

Polymer-Coated Nanoparticles for Enhanced Oil Recovery

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ABSTRACT: Enhanced oil recovery (EOR) processes aim to recover trapped oil left in reservoirs after primary and secondary recovery methods. New materials and additives are needed to make EOR economical in challenging reservoirs or harsh environments. Nanoparticles have been widely studied for EOR, but nanoparticles with polymer chains grafted to the surface—known as polymer-coated nanoparticles (PNPs)—are an emerging class of materials that may be superior to nanoparticles for EOR due to improved solubility and stability, greater stabilization of foams and emulsions, and more facile transport through porous media. Here, we review prior research, current challenges, and future research opportunities in the application of PNPs for EOR. We focus on studies of PNPs for improving mobility control, altering surface wettability, and for investigating their transport through porous media. For each case, we highlight both fundamental studies of PNP behavior and more applied studies of their use in EOR processes. We also touch on a related class of materials comprised of surfactant and nanoparticle blends. Finally, we briefly outline the major challenges in the field, which must be addressed to successfully implement PNPs in EOR applications. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2014, 131, 40576.

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INTRODUCTION

Energy consumption worldwide is expected to increase by 50% relative to current levels by the end of 2030.¹ This growth is unlikely to be met by renewable resources, and thus there is a strong and growing demand for oil as a predominant energy resource. Primary and secondary oil recovery methods typically produce only 15–30% of the original oil in place, depending on the compressibility of fluids and initial pressure of the reservoir.² This leaves large amounts of trapped oil in reservoirs, which in some cases is amenable to tertiary or enhanced-oil-recovery (EOR) processes.

Chemical EOR processes encompass a variety of mechanisms, including a reduction in the oil-water interfacial tension,^{3–5} surface wettability alteration,^{6–10} the use of high viscosity agents for mobility control,^{11–14} application of thermal methods whereby the viscosity of oil is decreased by increasing the temperature inside the reservoir,^{15–17} and the use of microbes for recovery of depleted reservoirs.^{18–21} EOR processes can include one or more of these mechanisms, and to be successful the approach must be economical, scalable, and reliable.

Nanoparticles have been explored for use in a remarkable range of applications,²² including polymer composites,²³ drug

delivery,^{24–29} solar cells,^{30–33} lipase immobilization,³⁴ metal ion removal,³⁵ imaging,^{28,36,37} and EOR.²² They can be interfacially active and used to modify surface properties. Nanoparticles have been shown to stabilize foams and emulsions or change the wettability of rock, but their successful implementation for EOR processes require considerations beyond interfacial properties. They must be able to migrate through porous media and be dispersible in water/brine, inexpensive, and injectable into a reservoir.

One approach to improve the dispersibility of nanoparticles and tailor their properties for a particular application is to covalently attach polymers to the nanoparticle surface, resulting in polymer-coated nanoparticles (PNPs). PNPs have received significant interest as additives and interfacially active materials, and more recently they have been investigated for EOR applications. PNPs are versatile materials that can be tailored for a particular application, such as EOR. While less work has been carried out with PNPs for EOR, recent work suggests they may be superior to unmodified nanoparticles for EOR. The aim of this article is to review work related to PNPs for EOR, including their use as mobility control agents and for wettability alteration (see Figure 1). We focus only on studies related to the use of PNPs for EOR. Other oilfield applications, such as

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hydrocarbon detection and estimation,³⁸ tracing, imaging,³⁹ etc. are beyond the scope of this study. A significant amount of work has been carried out on polymeric composites based on PNPs.⁴⁰⁻⁴⁴ For additional information, the reader is referred to recent reviews on polymer nanocomposites,⁴² on stimuli-responsive PNPs,⁴⁵ and on the synthesis of PNPs.⁴⁶⁻⁴⁸

We first discuss the use of polymer- and surfactant-coated nanoparticles in foams and emulsions, which can increase oil recovery through controlling the mobility of the injected fluid.

Next, we review work related to the use of PNPs for wettability alteration. We also discuss the stabilization and transport of PNPs through porous media, which will be important for all oilfield applications of PNPs. Finally, we outline challenges ahead and recommend directions for future study.

PNPs FOR MOBILITY CONTROL

In the terminology of fluid flow in porous media, mobility of a fluid is defined as the ratio of relative permeability of the

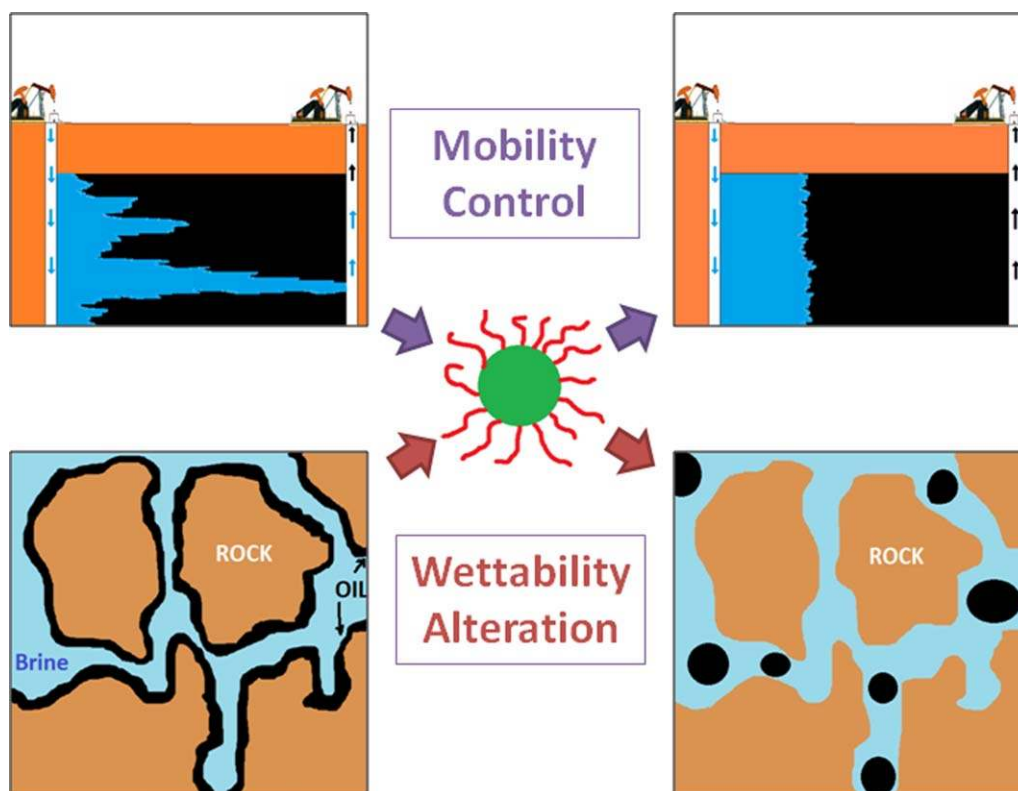


Figure 1. Schematic for the application of PNPs in EOR through mobility control and wettability alteration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

corresponding fluid to its viscosity. In EOR, mobility ratio is the mobility of the injected displacing fluid to that of the oil being displaced. Good mobility control is obtained when the viscosity of the injected fluid is higher than the viscosity of the oil in the reservoir and can lead to a piston-like displacement of the oil from the injection well to the production well, as shown schematically in Figure 1. However, poor mobility control due to a lower viscosity of the injected fluid can result in low recoveries due to viscous fingering.^{49,50} For instance, the viscous fingering effect may be observed if CO₂ is injected as an oil-miscible solvent. Injected CO₂ may find the path of less resistance to the production well and bypass most of the oil, leaving a huge portion of the oil in the reservoir behind.^{51–54} Achieving good mobility control in combination with other mechanisms including low interfacial tension or wettability alteration is therefore essential for successful chemical EOR.^{2,53}

A method for achieving high viscosities of the injected phases and good mobility control is through generation of foams and emulsions, which can form in the presence of surfactants or nanoparticles. Foams and emulsions are dispersions of one fluid in a second immiscible fluid, and they typically exhibit high viscosities and shear-thinning rheological behaviors.^{55,56} The high viscosity of the injected phase can lead to improved mobility control. In addition, the shear-thinning behavior of the injected foam or emulsion is advantageous for achieving high injection rates into the reservoir.

Similar to surfactants, nanoparticles can be used to generate foams and emulsions to increase the viscosity of the injected

phase. The stabilization of foams and emulsions using micron-sized particles was reported roughly 100 years ago by Ramsden and later by Pickering.^{57,58} Such emulsions are commonly known as Pickering emulsions. Unlike surfactants, nanoparticles have the advantage that they can irreversibly adsorb to a liquid-liquid or gas-liquid interface, forming very stable foams and emulsions. However, bare nanoparticles may be too hydrophobic or hydrophilic for stabilizing an interface. PNPs can be tailored for a specific interface and application. Below, we discuss the fundamental mechanisms involved in stabilization of foams and emulsions using PNPs and then discuss recent examples of their application for EOR. We begin by discussing surfactant-coated nanoparticles, which are closely related to PNPs and have been widely studied for EOR applications.

Foam and Emulsion Stabilization Using Surfactant- and PNPs

Surfactant-coated nanoparticles are closely related to PNPs and are prepared by blending surfactants and nanoparticles. Driven primarily by electrostatic interactions, the surfactant can form a monolayer on the nanoparticle surface, resulting in more hydrophobic particles. Figure 2 shows a schematic representation of surfactant adsorption onto a nanoparticle and examples of foams and emulsions stabilized by surfactant-coated nanoparticles. A number of studies have confirmed surfactant adsorption onto nanoparticles through contact angle measurements, adsorption isotherms of surfactants on nanoparticles, zeta potential measurements and dispersion stability measurements as a function of concentration of surfactant and nanoparticles.^{59–61} Surfactant-coated nanoparticles

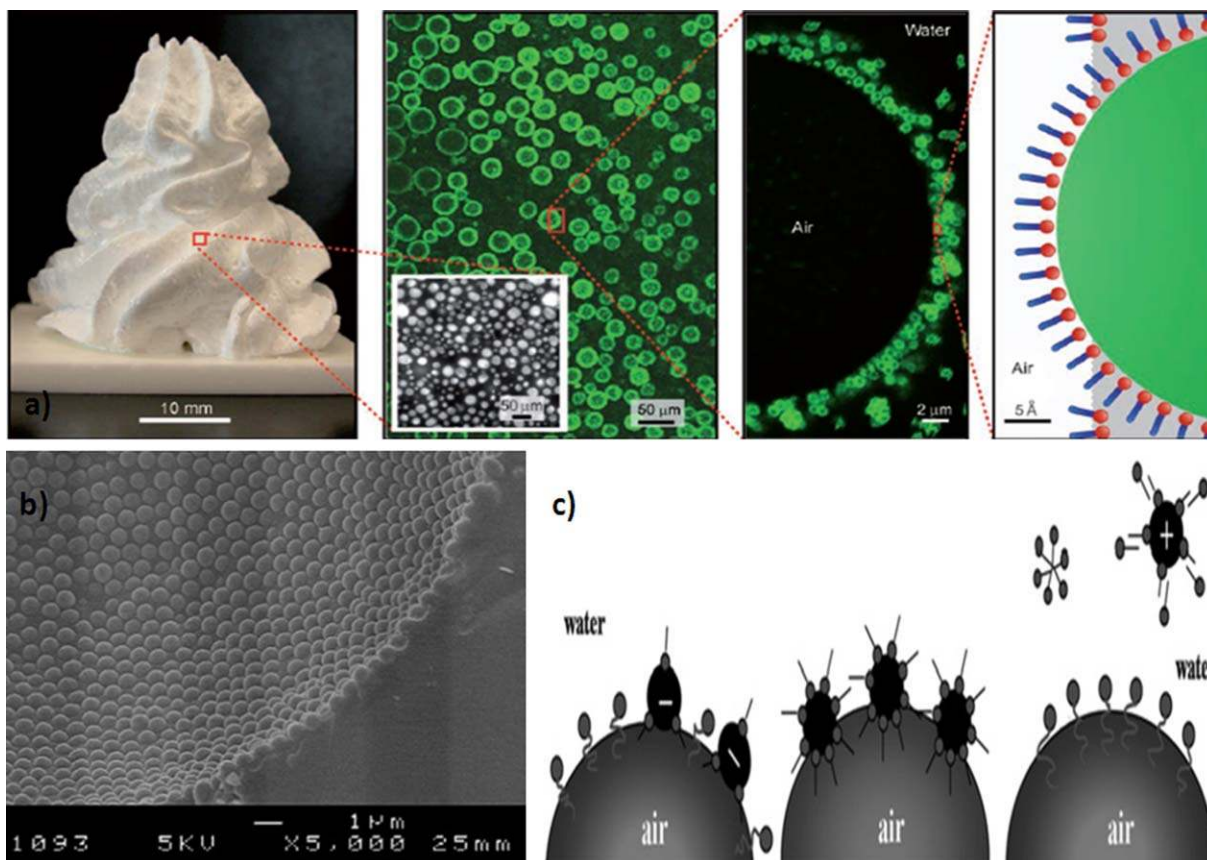


Figure 2. (a) Foam as a viscous fluid is a dispersion of air in water and each air droplet is surrounded by surfactant-coated nanoparticles; (b) Cryo-SEM image of a foam with nanoparticles closed packed; (c) schematic representation of the effect of concentration ratio of nanoparticle and surfactant. Reproduced with permission from Ref. 58 with permission from the Royal Society of Chemistry and Reproduced with permission Ref. 62 from Wiley. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

generate stable foams and emulsions in some cases where precursor nanoparticles or surfactants separately do not.^{59,62–64}

The properties of surfactant-coated nanoparticles are dependent on the relative concentrations of surfactant and nanoparticle. If the concentration ratio of surfactant to nanoparticle is low, only a fraction of nanoparticle surface is coated with surfactant. However, at much greater concentration ratios, the surfactant can form a double layer on the nanoparticle surface, resulting in a hydrophilic nanoparticle surface. Stable foams and emulsions are formed at a concentration ratio that results in maximum nanoparticle flocculation.⁶⁶ The most flocculated nanoparticle in this case corresponds to a low-charge, optimally hydrophobic nanoparticle, containing a monolayer of surfactant on the surface.^{59–61} Further, single chain surfactants are believed to be a better choice for foam formation when mixed with nanoparticles since double chain surfactants may lead to formation of double layer adsorption on nanoparticle at concentrations lower than that of single chain surfactants.⁶⁰

The rheology of foams and emulsions formed by surfactant-coated nanoparticles is also influenced by the surfactant to nanoparticle concentration ratio.⁵⁹ Viscoelastic behavior of the bulk is observed only over a range of concentration ratios. For instance, in a study of silica nanoparticles with a cationic surfactant (cetyl

trimethylammonium bromide), Limage et al. find that if the molar concentration of CTAB to silica nanoparticles is about 0.03, viscoelastic behavior is observed.⁵⁹ They also try to find a correlation between bulk rheology of nanoparticle and surfactant mixtures and that of the foam. Their rheological measurements are correlated with the structures forming at the interface using cryo-SEM imaging of the generated emulsions and foams.

Another role of the surfactant in this process is to lower the interfacial tension and form an initial dispersion of air/water or oil/water in case of foam or emulsion, respectively. Once this dispersion is formed due to shear and a decreased amount of interfacial tension, the stability of foam/emulsion is augmented by adsorption of nanoparticles at the interface.⁶²

Gonzenbach et al. provide a series of conditions which can result in formation of ultra-stable foams by means of surfactant-coated nanoparticles.⁶⁵ Apart from reporting the condition of optimal ratio between concentration of surfactant and nanoparticle, they find that a lower particle size or higher concentration of nanoparticle and surfactant leads to generation of more foam. Also, by comparing long-term stability of the foams treated with different length of surfactants, they find that long-term stable foams can be made by using surfactants with a short chain length ($n = 2–8$) rather than long chain length.

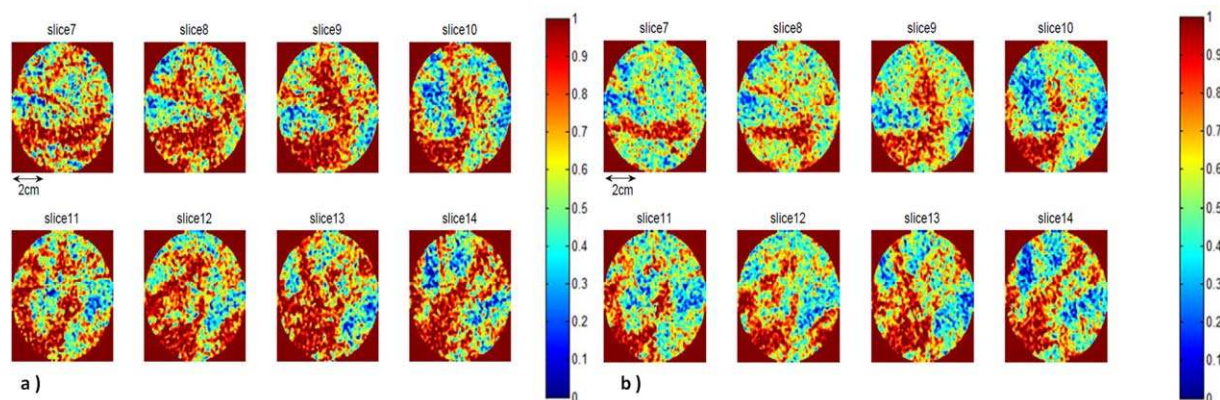


Figure 3. CT-scan of the cross section of a core flooded with CO_2 and (a) 2% NaBr brine and (b) 2% NaBr brine and 5% PEG-coated silica nanoparticles; pure brine and CO_2 are illustrated with red and blue, respectively. The scan is taken after 0.25 pore volume of CO_2 injected and each slice is 1 cm apart longitudinally (Reproduced with permission from Ref. 87 from the Society of Petroleum Engineers). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Similar to surfactant-coated nanoparticles, PNPs can be used to stabilize foams and emulsions. PNPs can decrease the interfacial tension of oil and water or water and air, which can lead to more stable emulsions. For example, in 2005 Saleh et al. reported the use of silica nanoparticles coated with a polyelectrolyte to stabilize oil-in-water emulsions.⁶⁷ More recently, Saigal et al. reported stable oil-in-water emulsions using silica nanoparticles coated with a pH responsive polymer, and they found that the most stable emulsions were formed at lower polymer chain grafting densities.⁶⁸ Related studies on star polymers,⁶⁹ bottlebrush polymers,⁷⁰ and paramagnetic particles with adsorbed amphiphilic polymers found stable emulsions⁷¹ and reductions in the oil-water interfacial tension at relatively low (0.1 wt %) particle contents.⁷² Alvarez et al. evaluated the dynamic reduction in interfacial tension of air and water in the presence of PNPs while changing the grafting density of the polymer brushes and showed that the polymer coating is a key factor in reducing the interfacial tension of air and water using PNPs.⁷² PNPs with stimuli-responsive polymer chains have also been reported. PNPs can respond to temperature, pH, and light through a change in surface properties.⁶⁸ Stimuli-responsive PNPs can potentially be used to design injectable fluids that respond to environmental changes before and after injection or in the presence of oil.

It should be noted that the reduction in interfacial tension by PNPs and star polymers is at most by one order of magnitude (from roughly 25 to 1 mN/m).^{68–70} By comparison, surfactant additives can lead to much greater reductions in oil-water interfacial tension, down to 0.001 mN/m² and below. Thus, irreversible PNP adsorption to the oil-water interface still plays a predominant role in emulsion stability with added PNPs, but the reduction in oil-water interfacial tension is modest compared with suitably chosen surfactant additives.

In addition to surface energy, entropy is important to the interfacial properties of PNPs. Polymers can exhibit conformational changes that influence the thermodynamics of PNP adsorption at the fluid-fluid interface.^{73–76} However, there are only a handful of studies on the effect of polymer entropy on nanoparticle

adsorption, although this has been studied more carefully in polymer-polymer blends⁷⁷ and in polymer nanocomposites.⁷⁸

Surfactant- and PNPs for Mobility Control

Prior studies and field tests have relied on the mechanisms explained above to increase the viscosity of the displacing fluid and the recovery of oil.^{79–85} Foams and/or emulsion formation in oil-rich porous media after injection of surfactant- or PNPs has been validated through CT-scans, an increased pressure drop across the core, and effluent analysis.^{86–88}

Figure 3 shows the CT-scan of different cross sections of a Boise sandstone core after flooding with brine and CO_2 , both with and without PEG-coated silica nanoparticles. The difference in these two experiments is only the presence or absence of PNP, and the same core has been scanned at the same injected pore volume of CO_2 . The CT-scan results show greater sweep efficiency in the presence of PNP [Figure 3(b)], while with no PNP added, large regions of the core are bypassed due to viscous fingering [Figure 3(a)].

One practical challenge in the application of foam and emulsions from PNPs is the energy needed for foam and emulsion formation.^{59,60} There is a threshold shear rate needed for nanoparticles to start generating foams and emulsions.⁸⁹ This threshold injection flow may be much greater than the practical injection rates in reservoirs. In addition, the pregeneration of foams and emulsions outside the reservoir before injection increases the cost and difficulty of injection into the reservoir.

It is noteworthy to mention that a type of polymeric nanoparticle with commercial name BrightWater was the first successfully field-tested nanoparticle to increase the sweep efficiency in an actual oil reservoir (Salema field, Campos Basin, Brazil).⁹⁰ Recently, other tests have confirmed the successful application of these nanoparticles in other reservoirs.⁹¹ BrightWater is a polymeric nanoparticle that hydrolyzes at a specific temperature and expands to many times its original volume. By blocking the pores in the high-permeability regions of a reservoir, the injected flow will be directed toward low-permeability zones of the reservoir, which may have been previously untouched.

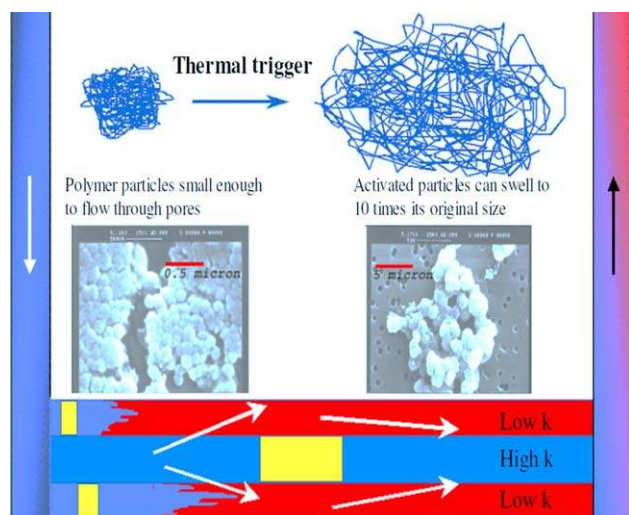


Figure 4. Schematic and SEM image of BrightWater polymeric nanoparticles. The particles expand at elevated temperatures, diverting flow to low permeability regions (Reproduced with permission from Ref. 90 from Society of Petroleum Engineers). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4 illustrates the basic idea behind the application of these polymeric nanoparticles, which can lead to significant increase in oil recovery. Although BrightWater is not a PNP, its successful implementation provides guidelines for the design of PNPs and demonstrates that PNPs do have potential for use in EOR.

PNPs FOR SURFACE WETTABILITY ALTERATION

Oil can more easily be extracted from water-wet rock than from oil-wet rock,⁹² and one approach to improve oil recovery is through changing the wettability of the reservoir rock from oil-wet towards water-wet. A surface is called water-wet if the water contact angle is $<90^\circ$ and oil-wet if the water contact angle is $>90^\circ$. Figure 5 demonstrates oil and water spreading on different surfaces. Below, we discuss how nanoparticles and PNPs can alter the wettability of surfaces and then discuss their potential use for wettability alteration in EOR applications.

Mechanisms of Surface Wettability Alteration by PNPs

Surface and interfacial energies determine whether a surface is water- or oil-wet. A spreading coefficient S of water on a solid in contact with both oil and water can be defined in terms of the interfacial tensions between each phase in eq. (1):

$$S = \gamma_{O/S} - \gamma_{W/S} - \gamma_{O/W} \quad (1)$$

where $\gamma_{O/S}$, $\gamma_{W/S}$, and $\gamma_{O/W}$ are the interfacial energies between oil/solid, water/solid, and oil/water. The contact angle formed results from a force balance at these interfaces.⁹⁴ Reducing the oil-water interfacial tension results in an increase in S and a more water-wet surface. “Rollup” is a well-known mechanism for removal of oily soils from solid surfaces by wettability alteration using surfactants.⁹⁵ If the initial contact angle is $<90^\circ$, it can be decreased to make the surface more water-wet by a reduction in oil-water interfacial tension alone. However, adsorption of surfactant to decrease water/solid interfacial

energy is needed to convert an initially oil-wet surface to a water-wet state.^{95,96}

However, in a fluid containing nanoparticles or spherical surfactant micelles, phenomena are observed that may not be fully explained through the previously known mechanisms. Kao et al. were the first to observe that in the case of an oil droplet on a surface immersed in a solution of nanoparticles, there are two contact lines instead of one.⁹⁷ Also, traditional mechanisms cannot accurately account for the faster spreading of a nanoparticle solution on a surface for higher nanoparticle concentrations and higher viscosities.⁹⁸ It is observed that the inner and outer contact lines move with a constant spreading velocity, which is a function of salt concentration, bulk volume fraction of nanoparticles, size, and polydispersity of nanoparticles, as well as interfacial tension between the drop and the spreading phase.^{94,99–101}

The underlying mechanism that can account for this unusual interfacial behavior is related to the size of nanoparticles. Adjacent to the wedge-shape inner contact line, the nanoparticles can form ordered structures, as shown in Figure 6.^{100–102} Chengara et al. claim that the ordering is a consequence of increase in entropy of the system.¹⁰⁰ These ordered, solid-like structures near the contact line lead to very high disjoining pressures that cause a wedge-like spreading of the nanoparticle solution, resulting in two contact lines (as shown in Figure 6). This structural disjoining pressure is oscillatory,¹⁰² and both period of oscillation and decay factor is dependent to the effective diameter of the nanoparticle.¹⁰³ Wasan and Nikolov showed that the structural disjoining pressure exponentially increases with a decrease in film thickness or number of nanoparticle layers between the solid and oil, as seen in Figure 6 (left).¹⁰² It is the high structural disjoining pressure that enhances the spreading of the phase containing nanoparticles and can lead to wettability alteration of an oil-wet surface to more water-wet states. Matar et al. showed this theoretically by applying the mass and momentum conservation equations under the lubrication approximation.¹⁰⁴

It is noteworthy that structural disjoining pressure which is discussed in these studies is just one of the components affecting disjoining pressure. Van der Waals, electrostatic, and solvation forces are other components that can affect the disjoining pressure. In particular, electrostatics can be very effective in increasing wettability alteration properties of nanoparticles. If the nanoparticle is coated by a polyelectrolyte, electrostatic repulsive forces can increase the disjoining pressure and may cause significant increase in spreading of the phase with dispersed nanoparticles.

In some of the studies that investigate wettability alteration through so-called “nanofluids”, a mixture of nanoparticle and surfactant is used.^{93,105} However, it is well-known that surfactants of different types are able to change the wettability of the rocks.¹⁰⁶ Therefore, such studies may not present conclusive evidence on wettability alteration using nanoparticles, especially when control experiments are lacking. In spite of this, there is conclusive evidence that shows nanoparticles can change the contact angle of an at least slightly oil-wet rock to more water-wet conditions.^{98,102}

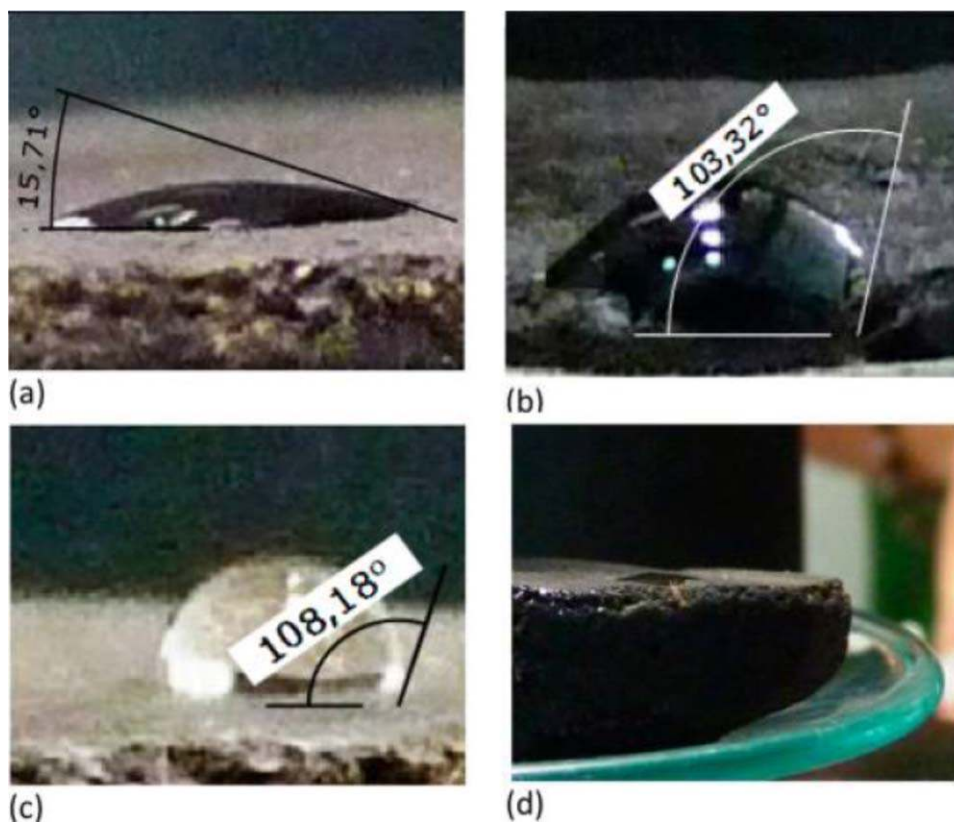


Figure 5. Contact angle on a rock (a) oil/air/rock before treatment, (b) oil/air/rock after treatment with silica nanoparticles, (c) water/air/rock before treatment, (d) water/air/rock after treatment with silica nanoparticles (Reproduced with permission from Ref. 93 from American Chemical Society). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

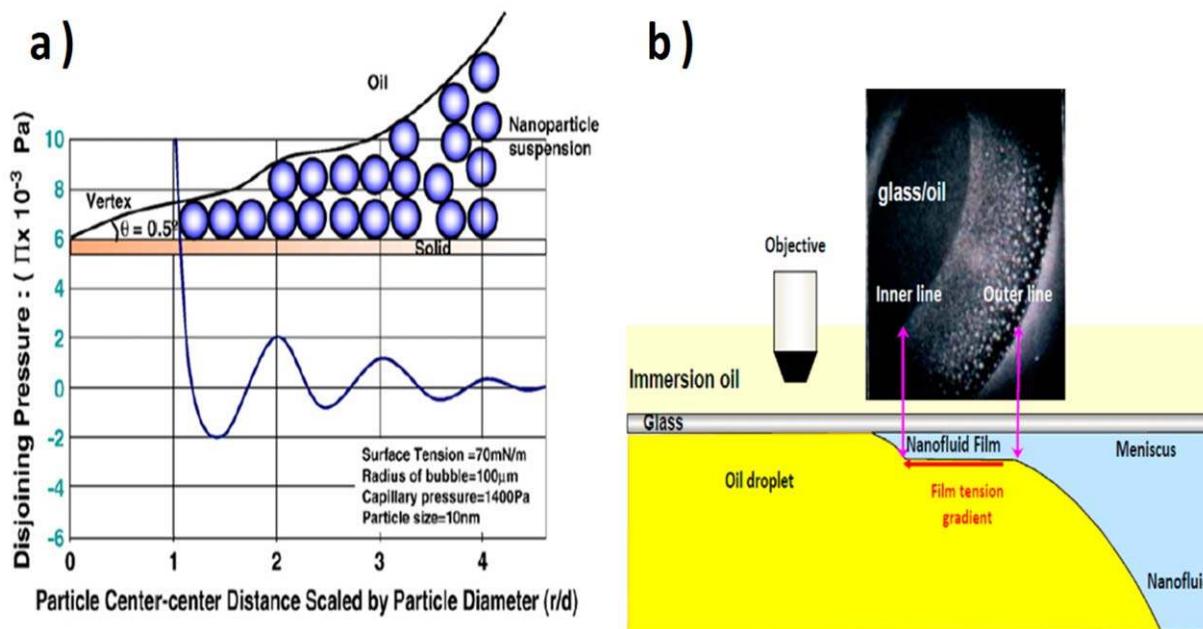


Figure 6. The inner and outer contact line due to ordering of nanoparticles; (a) the oscillatory disjoining pressure profile due to ordering of the nanoparticles near the wedge-like inner contact line; (b) visual and schematic pictures of inner and outer contact lines; (Reproduced with permission from Ref. 93 from Elsevier and from Ref. 96 from American Chemical Society, respectively). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Nanoparticle EOR Processes Through Wettability Alteration

A number of studies have reported the application of nanoparticles in EOR through wettability alteration,^{93,105,107,108} yet studies of the effect of PNPs on wettability is in the early stages. Here, we briefly review the current state of research on the effect of nanoparticles on wettability alteration and emphasize how a polymer coating in PNPs can potentially change the contact angle of the nanoparticles, increase electrostatic repulsion, and improve wettability alteration of nanoparticles.

Several studies measured the contact angle of oil-wet surfaces before and after treatment with nanoparticles, and it was found that nanoparticles can decrease the contact angle of various surfaces. Addition of nanoparticles to brine can also lead to spontaneous imbibition of the nanoparticle dispersion with resulting oil displacement from different rocks.^{105,109,110} Relative permeability curves of oil and water also change after contact with nanoparticles; that is, the relative permeability of oil and water increases and decreases, respectively.⁹³ Actual core flooding experiments where nanoparticles were injected in real cores found that recovery of oil can increase from 5 up to about 20% in some cases.^{93,107,109,110}

Ju et al. developed simulations to analyze wettability alterations caused by nanoparticles. They analyzed the effect of different physical and chemical properties of the nanoparticles, such as polymer coating, contact angle, and size in terms of empirical coefficients.^{108,111} They report that both permeability and porosity of the core decrease with injection of nanoparticles, and the decrease in permeability is more significant than porosity. However, the relative permeability of oil increases due to wettability alteration. Based on their simulations, oil recovery can be improved through wettability alteration by up to 20% when a high concentration of nanoparticle is injected. At the same time, increasing nanoparticle concentration leads to greater reductions in permeability. Therefore, they suggest an optimum concentration of nanoparticle (2–3%) for injection into the core.

TRANSPORT OF PNPs IN POROUS MEDIA

The sections above focused on the properties of PNPs that can improve oil recovery. However, nanoparticles must also be able to propagate deep into the reservoir to assist oil displacement. Previous studies have reported challenges in the transport of nanoparticles through porous media.^{112–116} Nanoparticles coated with various polymers including polyacrylic acid,^{117–123} cellulose,¹²⁴ starch,¹²⁵ and surfactants^{126–128} have been studied. In this section, a critical review of the mechanisms affecting transport of nanoparticles through porous media and current challenges are presented.

Mechanisms of Nanoparticle Transport Through Porous Media

Three mechanisms primarily affect propagation of nanoparticles in porous media: physical filtration, solution chemical stability, and adsorption on the rock/porous media surface. Each of these is discussed separately below.

Physical Filtration

Physical filtration occurs when the particles are larger than some of the pores in the porous media. This may even occur

for well-dispersed (nonaggregated) nanoparticles in case of injection in low-permeability rocks, such as tight sandstones. For nonaggregated nanoparticles, the size, shape and aspect ratio of the particle are relevant parameters that can affect filtration. The particle size-distribution is also important since filtration may be initiated with the larger particles. This can, in turn, cause further filtration due to decrease in the size of the pores after initial filtration.¹²⁹ In the case of PNPs, both nanoparticles and polymeric coatings can be polydisperse.

Solution and Chemical Stability of PNPs

By solution and chemical solution stability, we refer to the solubility and dispersibility of nanoparticles. In the presence of high salinity and hardness (which is often the case in oil reservoirs), poor chemical stability can lead to aggregation or precipitation of nanoparticles. From the molecular viewpoint, both van der Waals and hydrophobic attractions can result in precipitation and aggregation. Polymeric coatings on nanoparticles can potentially inhibit aggregation by providing electrostatic or steric repulsions.¹³⁰

Different polyelectrolytes, such as poly(acrylic acid), poly(vinyl pyrrolidone), poly(styrene sulfonate), and bilayers of ionic surfactants have been used to provide electrostatic repulsion between nanoparticles.^{131–134} The challenge with these types of coatings is that they are usually highly pH-dependent. Salinity and the presence of divalent ions can also affect the stability of PNPs. Some of these polymers [e.g., poly(vinyl pyrrolidone)] can actually stabilize the nanoparticles in high salinity brines; however, they may cause the nanoparticles to readily adsorb to the rock surfaces. Yan et al. studied the effect of salinity (based on KCl) on stability of a polyelectrolyte-coated PNP,¹³⁵ and Bagaria et al. conducted a comprehensive study on the effects of salinity (based on NaCl) and Ca^{+2} concentration on nanoparticles coated with different polyelectrolytes.¹³⁴ Also, Kim et al. studied the effect of pH and clay minerals on the stability of nanoparticles coated with both low molecular weight and high molecular weight polyelectrolytes (with negative charges).¹³⁶ The stability of PNPs with polyelectrolyte polymer coatings is found to depend on the pH, and to be adversely affected by increases in salinity and divalent ion concentrations.

Ionic surfactants have also been used to stabilize nanoparticles.^{126–128} However, as discussed above, stabilization of nanoparticles using surfactants is sensitive to the concentration ratio of surfactant to nanoparticle. At low concentration ratios of surfactant to nanoparticle, a monolayer of surfactant is adsorbed on the nanoparticle surface, making it hydrophobic, but if a bilayer of surfactant adsorbs to the nanoparticle, it can lead to more chemical stabilization due to electrostatic repulsion.

Some researchers have used long-chain polymers such as cellulose, starch, or polyacrylamide, as a coating on the surface of nanoparticles to stabilize them in the solution.^{124,125,130,137} This type of polymer coating leads to repulsion between nanoparticles based on steric inhibition and entropic effects. However, they have not been successfully shown to stabilize the nanoparticles at high salinities present in many reservoirs due to the poor solubility of the polymers under these conditions. Nanoparticles can also be coated with a combination of polymers to

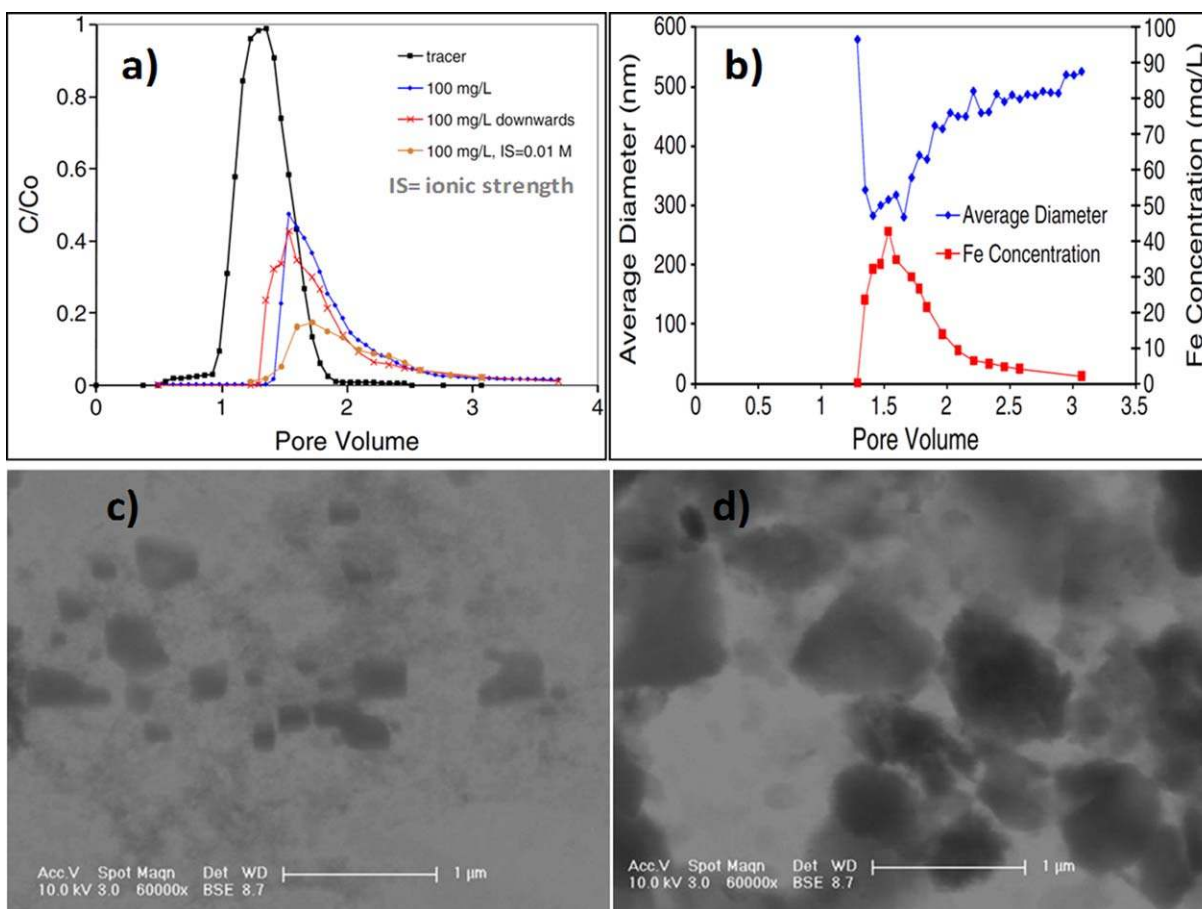


Figure 7. (a) The retardation of the poly(acrylic acid) coated iron nanoparticles in dynamic test; (b) the change in the effective size of nanoparticles as a function of injected pore volume; (c) ESEM images the size of nanoparticle before propagation through porous media; (d) the size of nanoparticle after propagation through porous media (Reproduced with permission from Ref. 131 from Elsevier). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

provide both providing steric inhibition and electrostatic repulsion to optimize the stabilization and adsorption.¹²⁹

Cirtiu et al. compared the stability of PNPs with the polymeric layer either postgrafted to a premade nanoparticle or through pregrafting, in which nanoparticle was synthesized while grafting polymers to the surface. They found that in most of the cases pregrafted samples led to a more stable PNP than the case of postgrafted PNPs.¹³⁷

Another factor to consider is that PNPs may behave differently and even have different sizes under static and dynamic conditions.¹³¹ Ersenkal et al.¹³¹ investigated the size of poly(acrylic acid)-coated iron nanoparticles in static (in solution) and dynamic conditions (passed through a porous medium). They found that the nanoparticle size appeared to depend on nanoparticle solution concentration in dynamic tests but not static measurements. In dynamic tests, they found retardation in nanoparticle propagation for initial nanoparticle concentrations lower than 600 mg/L (Figure 7). They hypothesized that these results reflect forces and torques acting on nanoparticles in a dynamic test that are absent in a static one and that these forces are most significant in the areas of flow convergence in porous media that favor nanoparticle filtration or particle aggrega-

tion.¹³⁸ This result highlights the complexity of the effects of dynamic factors (such as flow rate, permeability, etc.) on effective size of the nanoparticles and questions the validity of static measurements to determine the chemical stability of nanoparticles under dynamic conditions.

Hamedi Shokrlu and Babadagli have examined the effects of various dynamic parameters¹³⁰ on the transport of nanoparticles through porous media and found that for the system of their study, higher injection rates can lead to lower retardation of nanoparticles. More studies are needed in this area.

Adsorption on the Porous Media

Even for nanoparticles of appropriate size and shape and good stability in solution, adsorption onto solid surfaces may impede nanoparticle transport. Low adsorption of the injected chemicals on rock also improves the economics of the oil recovery process.¹³⁹ Prior work has shown that many of the polymer coatings which can stabilize nanoparticles in solution can also result in high adsorption and retardation of nanoparticles once injected into the porous media.^{129,132–134,136}

Electrostatic repulsions and reduced hydrophobic-hydrophobic interactions between PNPs and the rock surface can reduce

nanoparticle adsorption. PNPs with a surface charge that matches that of the rock surface^{132,134,136} or that are less hydrophobic¹³⁴ may exhibit reduced adsorption. However, this is challenging considering the different salinities, divalent ion concentrations, and pH values that must be considered. Further, adsorption should be reduced while maintaining the nanoparticle properties favorable to EOR. As an example, in the case of surfactant-coated nanoparticles, monolayer adsorption of surfactant can improve foam stability but also result in higher adsorption.

SUMMARY OF CHALLENGES AND DIRECTIONS FOR FUTURE RESEARCH

Nanoparticle-based technologies are promising for EOR processes and, in the case of BrightWater polymeric nanoparticles, have been field-tested for improving oil recovery. Polymer coatings can potentially offer significant advantages in terms of tuning nanoparticle surface properties, stability, and responsiveness, but more studies are needed to understand the potential of PNPs for EOR. Below, we prioritize areas of emphasis that need to be addressed for the eventual implementation of PNPs in EOR processes.

First, for the use of PNPs to improve mobility control, the energy required to stabilize a foam or emulsion should be commensurate with the energy required for injection into cores, with typical flow rates on the order of 10 ft/day. The role of different types and functionalities of polymers should be investigated to reduce the energy required for adsorption of nanoparticles at the fluid-fluid interface as well as for foam/emulsion stability.

Second, the thermodynamics of polymer rearrangement on the surface of PNPs located at an interface remains poorly understood. Thermodynamic models that consider the effects of rearrangement of polymers at the interface on the energy and entropy of the foam and emulsion systems should be further explored.

Third, studies are lacking on the effect of different types of polymers as coatings on nanoparticles for wettability alteration. Polymers can have different effects on energy and entropy of the system (structural, electrostatic, hydrophobic, and other effects), which change the disjoining pressure near the inner contact line and change the rate of wettability alteration caused by such PNPs.

Polymer coatings that can facilitate PNP propagation through a reservoir under harsh conditions, such as high salinity and high temperatures, are needed. A proper stabilizing polymer coating is one that not only stabilizes the nanoparticle in both static and dynamic conditions, but also has maximum long-term chemical stability and minimum adsorption on the rock.

Addressing these challenges may eventually lead to an optimized PNP polymer coating that minimizes the undesirable effects (adsorption, aggregation, etc.) and maximizes desirable effects such as increased viscosity, emulsion generation, and reduced interfacial tension under a variety of environmental conditions.

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