

Nanoparticle-Assisted Surfactant/Polymer Formulations for Enhanced Oil Recovery in Sandstone Reservoirs: From Molecular Interaction to Field Application

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ABSTRACT: There has been some success with polymer and surfactant injections into depleted sandstone reservoirs for reducing residual oil saturation and improving oil recovery. However, their microemulsion stability is compromised in the harsh conditions of high temperature and salinity. Nanoparticle addition to the polymers and surfactant has resulted in a nanofluid with more stability, improved rheological behaviors, reduced adsorption loss, and much more as a result of the synergistic effects of their components. In this work, the performance of polymeric and surfactant nanofluids and the factors that impair their efficacy were highlighted. Numerous surfactant adsorption mechanisms, such as ion pairing, ion exchange, hydrogen bonds, dipole interactions, and hydrophobic interactions, on the rock surface were illustrated. Synergistic interactions of ternary phases of surfactant, polymer, and nanoparticles to the interfacial tension reduction, wettability alteration, adsorption reduction, rheological enhancement, and nanofluid stability for enhanced oil recovery were also presented. Additionally, the prevailing challenges and their plausible interventions have been highlighted in this review. The summarized results from published papers based on experimental evidence and theoretical deductions presented in this review will uplift the understanding of the screening, designing, and formulation of nanofluids.



1. INTRODUCTION

Despite the rising global demand for fossil fuels, the number of new conventional oil reserve discoveries is currently dropping.¹ Just 20–35% of the original oil in place (OOIP) in the reservoir is retrieved when primary and secondary recovery techniques are applied, leaving the majority of the oil inside the reservoir.² One strategy for addressing the rise in oil use and demand in the oil and gas sector is to improve oil recovery from these reservoirs.³ Many enhanced oil recovery (EOR) techniques, including chemical, thermal, miscible gas, microbial injections, and many others, have undergone extensive research and demonstrated various recovery rates with promising futures.⁴

Chemical EOR for increasing both microscopic displacement and macroscopic sweep efficiency of crude oil has been in use for several decades.⁵ The chemical EOR methods, such as polymer and surfactant, exert their effects by the former viscosifying the water phase (displacing fluid), so that the mobility ratio can be lowered to below 1,⁶ and the latter reducing interfacial tension (IFT) and wettability.¹ Polymer flooding has been a reliable tool for recovering residual oil with the use of both synthetic polyacrylamide (PAM) and partially hydrolyzed polyacrylamide (HPAM) and natural polymers (xanthan and guar gum).⁷ However, the use of polymers and surfactants is currently faced with some challenges, such as

degradation as a result of high temperature and salinity and chemical adsorption to the formation surfaces.⁸ Therefore, systems of polymer, surfactants, and alkali have been proposed to harness their synergistic effects, although their performance and cost do not match.⁹

The invention of nanotechnology has also paved the way for petroleum industry applications in the area of drilling, cementing, and well completion, hydraulic fracturing, and EOR. Nanoparticles are particles of matter characterized by sizes between 1 and 100 nm with enhanced physical and chemical properties.¹⁰ They are used in chemical formulations to improve rheological and thermal properties of fluids in different environments. Nanofluids with varying physical properties can be designed and produced by combining these nanoscale materials (nanoparticles) with various base fluids and tailored for a specific scenario.¹¹ However, there have been a variety of reasons that have kept the application of nanoparticles in the field trial on hold, including their

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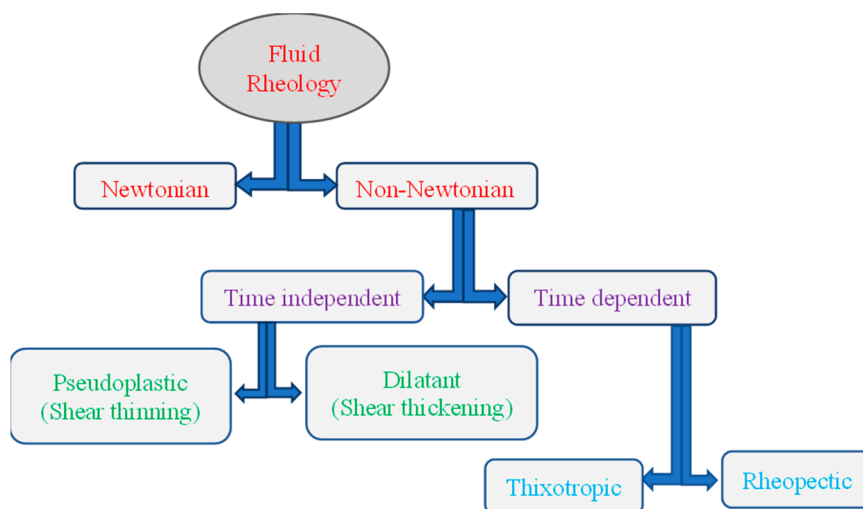


Figure 1. Schematic representation of the rheological behaviors of the fluid.

suspected ecotoxicity.¹² As a result of their large surface-to-volume ratio, nanoparticles are capable of adsorbing toxic compounds on their surface. The assessment of the risk presented by nanoparticles to organisms and the environment depends heavily upon data addressing nanoparticle mobility, transfer, and uptake, as impacted by environmental parameters.¹³ Considering the risks that some nanoparticles, such as titanium oxide, pose to health, the environment, and safety, their use for EOR processes needs to be carefully examined.

It has been reported elsewhere that binary and ternary systems of chemicals may synergistically enhance oil recovery.¹⁴ This can be achieved by combining the potentials of each ingredient in petroleum development, such as IFT reduction, wettability alteration, solubilization, mobility control (increasing viscosity of displacing fluid), and nanofluid stability.¹⁵ The unique performance success of polymer and surfactant floodings was merged with the nanoparticle outstanding properties, such as the small size, high diffusivity, and high surface area available for modification to suit specific reservoir conditions of high temperature and salinity.

The potential of nanotechnology in EOR was brilliantly highlighted in numerous previous works on nanoparticle-assisted surfactant and polymer formulations. However, molecular interactions, detailed rheological screening, and technical and economic limitations facing field applications have been partially reported in manuscripts. In this work, a comprehensive evaluation of nanoparticle-assisted polymer and surfactant formulations was conducted with their potentials for EOR in sandstone reservoirs. The comparison of various experimental and simulation results pertaining to nanofluid-assisted surfactant and polymer flooding highlighting the success and limitations is presented. The research gaps on the current experimental and simulation studies on the hybrid nanofluids are identified, and possible interventions are suggested. Additionally, various molecular interactions, rheological considerations during screening and limitations, and proposed interventions facing field applications are elaborated.

2. RHEOLOGICAL BEHAVIOR OF THE NANOPARTICLE-ASSISTED SURFACTANT/POLYMER

Rheology of a fluid refers to the change in the flow characteristics of a fluid caused by an applied force. It relates to the shear stress (τ), which is given as the tangential force applied per unit area, and shear rate ($\dot{\gamma}$), which is the change of shear strain per unit time. In addition, viscosity (η) can be defined as the ratio of shear stress to shear rate.¹⁶ Dependent upon the response to the applied shear force, fluids can be classified as Newtonian or non-Newtonian. Shear stress and shear rate for Newtonian fluids are linearly related, which means that the shear rate has no effect on the viscosity of these fluids. For non-Newtonian fluids, the change of the shear stress and shear rate is not constant, and therefore, their viscosity changes with the change in the shear rate.¹⁷ Various mathematical models used to describe the fluid behaviors include the power law model (eq 1), Bingham plastic model, Carreau model (eq 2),¹⁸ Hershel–Buckley model, and Casson model.¹⁹ However, careful selection of the model that gives the best fit should be done for various fluids based on the number of parameters involved in the equations, simplicity, and time. Additionally, on the basis of the value of their power law index (flow behavior index), fluids can be divided into three distinct types, such as $n < 1$ (shear thinning fluid), $n > 1$ (Newtonian fluid), and $n = 1$ (shear thickening fluid)

$$\eta = K\dot{\gamma}^{n-1} \quad (1)$$

$$\eta = \eta_0(1 + \lambda\dot{\gamma})^{\frac{n-1}{2}} \quad (2)$$

where η is the apparent viscosity, $\dot{\gamma}$ is the shear rate, η_0 is the zero shear viscosity, λ is the relaxation time, and K and n are the consistency index and power law index.²⁰ Figure 1 illustrates different fluid rheological behaviors encountered in the oil and gas industry.

Hojjat et al.²¹ investigated the rheological properties of a base fluid carboxymethyl cellulose (CMC) containing aluminum oxide, titanium dioxide, and copper oxide nanoparticles. It was found that the base fluid and all three nanofluids had a power index of less than 1 and, therefore, behaved as shear thinning fluids. The power law index declined with rise of the nanoparticle concentration. On the other hand,

Tie et al.²² performed a study on the rheological performances and other parameters of the three polymers [a linear polymer, a hydrophobic association of partially hydrolyzed polyacrylamide (HAHPAM), and a polymer–surfactant] under reservoir conditions for their potentials in EOR application. An increase in the shear rate leads to a decrease in the linear polymer viscosity, exhibiting pseudoplastic behavior, despite being a Newtonian fluid at a lower shear rate. A slight increase in viscosity was observed for the other two polymers at a low shear rate, and shear thinning was observed at a higher shear rate. There was a good fit of all three polymer samples to the Carreau equation and a satisfactory fit with the power law model. According to the study by Al-Hamairi et al.,²⁰ various rheological models have been compared to predict fluid viscosity of HPAM in different shear rates taking into account the concentration of polymers, fluid salinity, and divalent contents. However, as a result of their poor fit, the power law model was modified to fit the prediction of the polymer.

3. INFLUENCE OF CHEMICAL STRUCTURES IN FLUID–FLUID AND FLUID–ROCK INTERACTIONS

3.1. Nanoparticles (NPs). NPs are more reactive than their corresponding bulk materials as a result of their small particle size (1–100 nm), higher surface/volume ratio, and unstable bonds.²³ In addition, studies have shown that most NPs (silica, titanium, and aluminum) employed in oil recovery processes are well-matched with reservoir rock minerals and, therefore, do not pose significant environmental impacts.²⁴ Owing to their unique size and diffusion rate, nanoparticles can easily enter oil reservoirs and inflict changes that are intended in the specific reservoir.²⁵ They can change the rheological properties of the injected fluid and fluid–fluid interaction properties, such as IFT,²⁶ emulsification, and thermal responses, and also alter fluid–rock interaction properties (such as wettability alteration and dissolution). Nanoparticle application in EOR is categorized into three types of formulations, including nanofluids, nanoemulsions,²⁷ and nanocatalysts,²⁸ with nanofluids the focus of this work. Nanofluids refer to the fluid in which nanoparticle suspensions are introduced in a base fluid (water, alcohol, and oil) and stabilized by either a surfactant or polymer.²⁹

3.1.1. Nanoparticle Stability and Characterization Techniques. A nanofluid is stable if it maintains its basic properties, such as its morphology (size and shape), electrostatic repulsive forces, surface charge, hydrophobicity, and dispersion.³⁰ The Derjaguin–Landau–Verwey–Overbeek (DLVO) theory suggests that the stability of nanoparticles is determined by the balance between electrostatic double layers (repulsive forces) and London–van der Waals interactions (attractive forces). In this case, the van der Waals force promotes coagulation leading to instability, while the double-layer force stabilizes the suspension. When the repulsive forces outweigh the attractive forces, the colloidal system becomes stable, and vice versa is also true.³¹ As a result of the high surface energies of NPs, they aggregate in the aqueous solution to minimize their energy leading to agglomeration. The latter is caused by forces of a different nature (van der Waals and electrostatic) that interact among particles and the medium of dispersion, making it highly challenging to prepare stable nanofluids before injection.³² Salinity, which is typically present in the reservoir fluids, needs to be considered for nanoparticle stability in aqueous solution.³³ An anionic surfactant, such as sodium dodecyl sulfate (SDS), has been suggested to be able to

stabilize nanoparticles in a solution by inducing the formation of electrical double layers between the charged nanoparticles and the base fluid components. These layers protect the nanoparticles, allowing the hydrophilic groups of the anionic surfactant to adhere and bind to them. With their hydrophobic tails directed outward, the surfactants increase stability through steric repulsion.³⁴

Some studies have also suggested non-DVLO interactions that account for nanoparticle stability. These are (1) cation bridging formed between divalent cations between a negatively charged NP surface and a negatively charged molecule,³⁵ (2) steric effect derived from solvated films around the particles and other solute molecules in base liquids,³⁶ and (3) hydration force. It has been proposed that a number of techniques can be used to maintain the stability of nanoparticles dispersed in solution in high-temperature and high-salinity reservoirs. These include the use of polymers and surfactants to mix with nanoparticles as well as H⁺ protection³⁷ against high ionic strengths. Polymeric molecules provide steric stabilization by modifying the nanoparticle surface using polymers [e.g., polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG)]. They use their hydrophobicity to prevent the two particles from approaching one another, and in so doing, steric repulsion is exerted.³⁸ In another study, Sagala et al.³⁹ reported the surface coating of silica nanoparticles with various nanopyroxene functionalities to enhance their stability. Three different surface-modified silica, neutral nanopyroxene (NPNP), fully hydroxyl-functionalized nanopyroxene (HPNP), and half hydroxyl-functionalized Janus nanopyroxene (JPNP), were obtained. As a result of laboratory core flooding and stability tests, fully hydroxyl-functionalized nanopyroxene nanofluids showed an additional oil recovery of 10.57%, making them ideal for EOR applications.

Additionally, surfactants added to nanoparticle suspensions have the ability to self-assemble around surfaces of nanoparticles to provide stabilization. It is due to the formation of a monolayer of surfactant that the surface charges of the NPs cannot interact with each other, and the interactions between all NPs will be determined by the surfactant adsorbed on them. In H⁺ protection, Hutin et al.⁴⁰ investigated the stability of silica nanofluid at different pH values to evaluate its influence. It was concluded that silica nanofluids at a high ionic strength (42 000 ppm of NaCl and seawater) are stable for 1 day at basic pH and 3 weeks at pH 1.5, respectively. This was attributed to the increased electrostatic and/or steric repulsions in the base fluid to compensate for the loss of repulsive forces caused by increased salinity. A summary of the NP stabilization methods and mechanism involved, along with their strengths and challenges, can be found in Table 1.

In nanofluid stability analysis, various techniques are normally employed: direct visual observation, where nanofluid sedimentation over time is monitored with a very powerful tool for transparent samples, surface conductivity measurement, zeta potential, and particle size analysis [dynamic light scattering (DLS)].⁴¹ Particles with high zeta potential levels of ± 30 mV are electrically stable as a result of electrostatic repulsion and are said to be stable.⁴²

3.1.2. Key Performance Parameters of the Nanoparticle in EOR. For effective use of nanoparticles in EOR, the factors influencing their stability and performance must be explored. The factors include the concentration, size, temperature, salinity, mineralogy, pore size, and permeability.⁴⁷ The

Table 1. Methods of Enhancing Stability of Nanofluid Dispersions

technique	mechanism involved	stability against	weakness	strength	reference
polymer addition	steric and electrosteric stabilization	high temperature and salinity	surface modification sometimes expensive; PAM and HPAM polymers not stable at higher temperatures (>70 °C)	long-term stability of nanofluid enhances nanofluid viscosity	43–45
surfactant addition	surface adsorption	high temperature, salinity, and rock surface adsorption	some surfactants degrade easily at a high temperature	easily mixes with other components	46
HCl (H ⁺ protection)	H ⁺ ions prevent mono- and multivalent ions from accumulating in the EDL of NPs	high salinity	lower pH may induce mineral dissolution if pH rises, H ⁺ may be removed from the nanoparticle surface	lower price of HCl	37 and 40

following discussion will be made to some key factors, and the rest can be outsourced from the prescribed studies.

3.1.2.1. Nanoparticle Size. As a result of their greater charge density and stronger electrostatic repulsion, smaller nanoparticles have been shown to significantly improve oil recovery.⁴⁸ The intensity of the disjoining pressure that lifts the oil film from the reservoir surface is greatly influenced by their small size and charge density.⁴⁹ However, the too small nanoparticles and too big nanoparticles end up with mechanical entrapment or log jamming, respectively, as seen Figure 2. It was reported by Sun et al.⁵⁰ that silica

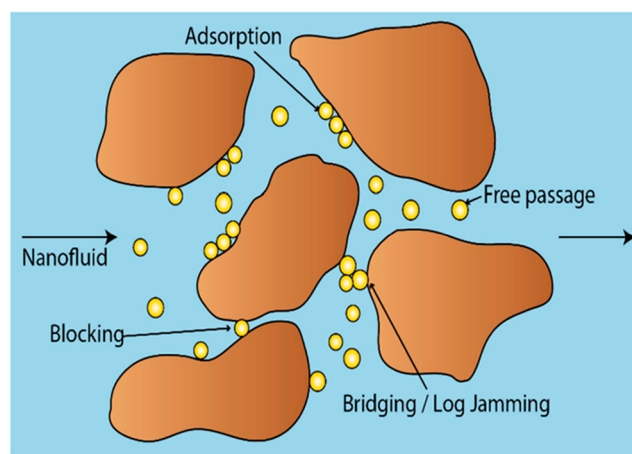


Figure 2. Effects of the nanoparticle size in porous media during nanoflooding. This figure was reproduced with permission from ref 52. Copyright 2021 American Chemical Society.

nanoparticles could induce higher oil recovery efficiency owing to their ability to alter wettability and lower IFT, as shown Figure 3. In another experiment, it was found that

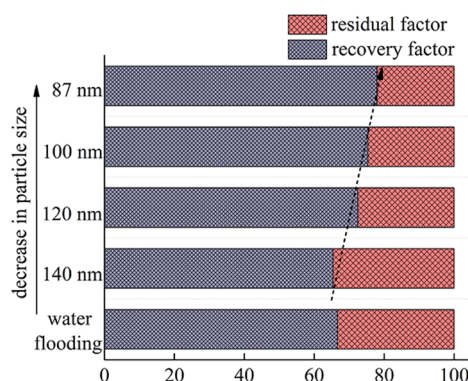


Figure 3. Oil recovery based on different SiO₂ nanoparticle sizes. This figure was reproduced with permission from ref 50. Copyright 2020 American Chemical Society.

smaller nanoparticles caused a decrease in the contact angle at the interface between rock and fluid as a result of higher structural disjoining pressure.⁵¹

3.1.2.2. Nanoparticle Concentration. Nanoparticle oil recovery efficiency rises with the increase in the nanoparticle concentration.⁵³ In this regard, wettability and oil displacement are more pronounced as the concentration of nanoparticles increases. This is due to the increase in the Brownian movement and disjoining pressure that exert a force on the

oil film attached on the rock surface, resulting into easy displacement of oil. However, the increase in the concentration will be up to the optimal value, where any further increase will add no value rather than inflating operational costs and plugging the pore throats. Lu et al.⁵⁴ investigated the effects of nanoparticle concentrations by varying the values between 5 and 30 ppm. It was evident that the tertiary oil recovery first increased (4.48–10.33%) and subsequently dropped as the injected nanoparticle concentration was raised. These findings suggest that increased oil recovery is not necessarily guaranteed by high nanoparticle concentrations after achieving the optimal concentration. Similar trends were also reported by Abe et al.,⁵⁵ as shown in Table 2. The optimal concentration of

Table 2. Nanofluid Core Flooding Test Results^{55 a}

NP	core ID	oil recovery (%)		
		LSWF	nanofluid	total
1000 ppm of NP-A	IDLS_7	33.20	5.98	39.18
1000 ppm of NP-B	IDLS_8	39.41	3.39	42.80
5000 ppm of NP-A	IDLS_9	36.65	5.34	41.99
10000 ppm of NP-A	IDLS_10	35.04	6.48	41.52

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nanoparticles must be determined through various screening techniques, such as rheology, IFT reduction, and adsorption behavior, prior to experiments.⁵⁶

3.1.2.3. Reservoir Temperature. Nanofluids used in EOR must be able to effectively disperse and resist aggregation long enough when transported through reservoirs with temperatures up to 150 °C. A higher formation temperature causes faster NP agglomeration, resulting in weakened stability of NPs. High temperatures lead to higher kinetic energies and collision frequencies of nanoparticles, which contribute to the aggregation of nanoparticles and adversely affect their stability.⁴⁰ A study by Zhou et al.⁵⁷ investigated the stability of nanoparticles under different temperatures. Nanofluid thermal stability was evaluated on the basis of particle size measurements at high temperatures (50–100 °C) to determine its thermal stability. A change in the nanoparticle size from 71 to 664 nm was observed after 5 days, indicating instability as a result of aggregation.

3.1.2.4. Fluid Salinity. The nanoparticle stability is severely affected by the increased salinity in the base fluid or connate water.³³ The zeta potential of nanoparticles decreases with rising base fluid salinity, which causes agglomeration. As a result of the strong attraction forces of the system and the rise in ionic interactions in the mixture, compression of an electric double layer occurs and is typically linked to the high salt concentration.⁵⁸ Ngouangna et al.⁵⁹ investigated the effect of brine salinity on recovery mechanisms for hydroxyapatite (HAP) nanoparticles. The change of IFT and wettability increased with the increase in brine salinity. The overall performance of the two mechanisms contributed to the higher incremental oil recovery, as shown in Figure 4.

3.1.2.5. Pore Size and Permeability. The reservoir pore size and permeability severely reduce nanoparticle effectiveness. A reservoir is made up of pore bodies and throats with a complicated and random structure that come in a broad range of sizes and can support adsorption, mechanical entrapment, and log jamming. The porosity and permeability of these formations are decreased by particle retention and cause the

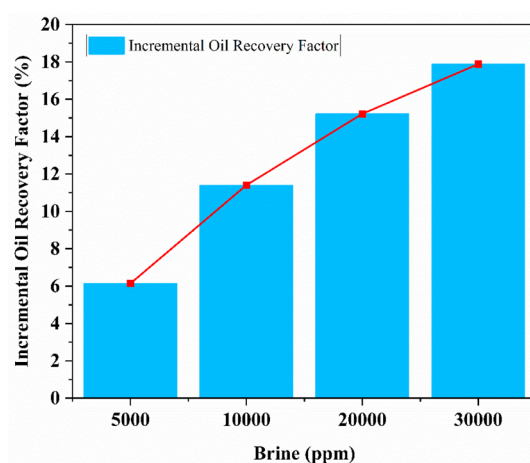


Figure 4. Effects of the brine concentration on the incremental oil recovery. This figure was reproduced with permission from ref 59. Copyright 2023 American Chemical Society.

formation damage. The adsorption on the wall is fast at the injection time, and the equilibrium will be established when no more adsorption occurs. That will also depend upon the injection flow rate and the size of the nanoparticles.⁶⁰

3.1.3. Nanoparticle Injection and Oil Recovery Mechanisms. For the purpose of removing oil films from the surface of rocks, various kinds of nanoparticles, including metal oxides and organic (dendrimers and biopolymers), inorganic, and composite particles, have been experimented.⁶¹ Research has shown that nanoparticles derived from the oxides of metals (Al_2O_3 , CuO , TiO_2 , and Fe_2O_3) can lower the oil/water IFT and also give rise to the disjoining pressure that pushes toward the solid surface and oil–water interface.⁶² IFT is reduced as nanoparticles separate out at the oil–water contact from the aqueous phase.⁶³ A number of factors were mentioned as contributing to the increase in EOR when nanoparticles are used, including the improvement in rock–fluid properties, altered rheological properties, high sedimentation, and thermal stability of nanoparticles.⁶⁴ Using nanoparticles, one can alter fluid flow characteristics from Newtonian to non-Newtonian,⁶⁵ increase oil mobility trapped by capillary force, improve wettability, and decrease IFT between oil and reservoir fluids,⁶⁶ as shown in Table 4.

Metal surfaces can be altered by silanol compounds derived from silica nanoparticles to enhance their capacity to attach organic substances, such as polymers, carboxylic acid, and the like. Free silanols are extremely labile, difficult to isolate, and

Table 3. Effects of Different Nanoparticles on Oil Recovery Mechanisms

category of NP	nanoparticle	mechanism of action	reference
inorganic	SiO_2	wettability change, IFT, emulsion stability, and increased viscosity	43 and 75
metal oxide	Al_2O_3	lower IFT and increased viscosity ^a	43 and 76
	TiO_2	wettability change ^a and IFT reduction	77 and 78
	Fe_2O_3		
organic (carbon based)	carbon nanotubes and graphene	IFT, wettability change, and viscosity reduction	79 and 80

^aDominant effect.

Table 4. Effects of Nanoparticles on Wettability and IFT^a

NPs	NP size (nm)	contact angle (deg)		NPs	NP size (nm)	IFT (mN/m)	
		blank	with NPs			blank	with NPs
NSP	7	166	130	FNP	7–16	16.41	12.61
Al ₂ O ₃	10	119.8	40	SiO ₂	7–12	20	1.87
ZrO ₂	24	180	40	SiO ₂	20–30	35	10.9
Al ₂ O ₃	4	142	0	SiO ₂	40	19.2	12.8
SiO ₂	40	131.2	38.82	TiO ₂	21	37.5	22.1
TiO ₂	21	131.2	21.64	Al ₂ O ₃	17	19.2	12.8
SiO ₂	14	100	0	SiO ₂	10–15	21.1	13.2
Al ₂ O ₃	20	70	52	TiO ₂	10–30	21.1	12.4
Al ₂ O ₃	20	92	75	SiO ₂	20	21.1	11.2
Al ₂ O ₃	20	85	62	HLP	10–40	26.3	1.75
ZrO ₂	40	70	60	NWP	10–20	26.3	2.55
ZrO ₂	40	92	84	Al ₂ O ₃	60	38.5	2.25
ZrO ₂	40	85	71	Fe ₂ O ₃	40–60	38.5	2.75
TiO ₂	10–30	90	46	SiO ₂	10–30	38.5	1.45
SiO ₂	10–30	134	82	SiO ₂	12	26.5	1.95
Fe ₂ O ₃	40–60	132.5	101	ZrO ₂	5–15	48	10

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therefore stored in the form of alkoxy silanes because they can be hydrolyzed on site to produce silanol-containing species when required.⁶⁷ Binshan et al.⁶⁸ studied the impact of lipophilic and hydrophilic polysilicon (LHP) nanoparticle injection for the oil recovery. It was observed that, the LHP adsorption changes hydrophobic pore walls into hydrophilic pore walls, resulting in a substantial reduction in oil retention while increasing the relative permeability of the oil phase (K_{ro}). In addition, as a result of LHP adsorption and wettability changes, oil in small pores would be displaced, increasing the effective pore diameter of the porous medium for oil flow and ultimately enhancing oil recovery. In addition, Lu et al.⁵⁴ observed that nanoparticle adsorption in the low-permeability core could result in increased flow of the oil phase, as shown in Figure 5. As a result of nanoparticle adsorption, residual oil saturation (S_{or}) decreased. After the adsorption of nanoparticles, the irreducible oil saturation of the core increased to 0.102 from 0.156. It was concluded that low-permeability cores

can be altered to strongly water-wet when exposed to nanofluids.

In some instances, the injection of silica nanoparticles through the openings of cores may result in particle retention as a result of log jamming. To minimize permeability limitations, it is crucial to take into account a variety of factors. These include the content of the nanoparticle concentration, the concentration of the good dispersion solution, the injection rate, and the pore volume injected.⁶⁹ Oil recovery factors are influenced by the type of NP, and proper selection of NPs for typical reservoir conditions needs special attention.⁷⁰ In EOR, nanoparticles are categorized into three main types, which are metal oxide and organic and inorganic particles.⁷¹ Their effects on different recovery mechanisms are summarized in Table 3. In their study, Song et al.⁷² tested the efficacy of different types of nanoparticles (Al₂O₃, SiO₂, TiO₂, and NiO) at varying concentrations on reducing oil/water IFT. The results indicated that SiO₂ NPs were the most efficient, resulting in the lowest IFT values for a specific NP concentration. The performance of SiO₂ and TiO₂ NPs was attributed to the higher surface area and large size, respectively.⁷³ It was reported by Zhou et al.⁷⁴ that, as the nanoparticle size increased, the IFT between the oil and nanofluid decreased. Furthermore, when nanoparticles become larger, the more contribution to oil and aqueous phase interactions leads to lowering of IFT. When the nanoparticle concentration is less than 0.3%, the oil–water IFT decreases gradually with a constant nanoparticle particle size. The variation of the nanoparticle sizes and concentrations and their effects on IFT are illustrated in Figure 6.

3.2. Polymer/Nanoparticle Formulation. During polymer injection into reservoirs, the viscosity of the displacing fluid (water/brine) is increased,⁸² high-permeable zones are blocked, and their permeability to the displaceable fluid phase is reduced; consequently, viscoelastic properties, the microscopic sweep and displacement efficiency of the oil, are improved.³ In this regard, the mobility ratio of water/oil is lowered to below 1, so that the fingering effect is eliminated and a uniform displacement front for the residual oil is ensured.⁸³ The viscoelastic behavior allows the polymer to flow

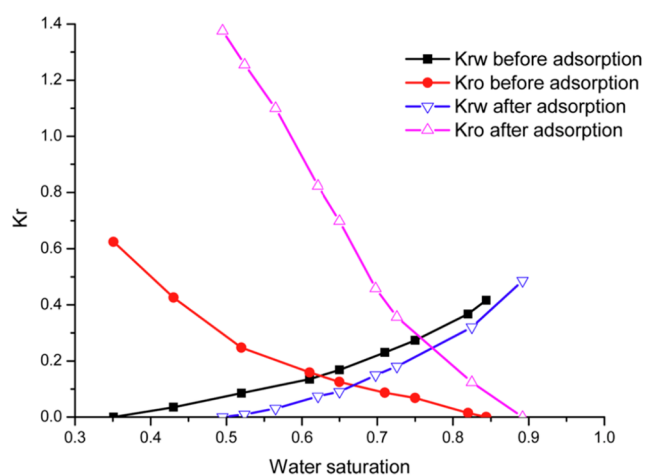


Figure 5. Oil and water relative permeabilities in hydrophobic rocks before and after nanoparticle adsorption. This figure was reproduced with permission from ref 54. Copyright 2017 American Chemical Society.

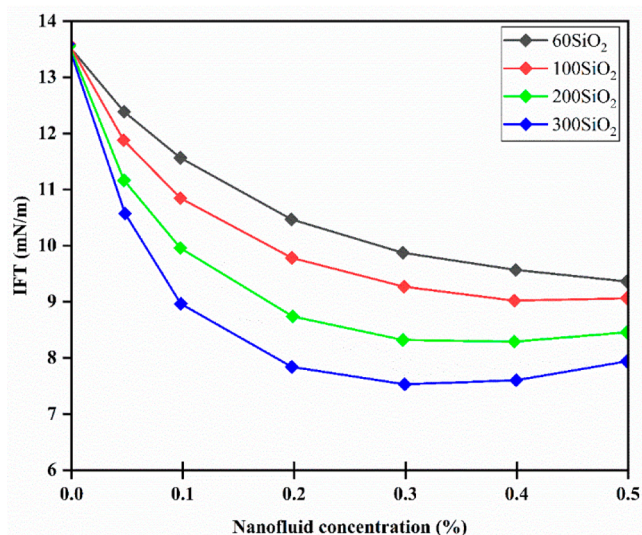


Figure 6. IFT reduction based on the concentration and size of nanoparticles. This figure was reproduced with permission from ref 74. Copyright 2023 American Chemical Society.

under an increased shear rate in the porous media and, subsequently, increase sweep efficiency.⁸⁴

However, the tolerance of most polymers to shearing and elevated temperatures (>80 °C) is significantly poor, leading to the loss of their rheological and viscoelastic behaviors.⁸⁵ This loss may be induced by the shearing actions during the polymer solution preparation and injection where the stirrer, surface injection pumps, and porous media cause mechanical loss of entangled structures.⁸⁶ Therefore, polymers and NPs can be coupled to produce synergistic effects that enhance the rheological characteristics of the displacement phase and enhance oil recovery.⁸⁷ The additions of nanoparticles and synthesis of more stable polymers have been the focus of researchers in recent years.⁸⁸ It has been shown that some polymers, such as associative polymers, can interact through hydrophobic associations to restore a significant amount of their solution properties after shear is applied. This enhances the shear tolerance of polymer solutions, and changes in rheological parameters and viscoelastic behavior do not impart a significant loss.⁸⁹ Both laboratory and simulation results have revealed the increase in oil recovery efficiency for hybrid formulation, as compared to conventional water or polymer flooding. On the basis of Figure 7, greater oil recovery was the outcome of improved rheology and stability. This resulted in higher sweeping and displacement efficiency for the hybrid formulation.⁹⁰ More experimental findings involving a variety of polymers and nanoparticles are shown in Table 5.

3.2.1. Rheological Enhancement. From the experimental results, it can be demonstrated that the addition of nanoparticles significantly enhances the rheological behavior of polymer–nanoparticle formulations.⁹¹ This depends upon both the type of nanoparticles added and the experimental conditions.¹⁴ According to Zhu et al.,⁹² it was observed that the addition of silica nanoparticles to hydrophobically associative polymer (HAHPAM) solutions increased their apparent viscosity and elastic modulus. These results are due to the formation of hydrogen bonds between the silanol moiety of silica nanoparticles and the amide groups in HAHPAM molecules. In this mixture, the concentration of polymer was kept below the critical association concentration (CAC) to

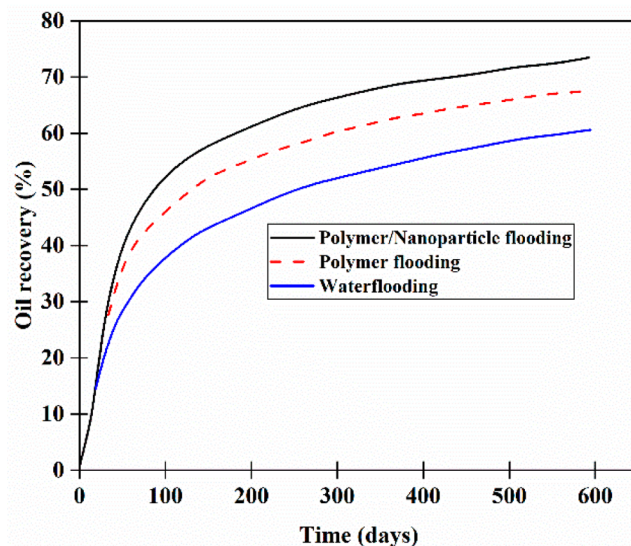


Figure 7. Oil recovery factor for hybrid and conventional flooding. This figure was reproduced with permission from ref 18. Copyright 2020 Elsevier.

Table 5. Synergism of the Polymer–Nanoparticle Hybrid Suspension

polymer	nanoparticle	properties	oil recovery (%)	reference
HPAM	SiO ₂	viscosity, improved viscoelasticity, thermal stability, and salt tolerance		90
HPAM	SiO ₂ /Al ₂ O ₃	increase in viscosity and viscoelasticity	67/68	93
PAAM	SiO ₂	viscosity, reduced IFT, and improved stability	2.52–7.82	102
xanthan gum	SiO ₂	viscosity increase, reduced IFT, and improved stability	6.4	103

avoid the effect of inter- and intramolecular interactions and focus on the hydrophobicity association. Similar findings were reported by Bilal Khan,⁹³ where a polyacrylamide–nanosilica mixed system undergoes microstructural changes to enhance elasticity of the polymer.

Bilal Khan⁹³ studied how nanoparticles may affect the rheological behavior of polyacrylamide and polymer surfactant solutions. It was found that nanoparticles strongly influence the rheological properties of solutions. Nanoparticles increase the shear viscosity of polyacrylamide solution by adsorbing polymer chains on their surfaces, resulting in complex micelle-like structures. Shear thinning was observed in the polymer solutions at low shear rates, but pseudo-plasticity was lost at higher shear rates, resulting in shear thickening. Also, Bera et al.⁹⁴ conducted a study on how silica nanoparticles affect the viscosity of the guar gum solution, behavior of the crude oil–nanofluid phase, and more oil recovery. It was discovered that silica nanoparticle addition increases guar gum solution viscosity, further noting that viscosity is a function of the nanoparticle concentration.⁹⁵

In addition, Wang et al.⁹⁶ investigated the HPAM/nanosilica suspension stability and rheological behaviors in various saline media, including deionized water (DIW), brine (NaCl), and simulated formation water (SFW). It was concluded that, when

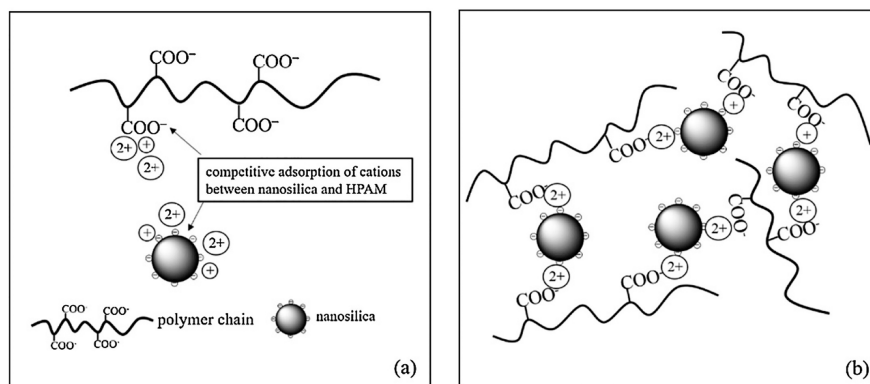


Figure 8. Chemical interaction of (a) divalent cations with carboxylate of HPAM and SiO_2 and (b) cationic cross-link of HPAM and SiO_2 . This figure was adapted with permission from ref 96. Copyright 2020 Elsevier.

the shear rate is less than 0.15 s^{-1} , the viscosities of HPAM/nanosilica suspensions were higher in the order of DIW < brine < SFW. Additionally, as the percentage of nanosilica rises, the viscosities of HPAM/nanosilica suspensions rise as well. The greater reserved viscosity of all HPAM/nanosilica suspensions compared to HPAM solutions suggests that nanosilica has improved the salt tolerance of the polymer. The addition of nanoparticles resulted into higher fluid viscosity owing to the cationic cross-links between the polymeric chains and the silica nanoparticles. The silica nanoparticle surface is negatively charged and can therefore provide the surface for the attachment of divalent cations. For an illustration, refer to panels a and b of Figure 8.

3.2.2. Thermal Stability Enhancement. As a result of the high-temperature formation, viscosity and recovery rates are significantly reduced. This is attributed to the increased movement of polymer chains as a result of the high kinetic energy, leading to the loss of cross-link bonds and the hydrophobic effect impairment.⁹⁷ Gbadamosi et al.⁹⁸ observed that, as the temperature rises from 25 to 90 °C, HPAM and nanoparticle-assisted HPAM behaved as non-Newtonian fluids, where their viscosities were reduced. However, as illustrated in Figure 9, at different temperatures, a hybrid dispersion

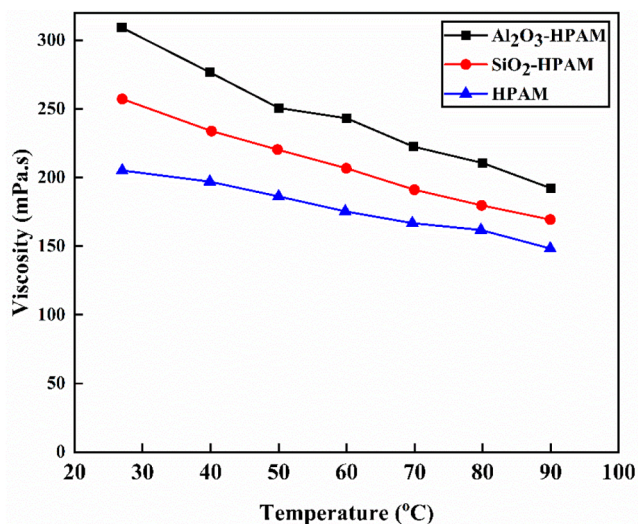


Figure 9. Variation of HPAM viscosity at different temperatures based on the inclusion of nanoparticles. This figure was reproduced with permission from ref 98. Copyright 2019 Elsevier.

incorporating NPs showed a higher viscosity than a control HPAM solution, demonstrating the influence of nanoparticles on the viscosity. A 51% increase in viscosity with Al_2O_3 and a 20.5% increase with SiO_2 polymeric nanofluids were observed at room temperature. This is attributed to the tendency of polymeric chain adsorption on the nanoparticle surface, which leads to the formation of polyion complex micelle flocs.

3.2.3. Salt Tolerance Enhancement. High-salinity environment, especially with the presence of divalent ions, such as Ca^{2+} and Mg^{2+} , can significantly affect the stability of both the polymers⁹⁹ and the nanoparticles. The stability of charged polymers, such as HPAM, depends among other factors upon the electrostatic repulsion between the chain molecules, and therefore, the addition of salts reduces the repulsive force. In this scenario, the polymer shrinks and loses its structure, leading to the decrease in viscosity.¹⁰⁰ The addition of nanoparticles in the polymer solution enhanced the polymeric structure by forming the ion–dipole interaction that ensures that no cation impairs the carbonyl group of the polymer, as illustrated by Figure 10.

3.3. Surfactant/Nanoparticle Formulation. Surfactant flooding has been shown in numerous studies to be an efficient method for recovering oil based on three major interactions: lowering the IFT between the oil and water phases, changing wettability, and emulsification.¹⁰⁴ The ratio of viscous forces to inertial forces, known as the capillary number, is directly linked to oil recovery. Lowering the IFT between water and oil to extremely low levels ($10^{-3} \text{ mN m}^{-1}$) will result in a capillary number high enough to release the trapped oil. Surfactants can precipitate by reacting with reservoir brine as a consequence of the high temperature and salinity, which can hinder the recovery process.¹⁰⁵ Another issue with surfactant EOR is the adsorption of surfactants onto formation surfaces. Higher adsorption can make a surfactant less effective at reducing the IFT and negatively affect the economics of the process, rendering the project unfeasible.¹⁰⁶ A nanofluid of the surfactant has been investigated to alleviate some of these challenges by improving the emulsion stability, foam stability, IFT, wettability, and adsorption.⁵⁰

3.3.1. IFT Reduction. To reduce IFT, surfactant nanofluids must align at the oil/water interface, where the surfactant adsorbs on the surface of the nanoparticle, creating a hydrophobic surface on the nanoparticles.¹⁰⁷ These complex molecules of surfactant–nanoparticles are transported from the bulk of the fluid to the oil/water interface by the Brownian motion of the nanoparticles, where the interfacial energy is

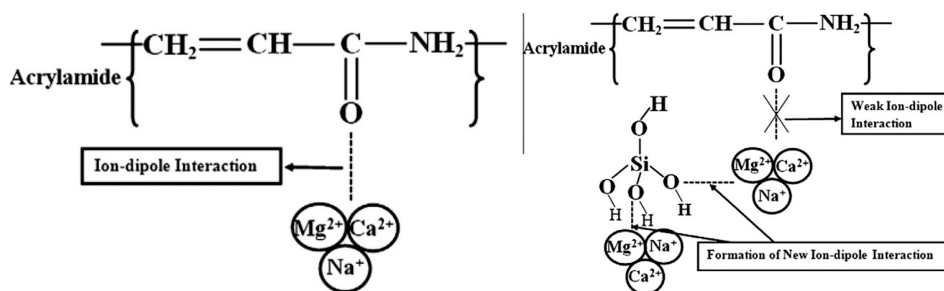


Figure 10. Polymeric enhancement by ion–dipole linkages with silica nanoparticles. This figure was reproduced with permission from ref 101. Copyright 2014 Elsevier.

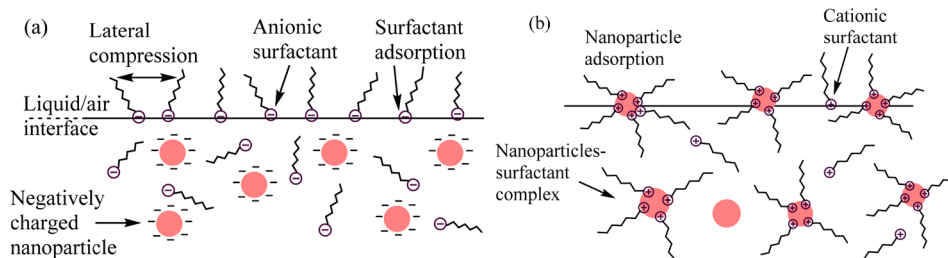


Figure 11. Nanoparticle interaction with (a) anionic and (b) cationic surfactants for surface tension. This figure was reproduced with permission from ref 111. Copyright 2018 American Chemical Society.

Table 6. Synergistic Effect of Nanoparticles and Surfactant on the Reduction of IFT^a

concentration (ppm)			concentration (ppm)		
SDS	nanoparticles	IFT ($\times 10^{-3}$, N/m)	C12TAB	nanoparticles	IFT ($\times 10^{-3}$, N/m)
2000	0	16	3000	0	18.5
2000	100	3.1	3000	100	5.4

^aThis table was reproduced with permission from ref 110. Copyright 2015 Elsevier.

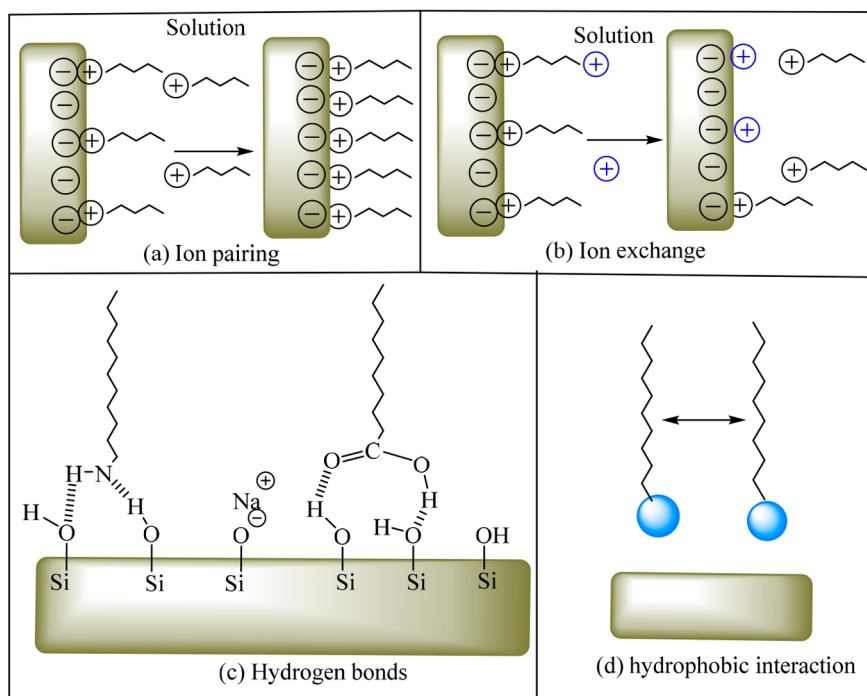


Figure 12. Surfactant non-covalent adsorption mechanisms on substrates: (a) ion pairing, (b) ion exchange, and (c) hydrogen bonds. This figure was reproduced with permission from ref 113. Copyright 2012 American Chemical Society.

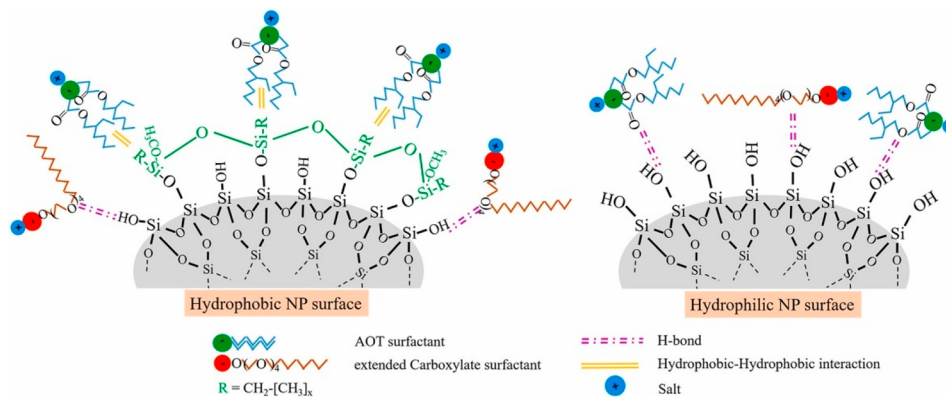


Figure 13. Differential surfactant adsorption on the nanoparticle surface. This figure was reproduced with permission from ref 115. Copyright 2023 Elsevier.

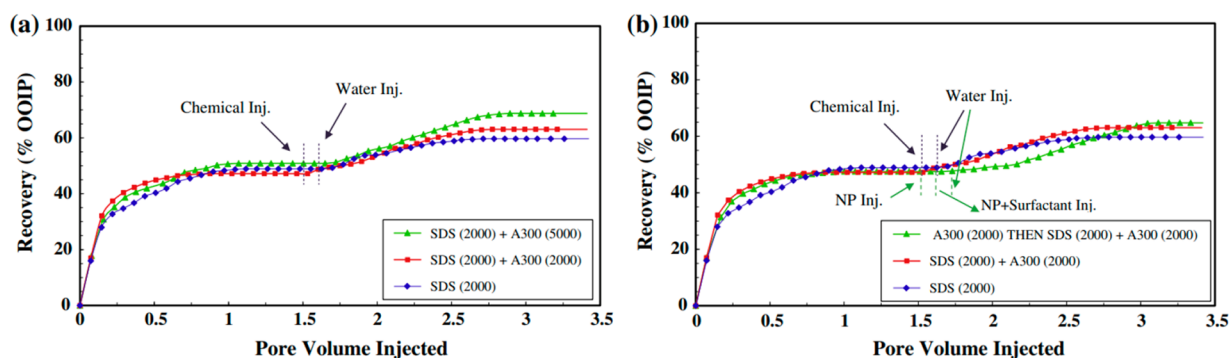


Figure 14. AEROSIL 300 nanoparticle–surfactant system for tertiary oil recovery with (a) unlike nanoparticle concentrations and (b) changed injection scenarios. This figure was reproduced with permission from ref 116. Copyright 2015 Elsevier.

reduced. According to Jingna et al.,¹⁰⁸ anionic surfactant adsorption at the liquid/air interface is facilitated by the electrostatic repulsion between the negatively charged surface of nanoparticles and the anionic surfactant. As a result, more surfactant molecules are drawn toward the liquid/air contact. This results in an increase in the surface concentration of surfactants and a subsequent decrease in surface tension.¹⁰⁹ On the other hand, the electrostatic attractive force between the nanoparticle and cationic surfactant reduces the effective surfactant concentrations at the liquid/air interface and leads to an increase of the surface tension. This attributed to the surfactant adsorption at the particle surface to form nanoparticle–surfactant assemblies. The mechanism is illustrated in Figure 11. The synergistic effect of nanoparticles and surfactant was further justified by ref 110, as illustrated in Table 6. The nanoparticles and surfactants reduced the IFT of oil and water, and a stabilized emulsion was formed, leading to enhanced oil recovery. The IFT was drastically decreased as a result of the adsorption of nanoparticles and surfactant at the oil/water interface. In this regard, an anionic surfactant (SDS) with an optimal concentration of 2000 ppm showed better performance than a cationic surfactant (C12TAB) with an optimal concentration of 3000 ppm than their individual nanoparticles.

3.3.2. Surfactant Adsorption Reduction. **3.3.2.1. Adsorption Mechanism for Surfactants.** Several mechanisms are involved in the adsorption of surfactants to the surfaces of solids, including nanoparticles. These include (i) ion pairing, where ionic surfactants are adsorbed on oppositely charged solid surfaces, (ii) ion exchange, in which the counterions

adsorbed on the substrate are displaced or exchanged by similarly charged ions, (iii) hydrogen bonding, (iv) dipole interactions, (v) conformation effects, and (vi) hydrophobic interactions as a result of the increased molecular weight.¹¹² Figure 12 illustrates some of the mechanisms stated above.

In their study of the adsorption interaction between NPs and surfactants, Rattanaudom et al.¹¹⁴ found that the hydrophobic and hydrophilic surfaces experienced two opposing effects. According to Figure 13, the capability of the surfactant for adsorption on the hydrophilic surface was less than that on the hydrophobic surface. This outcome might be a result of the hydrophobic–hydrophobic interaction having a lower surface coverage than the hydrogen-bond interaction.

3.3.2.2. Influence of Nanoparticles on the Adsorption Reduction. Nanoparticles derived from inorganics (silica), organics (carbon nanotubes and polymers), and metal oxides (Al_3O_4 , TiO_2 , and CuO) have surfaces with different characteristics that determine their potential to adsorb surfactants. The nanoparticle–surfactant complex plays a major role in the masking of the adsorption and then loss of surfactants in the reservoir. Zargartalebi et al.¹¹⁶ observed that the addition of the nanoparticle in the surfactant solution significantly improved the efficacy of surfactant flooding. Higher oil recovery was obtained at elevated concentrations of nanoparticles, where the greater addition as well as ultimate recovery of a binary system of nanoparticle–surfactant is attributed to the reduction of surfactant adsorption in the presence of nanoparticles. Panels a and b of Figure 14

demonstrate the influence of nanoparticles on the adsorption and incremental oil recovery. Low surfactant adsorption on the rock surface ensures the availability of enough surfactants to lower IFT and mobilize residual oils.

Pei et al.¹¹⁷ investigated the enhancement of heavy oil recovery through the addition of nanoparticles to surfactant-stabilized emulsions. Phase behavior, rheological studies, and core flooding tests demonstrated that the nanoparticle addition to the oil-in-water (O/W) emulsion offers three key advantages. It improved emulsion stability, minimizing electrostatic attraction among the droplets, viscosity enhancement, and mobility control that result in higher oil recovery, as shown in Figure 15. In another study by Kesarwani et al.,¹¹⁸

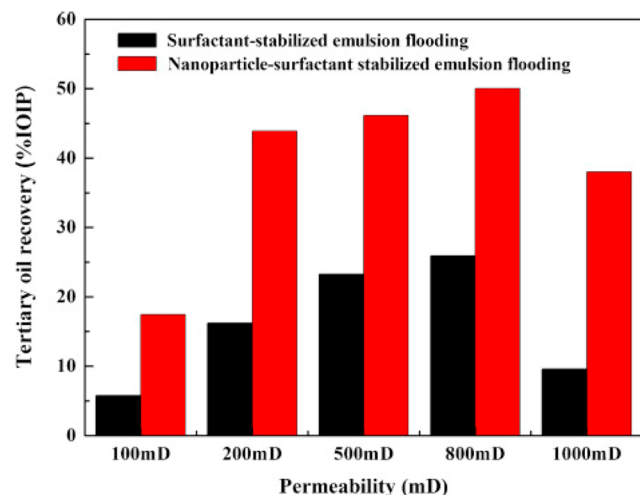


Figure 15. Surfactant-stabilized and nanoparticle–surfactant-stabilized emulsion flooding for EOR. This figure was reproduced with permission from ref 117. Copyright 2015 Elsevier.

the silica nanoparticles were used to reduce the adsorption of the surfactant (SDS) on the rock surface (sandstone or carbonate). It was observed that hydrogen bonding between negatively charged oxygen at the head of the surfactant molecules and hydrogen in the hydroxyl group of nanoparticles was formed. As a result, free SDS molecules in the aqueous solution that would have been adsorbed on the solid surface were reduced, leading to less adsorption, as illustrated in panels

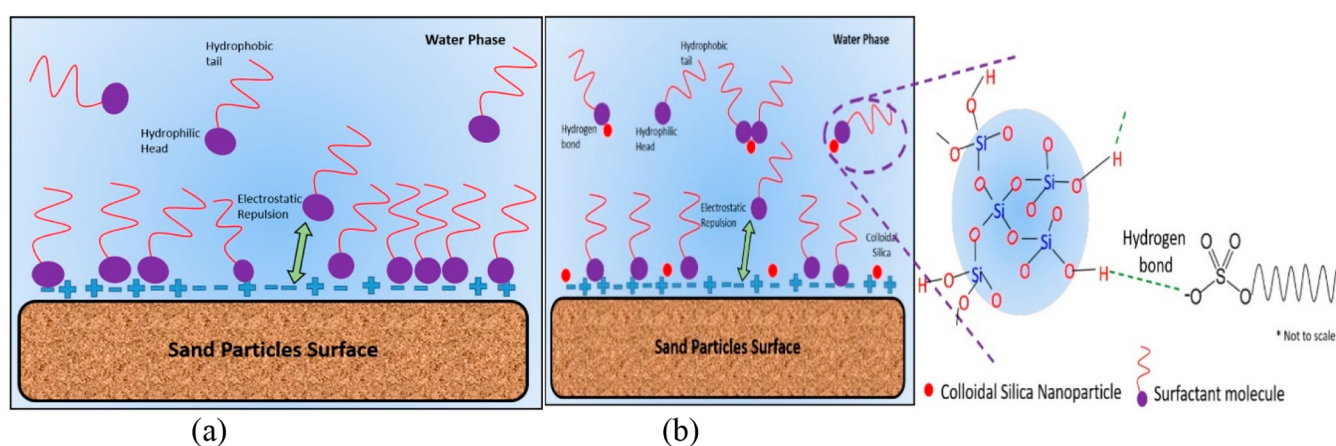


Figure 16. SDS adsorption on the solid surface in the (a) absence and (b) presence of SiO_2 nanoparticles. This figure was reproduced with permission from ref 118. Copyright 2021 American Chemical Society.

a and b of Figure 16. Alternatively, nanoparticle shielding and competitive adsorption could also explain the reason for the lowering of surfactant adsorption. It was further reported that a stable emulsion is a result of the interaction between nanoparticles and surfactants. The presence of suspended nanoparticles in a solution increases sedimentation stability because gravity is easily counterbalanced by surface forces. In addition, surfactants reduce IFT, thereby contributing to the stability of nanoparticles and emulsions.¹¹⁹

3.3.3. Wettability Alteration. The effectiveness of pore-scale displacement during oil recovery is significantly impacted by the wettability of the reservoir rock. The measurement of contact angles of rock–fluid interactions can be used to assess the wetting behavior.¹²⁰ Many variables, including reservoir pH, rock surface charge, salinity, NP concentration, NP adsorption to the rock surface, and NP surface charge density, have an impact on wettability.⁴ Wettability alteration by the surfactant can be achieved by ion pair formation and adsorption at the oil/water/rock interface.¹²¹ On the other hand, disjoining pressure has been proposed as a plausible mechanism for the wettability change from oil-wet to water-wet by the nanofluid.¹²² Moreover, the performance of nanoparticles in wettability alteration is influenced by different factors, including the particle size, concentration, and salinity of the base fluid. It has been shown that the contact angle of the aqueous phase decreased as the nanoparticle size diminished.¹²³

As suggested by the disjoining pressure theory, nanoparticles can induce wettability change when a wedge film is formed at the interface between the oil, water, and rock surface.¹²⁴ As illustrated in Figure 17, the spreading and wetting of nanofluids on solid surfaces are enhanced by the nanoparticle self-assembly within the region that is inside the wedge film between an oil drop, air, and solid surface. The interaction as a result of electrostatic, van der Waals, and structural forces between the nanoparticles within the wedge layer led to the formation of more organized structures than those in the bulk solution. The disjoining pressure becomes intense when the concentration of nanoparticles is high and the size is small. The structuring is associated with the increase in the entropy of the overall dispersion because ordering allows for free movement for the nanoparticles in the bulk liquid. Ultimately, the disjoining pressure exerted in a film toward the vertex by the

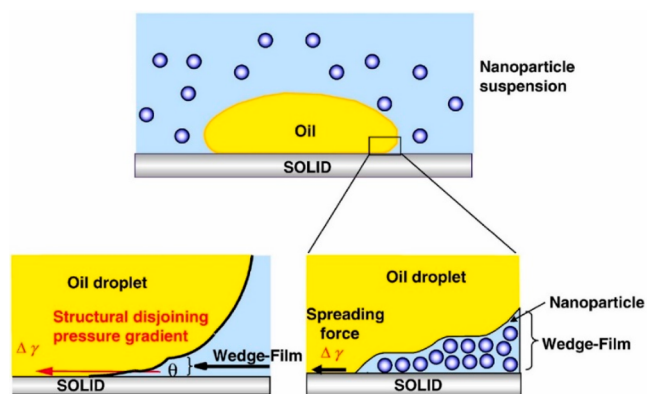


Figure 17. Nanoparticle arrangement in the wedge films exerting intense structural disjoining pressure toward the vertex. This figure was reproduced with permission from ref 125. Copyright 2020 Elsevier.

microstructures leads to separation of the two surfaces, keeping the nanoparticle solution.¹²⁵

3.4. Surfactant/Polymer Formulation. In their mixture, polymers and surfactants can interact to affect adsorption rates as well as their interfacial and rheological properties, where the molecular structure and charges of both components determine interactions between them.¹²⁶ The surfactant is known for its oil recovery mechanism of lowering IFT and altering wettability, while the polymer have a tendency of increasing the viscosity of water and then controlling the mobility ratio.¹²⁷ In their study, Samanta et al.¹²⁸ conducted a series of experiments to ascertain the additional recovery using a surfactant (SDS) and a hybrid system of a surfactant polymer (PHPA) slug. In comparison to the conventional oil recovery system, the hybrid system had higher additional oil recovery because of the synergistic reduction of IFT with SDS and improved mobility ratio with the PHPA solution. Additionally, Pandey et al.¹²⁷ conducted a core flooding experiment to compare the oil recovery efficiency of PAM + SDS + modified multi-walled carbon nanotubes (mMWCNTs) with SDS flooding for potential chemical enhanced oil recovery (CEOR) applications. As indicated in Figure 18, it was shown that a hybrid formulation of mMWCNT in a SDS +

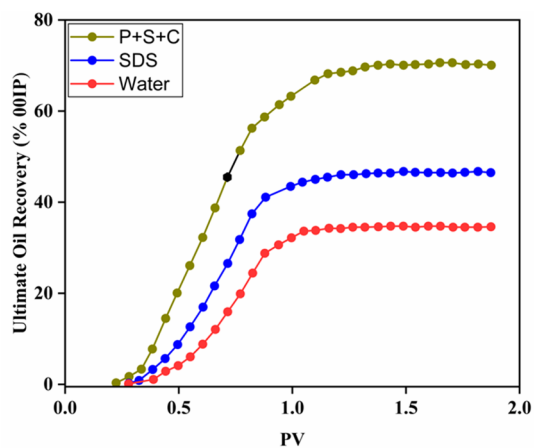


Figure 18. Overall oil recovery efficiency using water, SDS (S), and hybrid (S + P + C) flooding. This figure was reproduced with permission from ref 132. Copyright 2023 Elsevier.

polymer solution resulted in a higher oil recovery than SDS and water flooding. The increase in oil recovery was ascribed to the mMWCNT ability to lower SDS adsorption on the rock surface.

Khan et al.¹²⁹ also investigated the interaction of several surfactants and polymers based on the surface tension and conductivity measurements. The results indicated that there is a synergistic effect of lowering surface tension and increasing conductivity, which is attributed to the synergistic effects of the components.¹³⁰ When SDS was added to a polymer solution, the polymers interacted with the SDS, causing micellar aggregation. The micelles were more closely packed after the mixing than they were before, when the polymers were spreading out. The hydrophobicity of the polymer has a significant impact on how the SDS molecules assemble into the micellar aggregate because the hydrophobic side chains of hydrophobically modified (HM) polymers serve as SDS nucleation sites. Higher hydrophobicity causes the more compact packing of the micellar aggregate.¹³¹

4. SYNERGISM OF THE SURFACTANT/POLYMER/NANOPARTICLE FORMULATION

To enhance the performance of SP CEOR flooding, different types of nanoparticles are currently mixed to make hybrid nanofluids, where the combined influences are appreciated. Numerous studies have indicated that surfactant polymer flooding with nanoparticles significantly increases hydrocarbon recovery as a result of the synergistic effect that alters wettability, reducing IFT to an ultralow value and increasing sweeping efficiency¹³³ (Figure 19). It has been reported by Tang et al.¹³⁴ that polymeric nanofluids with a combination of surfactants and nanoparticles showed improved viscoelasticity and rheological properties compared to basic polymeric solutions and HPAM/NP solutions. In the formulation, surfactants were used to facilitate dispersion of nanoparticles in the polymer solution, where the nanoparticles acted as cross-linkers. This improved the viscosity and rigidity of the polymer solution by creating a complex network structure and preventing polymer chains from breaking. In another study by Yoon et al.,¹³⁵ silica/polymer dispersion was stabilized using a cationic surfactant [dodecyltrimethylammonium bromide (DTAB)]. Because DTAB and anionic polymer chains bind to silica surfaces, they enhance surfactant alignment at the oil–water interface. The lowering of the wettability of the surface of nanoparticles and particle–particle repulsion enhance the emulsion stability. Additionally, ZrO₂ nanoparticles were used to enhance the viscosity of polymeric solution. In this study, the NPs acted as a cross-linkers between polymer chains, forming a complex matrix of polymer solution.¹³⁶

The study by Sedaghat et al.¹³⁷ investigated the influence of TiO₂ and SiO₂ nanoparticles on the polymer (HPAM) and surfactant (SDS) formulations in terms of wettability change, IFT reduction, viscosity increase, and oil recovery. The results indicated that the wettability change during nanopolymer–surfactant flooding was much greater than when nanofluid alone was injected. SDS and nanoparticles acted synergistically in adsorption and disjoining pressure that dislodged the oil film from the surface. The polymer–surfactant solution viscosity increase resulted into the improved oil recovery as a result of the effective sweep efficiency of the solution. As sweep efficiency increases, nanoparticles are forced to adhere to a thin oily film on the rock and ultimately change its wettability.

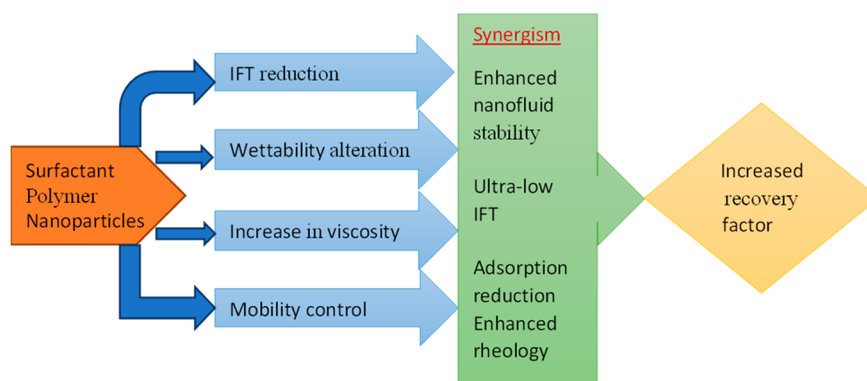


Figure 19. Synergistic effect of the S/P/NP system improved recovery.

Table 7. Oil Recovery Results Based on Synergistic Effects of Nanofluids

formulation	enhanced parameters	oil recovery of OOIP (%)	reference
SiO ₂ + SDS + HPAM	altered wettability and increased viscosity by cross-links	3.37–20.87	3
SiO ₂ + CAPB ^a + PHPA ^b	reduced IFT, altered wettability to be more water-wet, and increased viscosity	28.6	4
SiO ₂ + SDS + PAM	viscosity, IFT, and stable emulsion	21	141
SiO ₂ + AOT ^c + PVP-K30	reduced IFT and altered wettability to be more water-wet	5.74–13.62	143
Al ₂ O ₃ + SAILS ^d + PVP	adsorption, IFT reduction, and increased viscosity	11.96	144
SiO ₂ + SDS + PAM	lowered IFT and increased viscosity		145
SiO ₂ + 14-6-14 GS ^e + PHPA	wettability change to be more water-wet and increased viscosity	26.25	146
silica + Reetha + xanthan gum	IFT reduction, emulsification, creaming index, increased viscosity, sweep efficiency, and wettability alteration	27.33	147

^aCocoamidopropyl betaine. ^bPartially hydrolyzed polyacrylamide. ^cDiocetyl sodium sulfosuccinate. ^dSurface-active ionic liquids. ^eGemini surfactant.

Son et al.¹³⁸ investigated the interactions of different sizes of silica nanoparticles with an anionic polymer and zwitterion surfactant. Their synergistic effects on wettability, rheology, and oil recovery factor were observed. The emulsion stability was enhanced by the silica nanoparticles, and wettability was changed to more water-wet as a result of the disjoining pressure exerted on the solid–liquid–air interface.¹³⁹ The wettability, rheology, and oil recovery increased with a decline in the nanoparticle size.¹⁴⁰ The overall performance of the ternary system was the combined influence of each component.

In another study by Sharma et al.,¹⁴¹ they studied the use of SiO₂ nanoparticles to stabilize the emulsion formed by PAM and surfactant. It was noted that a significant decrease in IFT with the addition of nanoparticles and fairly lower IFT values were observed. A substantial synergistic effect can be observed when nanoparticles are added to SP solution.¹⁴² Therefore, Pickering emulsions stabilized with nanoparticles may be useful for the EOR process. The summary of numerous core flooding results generated as a result of the synergistic behavior of nanofluid components is shown in Table 7.

5. CHALLENGES, RESEARCH GAPS, AND FUTURE PERSPECTIVES

The field application of nanofluids of SP has been stalled, despite the available abundant laboratory and simulation results that suggest the huge potential for EOR. This is presumably due to the lack of convincing and practical experimental results that are technically and economically justifiable and the mismatch of trial fieldwork data. In the field, reservoir petrophysical and fluid parameters can change from one oil reservoir to the next, and thus, the chemistry of the nanofluid in a given reservoir will definitely differ. The

application of hybrid nanofluids is challenged by several factors, including the following:

The temperature and salinity of the reservoir as well as the heterogeneity of the reservoir affect the stability and recovery mechanisms of polymer and surfactant nanofluids, thereby reducing the efficiency of their recovery. Injections of these nanofluids into deep reservoirs are also susceptible to adverse effects from fluctuating conditions at the injection point, middle, and end of the reservoir.

The use of more additives in the current formulation of hybrid nanofluids has improved the oil recovery compared to their individual performances. However, the cost of these additives (nanoparticles and surfactants) in comparison to the global oil price renders some of these findings unfeasible for field application. This is probably why economists are placing their brake pedal for further implementation of nanofluids as a result of unjustifiable project costs.

An adequate evaluation of the feasibility at a large-scale implementation of the nanofluid involving polymers and surfactants has not been done. Some proposed recovery mechanisms and results derived from experimental and simulation data do not reflect the reality of the reservoir in the fields. Furthermore, some findings for example of effects of the nanoparticle size on the oil recovery are contradicting each other.

As a result of their incredibly small size, the nanomaterials may cause serious health effects to both the organism and the environment. There have been a variety of reasons that have kept the application of nanoparticles in the field trial on hold, including their suspected ecotoxicity. The assessment of the risk presented by nanoparticles to organisms and the environment depends heavily upon data addressing nanoparticle mobility, transfer, and uptake, as impacted by

environmental parameters. Considering the risks that some nanoparticles, such as titanium oxide, pose to health, the environment, and safety, their use for EOR processes needs to be carefully examined. As a result of their large surface/volume ratio, nanoparticles are capable of adsorbing toxic compounds on their surface.

The research gaps that can be noted from the current use of nanofluids of polymers and surfactants are inadequate reaction mechanisms for deducing the chemistry and reaction kinetics behind fluid–fluid and fluid–rock. Most of the proposed mechanisms are based on the physical interaction evidence that does not tell the certainty of the chemical interaction. How different nanofluids bond with polymers and surfactants under stressful conditions of reservoir turbulence, salinity, and high temperature needs attention and more investigation.

There is a mismatch of experimental and simulation results derived from different researchers. For example, with similar experimental parameters, different effects of Al_2O_3 or TiO_2 nanoparticles on oil recovery mechanisms have been reported.

In an attempt to address the aforementioned challenges, intensive studies of the nanoparticle surface functionalization, characterization, and testing must be emphasized. On the basis of experiments and simulations, polymers with different functionalities can impart a variety of properties, such as stability, minimal retention, and overall flow behaviors, in the porous media. An optimized polymer-coated nanoparticle suspension provides and enhances charge screening. However, large polymeric chains lead to poor injectivity in the reservoir as a result of their bulkiness. Therefore, a detailed investigation on the optimal size of polymeric chains with respect to the pore sizes must be selected for nanoparticle surface coating.

Nanoparticle synthetic methods can be improved to yield less cost and plenty of particles too with the surface tailored to suit specific harsh reservoir conditions. The bulk production techniques using green methods must be researched to lower the cost and toxicity and ensure availability for large-scale field trials.

Studies on the toxicity level of various nanoparticles have to be conducted to ascertain their health, safety, and environmental effects. Even unarmful materials when reduced to the nanoscale may pose a serious threat to humans and the environment.

Field trials of flooding involving nanoparticle-assisted surfactant/polymers based on the available up to date data for the performance gap need to be identified and conducted. The execution will reveal the challenges that will enlighten the researchers on what are the real obstacles. There has been numerous laboratory and simulation data with great potential, which could be upscaled in terms of fluid preparation, injection, and monitoring of their efficiency in the reservoirs.

6. CONCLUSION

In this work, a detailed review of molecular interactions of nanoparticles and the hybrid surfactant/polymer solutions and their synergistic influence on EOR was presented. The combined influences of the nanofluid of the surfactant and polymer were observed to change the wettability, reduce IFT, lower adsorption tendencies, and improve rheology and nanofluid stability. The following deductions were made from this study:

Apart from the injection flow rate, rheology, and differential pressure, the successful injection of the hybrid system of the SPNP slug depends primarily upon its preparation stage. In

this stage, proper dissolution, stability of suspension, and selection of the optimal concentration of the ingredients are crucial.

Whether the nanofluid is used standalone or in hybrid mode, the size and concentration of nanoparticles make a significant difference in the performance. When mixed with a surfactant, the smaller nanoparticles at the optimal concentration will determine the formation and stability of microemulsions with high solubilization parameters. The performance of nanoparticles in EOR can be appreciated when combined with the suspension of other chemicals, such as surfactants and polymers. Their synergistic interaction results in wettability alteration, IFT reduction, emulsification, reduced adsorption, improved rheological behaviors, and fluid mobility control, culminating in higher oil recovery.

The suggested polyelectrolytes and anionic polysulfonates as nanoparticle stabilizers are efficient at low to moderate temperatures and salinity. This is due to their shrinkage behavior when brine salinity and temperature increase, resulting in the loss of fluid viscosity. A substitute zwitterion polymer (polyampholyte) grafted on the nanoparticles is recommended for surface functionalization. This is attributed to their swelling behavior as the temperature and ionic strength increase. This results in a significant increase in the excluded volume as well as improved salt and thermal tolerance. The nanofluid injection performance is severely affected by the reservoir temperature and salinity. As a result of reservoir heterogeneity, the initial data collected may not be the same throughout the reservoir. The fluid flow in the porous media will likely be diluted before its breakthrough.

The rheological properties of polymers are enhanced by adding nanoparticles to their solutions, where the polymer chain adsorbs onto their surfaces, resulting in complex micelle formation. As a result of this interaction, the polymer becomes viscous, leading to increased sweep and displacement efficiency and ultimately higher oil recovery.

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