown in Figure 15, after seawater breakthrough and reaching the steady state, residual oil droplets were distributed in the swept region. Under the NP suspension flood, the generation of water-in-oil-in-water emulsion was spontaneously initiated and residual oil droplets swelled along with dewetted. Although the swelled and dewetted residual oil droplets could not be mobilized through the pore-throat, they increased the resistance of the water phase to flow through those swept channels.

4. CONCLUSION

By conducting visualized experiments in both single-pore scale and "reservoir-on-a-chip" scale, we discovered a surprising

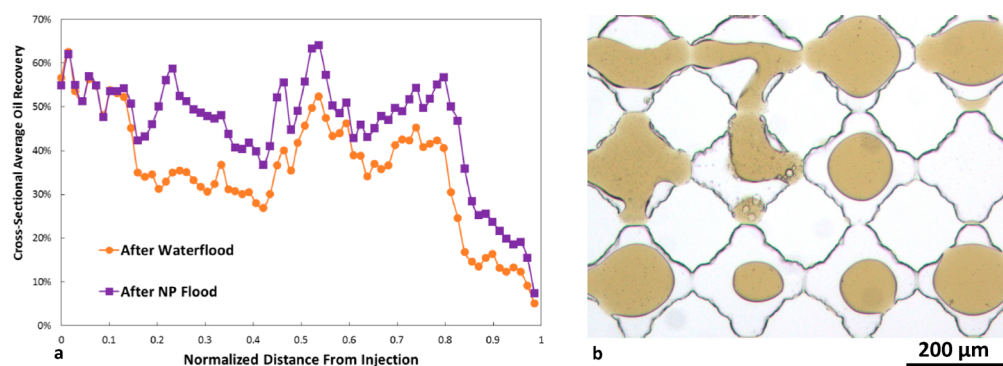


Figure 12. (a) The local oil recovery at different cross sections that were vertical to the flow direction, after seawater injection (orange circles) and after NPs suspension injection (purple squares). (b) Microscopic image of swept region after 2000 ppm negatively charged NPs suspension flooding. The spontaneous emulsification occurred (the dark dots and small water droplets in the oil phase), and the dewetting also occurred (the oil droplets are mostly nonwetting).

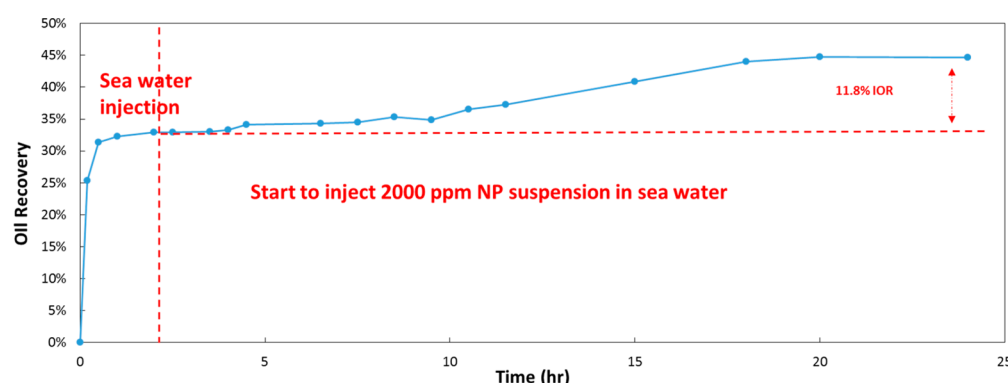


Figure 13. Oil recovery curve during the reservoir-on-a-chip experiment. The vertical dashed red line indicates the end of seawater injection and the start of NPs suspension injection. The horizontal dashed line indicates the oil recovery at the end of seawater injection and before the start of NP suspension injection.

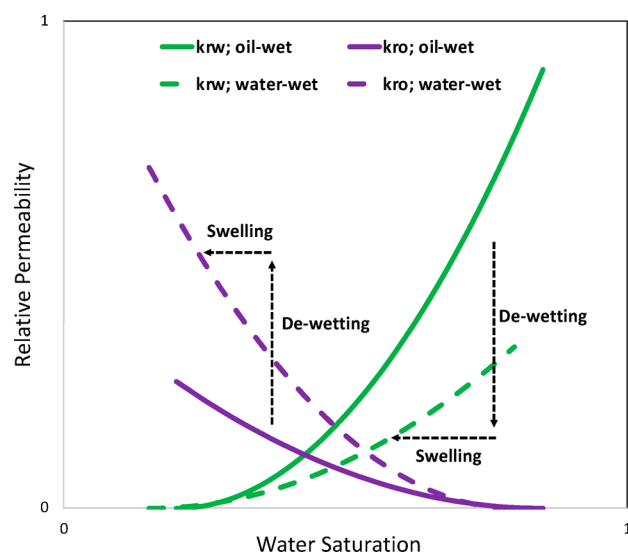


Figure 14. Typical relative permeabilities at different wetting conditions. The solid lines are relative permeabilities when oil is more wetting, and the dashed lines are relative permeabilities when oil is less wetting. When apparent oil saturation increases and oil become less wetting, the relative permeability of oil increases and the relative permeability of water decreases. The curves shown here are qualitative rather than quantitative.

interaction between negative-charged hydrophilic NPs' suspension and crude oil containing a moderate amount of polar components. This interaction swells and dewets crude oil. By conducting flooding experiments on porous micromodels, we showed that this interaction can significantly improve oil recovery with relatively low NP concentration.

On the basis of observations in the dead-end-pore microchannel, a significant but slow (last for more than 10 h) swelling of crude oil under contact with NPs suspensions was confirmed. This swelling was caused by spontaneous generation of a large amount of small aqueous droplets inside the crude oil phase, and the swelling rate increased with increased negatively charged NPs concentration and with decreased salinity in the aqueous phase. Positively charged NPs showed little effect. The interplay of water chemical potential in the aqueous phase and in the crude oil phase under different NPs/salinity environment is proposed to be the mechanism of this swelling, which is supported by much experimental evidence. The swelling ratio of crude oil can be as significant as 30% in 16 h under ideal conditions (when DI water containing 5 wt % NP was applied) and not negligible (~4% in 16 h) under practical conditions (seawater with 500 ppm of NP was applied).

We further investigated the effect of this swelling on oil recovery performance in a homogeneous porous micromodel "reservoir-on-a-chip" that contained a regular array of 10^4 identical pores. Visualization and local saturation data showed a great increase in sweep efficiency and little change in residual

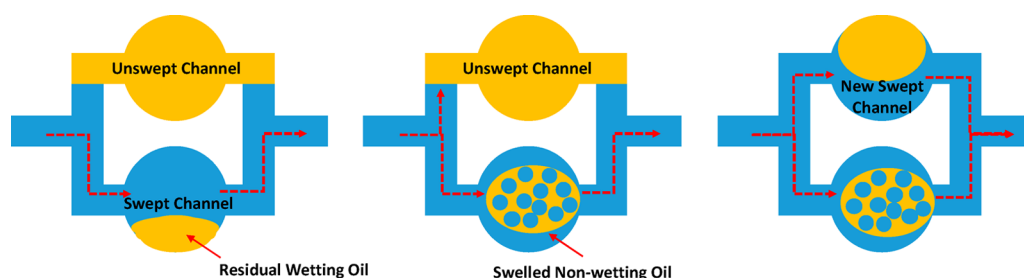


Figure 15. Illustrations to show the sweep efficiency improvement induced by NPs-induced residual oil swelling and dewetting. Yellow indicates crude oil, blue indicates aqueous phase, and dashed red lines indicate the flow path.

oil saturation under 2000 ppm negatively charged NP seawater suspension flooding. This improvement in sweep efficiency brought an 11.8% incremental oil recovery and lasted for more than 20 h, which matched the swelling dynamics of crude oil under the corresponding NPs suspension. From a pore-scale perspective, this improvement in sweep efficiency can be explained by the blockage effect of swelled residual oil in the swept region, which redirected flooding fluid into the unswept region. This pore-scale hypothesis can also be translated to a reservoir scale model that the swelling and dewetting of oil increases the oil relative permeability and decreases the water relative permeability, which finally reduces the mobility ratio and thus improves the sweep efficiency.

On the basis of this work, we not only revealed an important and previously unobserved mechanism of NP-induced oil recovery, but also constructed a benchmark to study complex EOR mechanisms using a multiscale microfluidic approach. The pore-scale observations can be connected to porous media scale displacement performance, and reservoir-scale models can be derived from relatively small-scale experiments on a microfluidic platform.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.energyfuels.8b02496](https://doi.org/10.1021/acs.energyfuels.8b02496).

A video showing the evolution of trapped oil (AVI)

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Notes

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