

A review on the application of nanofluids in enhanced oil recovery

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Abstract Enhanced oil recovery (EOR) has been widely used to recover residual oil after the primary or secondary oil recovery processes. Compared to conventional methods, chemical EOR has demonstrated high oil recovery and low operational costs. Nanofluids have received extensive attention owing to their advantages of low cost, high oil recovery, and wide applicability. In recent years, nanofluids have been widely used in EOR processes. Moreover, several studies have focused on the role of nanofluids in the nanofluid EOR (N-EOR) process. However, the mechanisms related to N-EOR are unclear, and several of the mechanisms established are chaotic and contradictory. This review was conducted by considering heavy oil molecules/particle/surface micromechanics; nanofluid-assisted EOR methods; multiscale, multiphase pore/core displacement experiments; and multiphase flow fluid-solid coupling simulations. Nanofluids can alter the wettability of minerals (particle/surface micromechanics), oil/water interfacial tension (heavy oil molecules/water micromechanics), and structural disjoining pressure (heavy oil molecules/particle/surface micromechanics). They can also cause viscosity reduction (micromechanics of heavy oil molecules). Nanofoam technology, nanoemulsion technology, and injected fluids were used during the EOR process. The mechanism of N-EOR is based on the nanoparticle adsorption effect. Nanoparticles can be adsorbed on mineral surfaces and alter the wettability of minerals from oil-wet to water-wet conditions. Nanoparticles can also be adsorbed on the oil/water surface, which alters the oil/water interfacial tension, resulting in the formation of emulsions. Asphaltenes are also adsorbed on the surface of nanoparticles, which reduces the asphaltene content in heavy oil, resulting in a decrease in the viscosity of oil, which helps in oil recovery. In previous studies,

most researchers only focused on the results, and the nanoparticle adsorption properties have been ignored. This review presents the relationship between the adsorption properties of nanoparticles and the N-EOR mechanisms. The nanofluid behaviour during a multiphase core displacement process is also discussed, and the corresponding simulation is analysed. Finally, potential mechanisms and future directions of N-EOR are proposed. The findings of this study can further the understanding of N-EOR mechanisms from the perspective of heavy oil molecules/particle/surface micromechanics, as well as clarify the role of nanofluids in multiphase core displacement experiments and simulations. This review also presents limitations and bottlenecks, guiding researchers to develop methods to synthesise novel nanoparticles and conduct further research.

Keywords nanofluid, EOR mechanism, nanoparticle adsorption, interface property, internal property

1 Introduction

Unconventional oil resources show potential application value in crude oil recovery. Although primary/secondary oil recovery processes improve the oil recovery, 50% of the crude oil still remains in the reservoir pores and channels [1]. Enhanced oil recovery (EOR) was also known as ‘tertiary recovery’, is a process for extracting oil that has not already been retrieved through the primary or secondary oil recovery techniques. During the EOR process, the oil-solid interaction force significantly affects the oil recovery [2,3], and several researchers have focused on novel methods to decrease the oil-solid force [3–18]. Traditional EOR primarily includes three methods: miscible flooding [19–22], thermal flooding [23,24] and chemical flooding [25–30]. Miscible solvents and gases

are necessary for miscible flooding [31]. Conversely, thermal methods require a high temperature to decrease the viscosity of the oil, which results in significant energy consumption [32].

When compared to miscible and thermal flooding processes, chemical EOR (C-EOR) has been industrialised, and several chemicals are used during the C-EOR process, such as surfactants [28,33–40], polymers [41–44], alkalis [29,45,46], ions [47,48], foams [49–61], and nanofluids [62–64]. Surfactants are the most commonly used chemicals during the EOR process [34,50–59,65–72]. However, surfactant EOR exhibits several limitations; for example, surfactants are easily adsorbed on mineral surfaces, and the loss of adsorption sites caused by ineffective adsorption limits the utilisation of the surfactant [73–75]. Moreover, surfactants are expensive and unstable at high-salinity or high-temperature environments [76,77]. Furthermore, chemical surfactants are difficult to degrade and cause serious environmental pollution [78].

Polymer EOR can decrease the water mobility ratio and displacement efficiency, resulting in increased oil recovery [41,43]. However, the polymer synthesis process is complex and expensive and can cause environmental pollution and other problems.

Nanoparticles include non-metallic oxide nanoparticles (SiO_2) [79] and metal oxide nanoparticles (ZrO_2 , NiO , TiO_2 , Al_2O_3) [80–82]. Nanoparticles have several unique properties, such as small size (1–100 nm), stability, mechanical properties, and low cost [83–86], which have been widely used in catalysis and materials synthesis [87–90]. Several engineered nanomaterials, such as anti-temperature [65,91–93], anti-salinity [65,91–94], and magnetic responsive materials [95,96], have been used for EOR. Nanoparticles can be dispersed in deionised water to form nanofluids. When compared to other methods, nanofluids have several advantages. For instance, nanoparticles can penetrate the pore throat, alter several properties, such as the oil/water interface properties [97], surface tension [98], viscosity of aqueous solutions [99,100], and mineral wettability, and significantly increase oil recovery [101,102]. Therefore, nanofluid EOR (N-EOR) has been extensively studied [65,103–105].

The mechanisms by which nanoparticles enhance oil recovery are shown in Fig. 1. Nanoparticles can be adsorbed on the solid/gas, oil/water, and oil/water/solid interfaces [106], which alters the wettability of the minerals, oil/water interfacial tension, and structural disjoining pressure. Moreover, nanoparticles can alter the internal properties of the oil because asphaltenes are adsorbed on the surface of nanoparticles, which reduces the oil viscosity. The nanoparticle adsorption phenomenon is the basic mechanism by which nanofluids enhance oil recovery, as shown in Fig. 1.

Several reviews have been previously published on N-EOR [1,30,84–86,107–122]. Olayiwola and Dejam summarised the interaction effects of nanoparticles with low-salinity water (LSW) and surfactant for EOR in sandstone and carbonate reservoirs. They reviewed the nanoparticle behaviour in deionised and low/high-salinity water, and the role of surfactants (cationic/anionic/non-ionic surfactant) in nanoparticle stability and oil recovery [85]. Peng et al. reviewed the role of nanomaterials in EOR [1]. They divided nanomaterials into zero-, one-, and two-dimensional nanomaterials, and the functional factors of nanomaterials in nanoflooding were analysed. Corredor et al. reviewed the role of polymer nanohybrids in oil recovery [107]. They reviewed the polymer nanohybrid preparation process and determined that the mechanisms that improved oil recovery were primarily due to the effect of polymer nanohybrids on the improvement of rheological properties, fluid–fluid interactions, and reduction of polymer retention. Cheraghian and Hendvaningrat reviewed the role of nanoparticles in interfacial tension and flooding during the EOR process [108,109]. Agista et al. reviewed the application of nanoparticles in an EOR process [86], and analysed the parameters affecting the nanotechnology-assisted and nanotechnology-enhanced EOR processes. Moghadam and Salehi reviewed the effect of nanoparticles on mineral wettability during the EOR process and emphatically analysed the mineral type and wettability measurement methods [113]. Irfan et al. reviewed a mathematical model on N-EOR, and different models were compared and analysed [115]. Almahfood and Bai studied the synergistic effect between

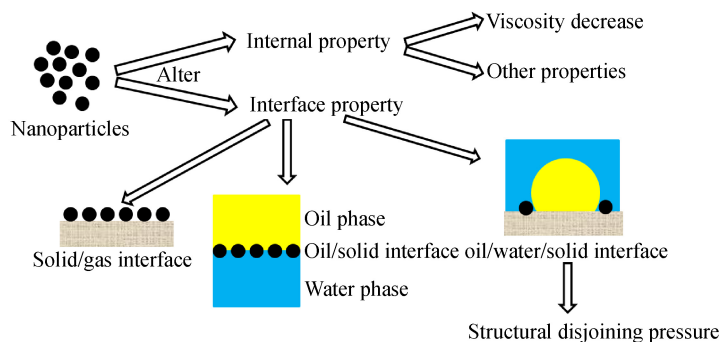


Fig. 1 Mechanisms of nanoparticles that enhance oil recovery.

nanoparticles and surfactants on EOR, and the corresponding mechanisms were analysed [122]. The published reviews focused on the role of nanofluids in EOR; however, nanoparticle adsorption was ignored. Wettability alteration, structural disjoining pressure, interfacial tension alteration, emulsion formation, and viscosity are affected by the adsorption of nanoparticles on the mineral surface, oil/water interface, and oil components. Most previous reviews only focused on nanofluids that decrease oil/water interfacial tension; however, certain studies indicated that nanofluids can increase the oil/water interfacial tension.

In this review, N-EOR mechanisms are systematically reviewed, as shown in Fig. 2. The contradictory mechanisms are summarised as heavy oil molecules/particle/surface micromechanics. Moreover, the role of nanofluids during the multiphase core displacement process is reviewed, and the related simulation is discussed. Finally, potential mechanisms and future research directions are proposed.

However, this review has certain limitations. On one hand, a novel synthesis method for nanoparticles which can remain stable under high temperature, high salinity, and high pressure has not been discussed. On the other hand, the industrial application of N-EOR is rare. Consequently, the N-EOR in industrial applications has not been discussed.

Thus, based on the interface and internal aspects, this review can be summarised as follows. First, the interface characteristics are described. The interface properties include wettability, structural disjoining pressure, interfacial tension, and emulsion formation. Then, the internal property alteration is reviewed, which includes the reduction of viscosity and injected fluid mobility ratio. Finally, the potential mechanisms and future research directions are discussed.

2 Heavy oil molecules/particle/surface micromechanics

2.1 Particle/surface micromechanics: wettability alteration

Wettability controls oil recovery in the EOR process, which is measured by the water/solid/air and oil/solid/water three-phase contact angles (Fig. 3). In an air atmosphere, when a water drop is dripped onto minerals, a water/solid/air three-phase contact angle is formed. When the contact angle (θ) is less than 90° , the minerals (solids) are hydrophilic. When the contact angle increases to 90° or is greater than 90° , the minerals become neutral or hydrophobic, respectively. Because the liquid drop evaporates easily in an air atmosphere, only the initial contact angle can be measured, and the equilibrium contact angle is difficult to measure. Therefore, to measure the equilibrium contact angle, an oil drop is dripped on minerals in the aqueous phase. When the contact angle is less than 90° , the minerals are lipophilic. When the contact angle is higher than 90° , the minerals are oleophobic.

2.1.1 Concepts of nanofluids that affect wettability

Several researchers have focused on the effect of nanoparticles on wettability alteration in minerals [123–127]. The wettability of minerals influences oil recovery. On one hand, several researchers speculate that oil recovery increases when minerals become more hydrophilic. Thus, as the contact angle decreases, oil recovery correspondingly increases. On the other hand, certain studies have indicated that oil recovery is optimum when the mineral is media-wet rather than water-wet [128]. Nanofluids can alter wettability because nanoparticles can be adsorbed on the surface of minerals [129,130] (Figs. 4

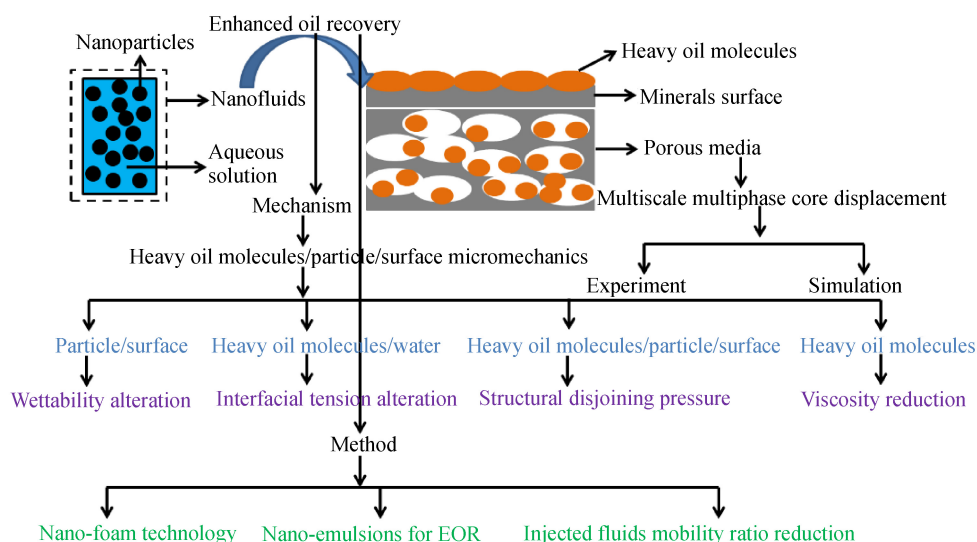


Fig. 2 General sketch of this review.

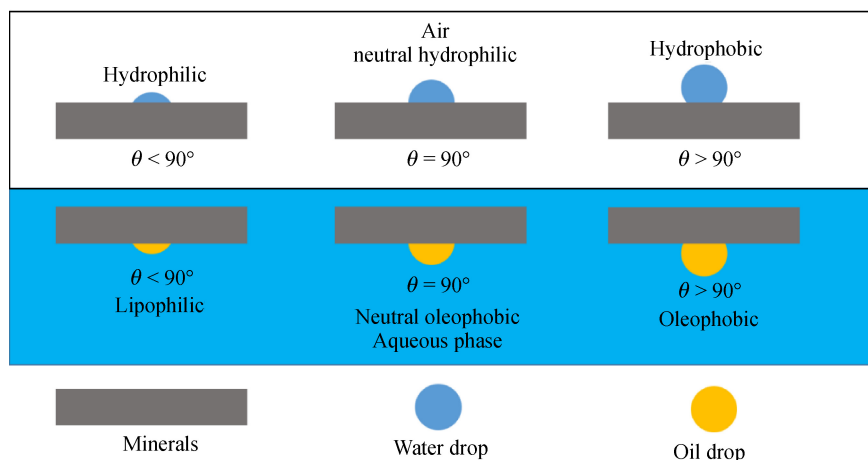


Fig. 3 Water/solid/air and oil/solid/water three-phase contact angles.

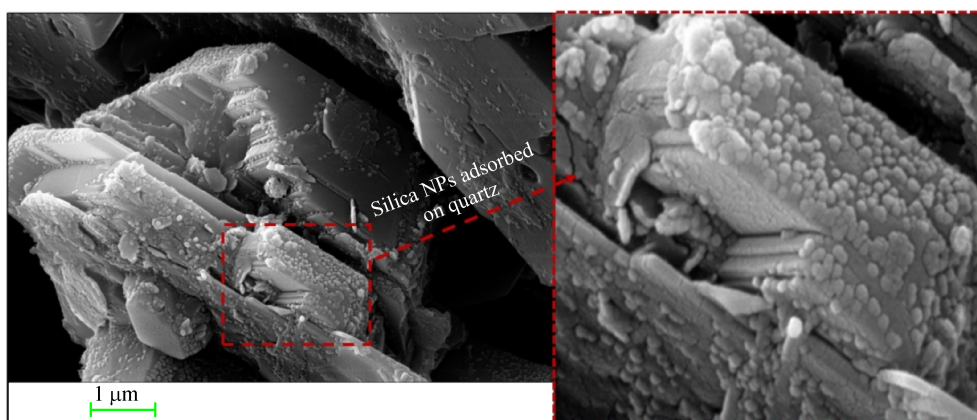


Fig. 4 Scanning electron microscopy (SEM) images of SiO_2 nanoparticles that are adsorbed on quartz. Reprinted with permission from ref. [132], copyright 2018, Elsevier.

and 5), which was verified by microfluidic flooding experiment results [131].

Abhishek et al. studied the adsorption of SiO_2 nanoparticles on rock sandstone in low-salinity flooding [132]. The isothermal static adsorption indicated that more nanoparticles were adsorbed on the quartz surface than on kaolinite. The adsorption of nanoparticles was verified by SEM images, as shown in Fig. 4. When the aqueous-phase salinity increased, the adsorption of nanoparticles increased. The desorption rate was only 21.2 wt% when the nanoparticles were 35 wt%. The adsorption and desorption of nanoparticles are controlled by the pH; thus, a higher pH aids in desorbing nanoparticles from minerals. The authors also studied the adsorption kinetics and type of adsorption [130]. They determined that the nanoparticle adsorption process is influenced by intraparticle and film diffusion processes.

Li et al. studied the adsorption of nanoparticles on Berea sandstone, and the wettability alteration was related to the

adsorption of nanoparticles [134]. The hydrophobic nanoparticle injection process can cause significant adsorption and retention of nanoparticles in the core plug; however, hydrophilic nanoparticles do not exhibit the desorption phenomenon. Conversely, hydrophilic nanoparticles demonstrate lesser adsorption and higher desorption. Thus, the adsorption of nanoparticles alters the wettability. However, nanoparticle adsorption and wettability alteration are not closely related.

2.1.2 Analysis of factors that influence wettability

During the N-EOR process, several parameters influence mineral wettability, such as temperature, aqueous environment (pH, salinity, nanoparticle species, and nanoparticle concentration), oil and mineral properties, as listed in Table 1.

In recent years, several researchers have focused on the effect of nanofluids on mineral wettability alteration. The

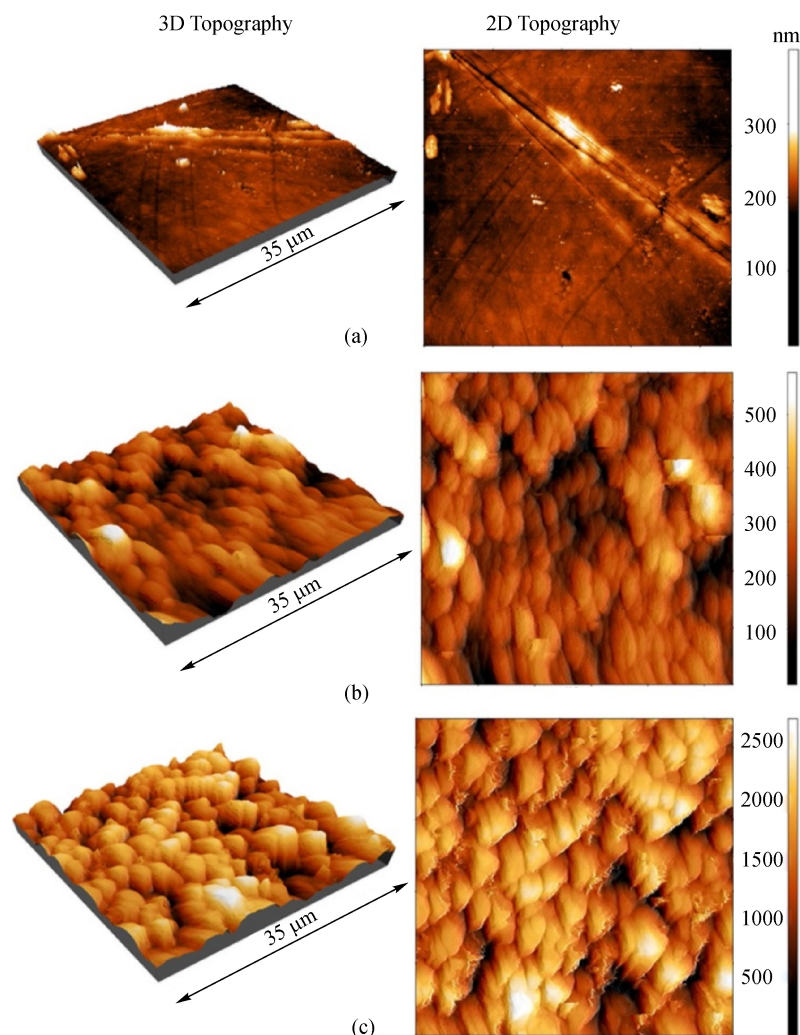


Fig. 5 Calcite surface atomic force microscopy image. (a) Before nanofluid-based treatment; nanofluid-based treatment at (b) 23 °C and (c) 60 °C. Reprinted with permission from ref. [133], copyright 2017, Elsevier.

detailed description is as follows. Mousavi et al. [135] synthesised fluorinated SiO_2 nanoparticles, which were used to alter the rock wettability in the near-wellbore region from a highly liquid-wet to an intermediate gas-wet state. Without the fluorinated SiO_2 nanoparticle-based treatment, the surface cannot be used to measure wettability. The water/*n*-decane contact angle was 147°/61°. Giraldo et al. [136] studied the effect of alumina-based nanofluids on the wettability alteration of sandstone cores; the anionic surfactant could disperse alumina-based nanoparticles and make the sandstone cores more hydrophilic. The effect of the anionic surfactant on wettability alteration could be improved by adding nanoparticles (concentration ≤ 500 ppm (10^{-6})). The core displacement proved the effect of the alumina nanoparticles.

Hendraningrat et al. [137] used SiO_2 nanofluids (in brine solution) to alter sandstone wettability; the contact angle decreased from 54° to 22°, and the oil recovery increased by 36.49%. Ehtesabi et al. [138] used TiO_2 nanoparticles to

improve the recovery of heavy oil from sandstone cores, and the oil recovery was improved from 49% to 80%. The rock wettability was changed from oil-wet to water-wet state after nanofluid-based treatment, and the nanoparticles were homogeneously adsorbed onto the core plug surface (observed through SEM-energy dispersive X-ray spectroscopy). Hendraningrat and Torsaeter [139] studied the initial rock wettability in a study based on SiO_2 -based nanofluid alteration of the wettability of quartz plane. The SiO_2 nanofluids decreased the contact angle from 39° to 26°. Optimal oil recovery occurred when the initial wettability of the minerals was in the intermediate-wet state. It was also observed that oil recovery increased at a higher temperature.

Joonaki and Ghanaatian [64] used Al_2O_3 , Fe_2O_3 , and SiO_2 to enhance oil recovery from sandstone rocks, and the oil recovery increased by 20.2%, 17.3%, and 22.5%, respectively. Moreover, the contact angle decreased significantly. To explore the effect of temperature on

Table 1 Contact angle alteration and oil recovery with different nanoparticles, minerals, aqueous phases, and temperatures

Ref.	Nanoparticle	Mineral type	Aqueous phase	Temperature	Oil recovery increase	Contact angle alteration
[135]	Fluorinated nano SiO ₂	Limestone	Deionised water	80 °C	–	–
[136]	Al ₂ O ₃	Sandstone	PRNS	Ambient temperature	–	142° to 0°
[137]	SiO ₂	Sandstone	Brine	20 °C	36.49%	54° to 22°
[138]	TiO ₂	Sandstone	Brine	Ambient temperature	–	125° to 90°
[139]	SiO ₂	Quartz plane	Brine	Ambient temperature	–	39° to 26°
[64]	Al ₂ O ₃	Sandstone	Synthetic brine	Ambient temperature	20.2%	Higher than 82°
	Fe ₂ O ₃				17.3%	134° to 100°
	SiO ₂				22.5%	134° to 82°
[81]	Al ₂ O ₃	Limestone	Deionised water	26 °C, 40 °C, 50 °C, 60 °C	9.9%	82° to 61°
	TiO ₂				6.6%	82° to 46°
	SiO ₂				2.9%	82° to 18°
[140]	γ -Al ₂ O ₃	Calcite	Deionised water	Ambient temperature	11.25%	119° to 38° (0.5%)
[141]	TiO ₂	Carbonate	Deionised water	Ambient temperature	–	144° (water), 95° (oil)
	SiO ₂					139° (water), 88° (oil)
	CNT					140° (water), 85° (oil)
[80]	Al ₂ O ₃ /TiO ₂ /SiO ₂	Sandstone	3 wt% NaCl, PVP	Ambient temperature	6%	56.09° to 21.64°
[142]	SiO ₂	Calcite	0.05 mol·L ⁻¹ NaCl	Ambient temperature	–	156° to 41.7°
[172]	SiO ₂	Carbonate	Brine	Ambient temperature	–	122° to 18°
[144]	SiO ₂	Glass	Ethylene glycol	Brine, SDS	18.1%	88° to 25°
[145]	SiO ₂	Sandstone	PAM, SDS	30 °C, 90 °C	24.7%	–
[82]	ZrO ₂ , NiO	Limestone	C ₁₆ TAB, TX-100	Ambient temperature	–	152° to 35°
[146]	FSPNs/SiO ₂	Plate	Ethanol	Ambient temperature	28%	134.4° to 23.7°
[173]	SiO ₂	Quartz	Brine	Ambient temperature	4.48% to 10.33%	–
[133]	SiO ₂	Calcite	Brine	23 °C to 60 °C	–	145° to 56°
[147]	Al ₂ O ₃ (ZrO ₂)	Carbonate	TX-100	Ambient temperature	–	85° to 62° (71°)
			SDS			92° to 75° (84°)
			CTAB			70° to 52° (60°)
[149]	SiO ₂	Sandstone	Brine, Tween® 20	Ambient temperature	–	121.7° to 39.7°
[150]	SiO ₂	Carbonate	Brine	Ambient temperature	–	138.7° to 50.8°
[151]	SiO ₂	Glass substrate	Brine	60 °C	25%	142° to 35°
[152]	Fe ₃ O ₄ /chitosan	Sandstone	Brine	Ambient temperature	10.8%	127° to 92°
[153]	SiO ₂ particles	Berea core slice	Xanthan gum	Ambient temperature	20.82%	86.2° to 50.4°
[154]	ZnO	Calcite	SDS	Ambient temperature	11%	11.82°
[65]	SiNP-NH ₂	Sandstone	Soluterra 964, brine	65 °C	17.23%	130.2° to 43.4°
[155]	CaCO ₃	Calcite	Surfactant	25 °C to 80 °C	–	106° to 50°
[156]	SiO ₂	Sandstone	HPAM, brine	Ambient temperature	6.7%	55.7° to 31°
	Al ₂ O ₃				11.3%	55.7° to 25.1°
[159]	ZnO/SiO ₂ /xanthan gum	Carbonate	LSW	Ambient temperature	19.28%	137° to 34°
[83]	SiO ₂	Glass	Deionised water	Ambient temperature	9%	135° to 88°
[160]	Hydrophilic SiO ₂	Limestone/dolomite	SDS, brine	Ambient temperature	15%	165.65° to 65.75°
[161]	SiO ₂	Carbonate	Saline	80 °C	8% to 17%	141° to 23°
[166]	MnZn ferrite	Glass plate	Brine, SDBS	Ambient temperature	–	48.64° to 11.97°
[167]	SiO ₂	Berea sandstone	Brine, rhamnolipid	Ambient temperature	5.3% to 6.8%	145° to 54°

(Continued)

Ref.	Nanoparticle	Mineral type	Aqueous phase	Temperature	Oil recovery increase	Contact angle alteration
[162]	SiO ₂	Calcite	NaCl	Ambient temperature	18%	140° to 38°
[157]	Al ₂ O ₃	Sandstone	HPAM	27 °C, 60 °C, 90 °C	10.6%	100.3° to 60.6°
	SiO ₂				6.11%	100.3° to 78.6°
[158]	CuO/TiO ₂ /PAM	Carbonate Sandstone	Deionised water	Ambient temperature	–	151° to 14.7° 135.25° to 11.75°
[168]	NiO/SiO ₂	Carbonate rocks	Deionised water/poly-ethylene glycol	Ambient temperature	–	176° to 40°
[148]	Al ₂ O ₃	Rock samples	TX-100/SDBS	Ambient temperature	–	16.0° (TX-100), 25° (SDBS)
	CuO					13.7° (TX-100), 22.3° (SDBS)
	TiO ₂					12.5° (TX-100), 25.9° (SDBS)
	CN					7° (TX-100), 20.5° (SDBS)
	SiO ₂					16.9° (TX-100), 25.8° (SDBS)
[169]	TiO ₂ /quartz	Carbonate pellets	Seawater	30 °C, 50 °C, 70 °C	21%	103° to 48°
[170]	Fe ₃ O ₄ @SiO ₂ @xanthan	Carbonate rock	Deionised water	Ambient temperature	–	134° to 28°
[171]	Fe ₃ O ₄	Carbonate rock	Polyvinyl alcohol, hydroxyapatite	Ambient temperature	–	116° to 62°
[164]	SiO ₂	Glass surface	Brine water	Ambient temperature	75% (brine)	120° to 0° (oil-wet)
[165]	SiO ₂	Sandstone rock	Brine water	70 °C	18.46% (LNS)	180° to 65°
[163]	SiO ₂	Carbonate rock	Brine water	70 °C	2.8% (LNS)	180° to 120°

mineral wettability and oil recovery, Bayat et al. [81] used Al₂O₃, TiO₂, and SiO₂ to increase oil recovery, which increased by 9.9%, 6.6%, and 2.9%, respectively. The contact angles of a water drop on a limestone surface decreased from 82° to 61°, 82° to 46°, and 82° to 18°, respectively. Further, the contact angle decreased as the temperature increased. Naseri [140] used γ -Al₂O₃ nanofluids to alter the wettability of calcite, and the contact angle decreased from 119° to 38°, and the oil recovery improved by 11.25%. Esmailzadeh et al. [141] studied TiO₂, SiO₂, and carbon nanotube (CNT) nanofluids on the wettability alteration of carbonate rocks; they measured the water and oil-drop contact angles. Hendraningrat and Torsaeter [80] studied the effect of hydrophilic metal oxide nanoparticles in brine solutions on sandstone wettability alteration. Polyvinyl pyrrolidone (PVP) could effectively improve the stability of nanofluids. The Al₂O₃, TiO₂, and SiO₂ nanofluids could significantly decrease the sandstone contact angle.

Tabar et al. [142] and Al-Anssari et al. [143] studied the effect of SiO₂ nanofluids on the alteration of carbonate rock wettability in brine solutions. The results showed that SiO₂ nanofluids could effectively alter the wettability from strongly oil-wet to water-wet state. Zhang et al. [144] studied the effect of SiO₂ nanofluids on the wettability alteration of glass, and determined that the oil recovery could be improved by 18.1%, while the contact angle decreased from 88° to 25°. In this experiment, sodium

dodecyl sulfate (SDS) and brine were used to disperse the nanofluids. To explore the effect of temperature on mineral surface wettability, Sharma et al. [145] used SiO₂ nanofluids to alter the sandstone wettability under polyacrylamide (PAM) and SDS solutions at temperatures ranging from 30 °C to 90 °C. Nwdee et al. [82] studied the effect of ZrO₂ and NiO nanofluids on limestone wettability alteration; they used Triton X-100 (TX-100) and cetyltrimethylammonium bromide (CTAB) as the dispersant, and a contact angle reduction from 152° to 35° was measured. Azarshin et al. [146] used composite nanoparticles (functionalised SiO₂ nanoparticles/SiO₂) to enhance oil recovery at room temperature; the dispersant used was ethanol. The oil recovery improved by 28% and the water drop contact angle on the plate surface decreased from 134.4° to 23.7°. Al-Anssari et al. [133] used SiO₂ nanofluids to alter oil-wet calcite surface wettability under a saline environment at a temperature range of 23 °C–60 °C, and measured a decrease in contact angle from 145° to 56°. Mohd [147] studied the effects of different surfactants and nanoparticles on the wettability alteration of carbonate rocks. For Al₂O₃ nanofluids, CTAB, SDS, and TX-100 could reduce the contact angle from 70° to 52°, 92° to 75°, and 85° to 62°, respectively. For ZrO₂ nanofluids, CTAB, SDS, and TX-100 could decrease the contact angle from 70° to 60°, 92° to 84°, and 85° to 71°, respectively.

Yekeen et al. [148] studied the synergistic effect of

nanoparticles and surfactants on the wettability alteration of rocks. Four nanofluids, Al_2O_3 , CuO , TiO_2 , CNT, along with TX-100, sodium dodecylbenzene sulfonate (SDBS) were used. Huibers et al. [149] studied the effect of SiO_2 nanoparticles on sandstone surface wettability, and observed a reduction in the contact angle from 121.7° to 39.7° . Jang et al. [150] used SiO_2 nanoparticles to alter the wettability of a carbonate surface. The SiO_2 nanoparticles were dispersed in a brine solution at ambient temperature, and the water contact angle was observed to decrease from 138.7° to 50.8° . Li et al. [151] studied the effect of SiO_2 nanoparticles on glass substrate wettability at 60°C , and a 25% increase in oil recovery and a decrease in contact angle from 142° to 35° were observed. Rezvani et al. [152] used composite nanoparticles (Fe_3O_4 /chitosan) to alter the wettability of sandstone; the aqueous environment was brine. They observed that the oil recovery increased by 10.8% and the contact angle decreased from 127° to 92° . Saha et al. [153] studied the effect of xanthan gum and SiO_2 nanoparticles on the wettability of the surface of a Berea core slice; they observed that the oil recovery increased by 20.82% and the contact angle decreased from 86.2° to 50.4° . Soleimani et al. [154] studied the effect of ZnO nanoparticles and SDS surfactant on calcite surface wettability at ambient temperature; they determined that the oil recovery increased by 11% and contact angle decreased by 11.82° . Zhou et al. [65] studied the effect of nanoparticle surface modification on the alteration of mineral wettability. They grafted $-\text{NH}_2$ functional group on the surface of SiO_2 nanoparticles, which remained stable in Soloterra 964 and brine solution at 65°C . The oil recovery increased by 17.23% and the contact angle decreased from 130.2° to 43.4° . Ahmadi et al. [155] used CaCO_3 nanoparticles and a surfactant to alter calcite surface wettability at a temperature range of 25°C – 80°C , and observed a decrease in the contact angle from 106° to 50° . Gbadamosi et al. [156] studied the effect of SiO_2 and Al_2O_3 nanofluids (hydrolysed PAM (HPAM), brine) on sandstone wettability at ambient temperature. The results showed that Al_2O_3 nanofluids showed a superior effect with an 11.3% increase in oil recovery and a decrease in contact angle from 55.7° to 25.1° . For SiO_2 nanofluids, the oil recovery increased by 6.7% and contact angle decreased from 55.7° to 25.1° . Similarly, Gbadamosi et al. [157] concluded that Al_2O_3 nanofluids showed better effect than SiO_2 nanofluids. Al_2O_3 nanofluids (HPAM) and SiO_2 nanofluids (HPAM) were used to alter sandstone wettability at different temperatures, and the oil recovery increased by 10.6% and 6.11%, respectively. The contact angle decreased from 100.3° to 60.6° and 100.3° to 78.6° , respectively.

Bahraminejad et al. [158] used composite nanoparticles ($\text{CuO}/\text{TiO}_2/\text{PAM}$) to alter the carbonate and sandstone surface wettability at ambient temperature, the contact angle decreased from 151° to 14.7° (carbonate) and 135.25° to 11.75° (sandstone). Ali et al. [159] used

composite nanoparticles ($\text{ZnO}/\text{SiO}_2/\text{xanthan gum}$) to alter the carbonate surface wettability at ambient temperature, the aqueous solution was LSW. They observed that the oil recovery increased by 19.28% and contact angle decreased from 137° to 34° . Rostami et al. [83] used SiO_2 nanofluids to alter the surface wettability of glass at ambient temperature; they determined that the oil recovery increased by 9% and the contact angle decreased from 135° to 88° . Aghajanzadeh et al. [160], Keykhosravi and Simjoo [161], Hou et al. [162] and Olayiwola and Dejam [163] studied the effect of SiO_2 nanofluids on the wettability alteration of carbonate surface, and identified a significant decrease in the contact angle. Rostami et al. [164] and Olayiwola and Dejam [165] studied the effect of SiO_2 nanofluids (brine) on sandstone surface wettability, and identified an obvious effect. Mokhtar et al. [166] used MnZn ferrite nanofluids (brine, SDBS) to alter the surface wettability of a glass plate; they discovered that the contact angle decreased from 48.64° to 11.97° . To study the biosurfactant effect on sandstone surface wettability, Wang et al. [167] studied the synergistic effect of SiO_2 nanofluids and rhamnolipid on oil recovery and wettability. The results showed that the oil recovery increased by 5.3%–6.8%, and the contact angle decreased from 145° to 54° . Dahkaee et al. [168], Zargar et al. [169], and Ali et al. [170] studied the effect of composite nanoparticles on the wettability of carbonate rocks; the results indicated that the composite nanofluids showed a superior effect on the wettability alteration of carbonate rocks. Safaei et al. [171] studied the effect of Fe_3O_4 nanofluids (polyvinyl alcohol, hydroxyapatite) on the surface wettability of carbonate rock and observed that the contact angle decreased from 116° to 62° .

Although several studies have focused on the effects of nanofluid species, mineral type, surfactant species, salinity, and temperature on oil recovery and wettability alteration, these conclusions are contradictory. Moreover, the detailed mechanism is unclear.

2.1.3 Effect of nanoparticle species on wettability alteration

Different species of nanoparticles have unique properties and different adsorption effects on mineral surfaces, which can alter the wettability of minerals. Several researchers have focused on the effects of nanoparticle species on mineral wettability.

Moghaddam et al. [174] used different nanofluids to enhance the oil recovery of carbonate rocks and compared the wettability of different nanofluids. The results indicated that the optimum nanoparticles were SiO_2 and CaCO_3 , which increased oil recovery by 8%–9% with hydrophilic wettability. However, certain researchers have presented different opinions on the effect of nanoparticle species on wettability alteration. Bayat et al. [81] indicated that Al_2O_3 and TiO_2 nanofluids have a better effect than SiO_2 nanofluids on EOR.

2.1.4 Influence of salinity on wettability alteration

Salinity can influence the N-EOR process because of different reasons. Different salinities show different ionic strengths, which can influence the adsorption of nanoparticles on minerals and subsequently alter the wettability of minerals. The salt ions influence the oil/water/solid interface property, resulting in a change in the surface energy of minerals; therefore, the wettability of minerals is altered. Moreover, salinity influences the stability of nanofluids.

Rostami et al. studied mineral wettability alteration at different salinities using static/dynamic contact angles [164]. Salt ions can compress the electrical double layer; then, more nanoparticles are adsorbed onto the solid surface in saline solution. Consequently, a greater water-wet state is observed on the sandstone surface.

Tabar et al. investigated the effect of SiO_2 nanofluids on carbonate wettability under different salinities [142]. SiO_2 nanofluids ($2000 \text{ mg}\cdot\text{L}^{-1}$) can alter the wettability of minerals from oil-wet (156°) to water-wet state (41.7°), thereby increasing oil recovery.

Although several studies have focused on the effect of nanofluids on mineral wettability, the effects of divalent and mixed salt ions were ignored; moreover, the change in mineral surface morphology after nanofluid treatment at different salinities should be measured using SEM or other methods.

2.1.5 Effect of temperature on wettability alteration

Temperature can influence mineral wettability as it influences the speed of nanoparticles, which enhances the adsorption of nanoparticles on minerals.

Al-Anssari et al. indicated that the size of nanoparticles has no effect on mineral wettability, but temperature influences the wettability, as shown in Fig. 6 [133]. The contact angle decreased with increasing immersion time.

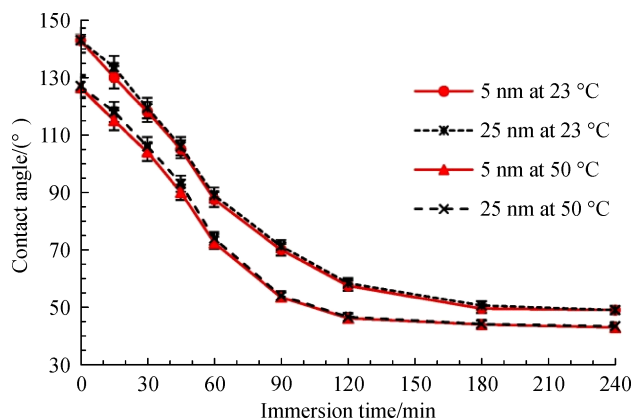


Fig. 6 Effect of nanoparticle size, temperature on the contact angle of water. Reprinted with permission from ref. [133], copyright 2017, Elsevier.

The contact angle also decreased with increase in temperature for the same immersion time. To obtain the same contact angle, the immersion time should decrease as the temperature increases.

2.1.6 Wettability alteration for different minerals

Sandstone and carbonate minerals have different properties, resulting in different behaviours of oil drops on these minerals.

Currently, several researchers have focused on sandstone oil rocks. Oil-solid interactions in sandstone oil rocks are weak, and oil is easily liberated from the solids. Conversely, the oil-solid interactions in carbonate rocks are strong; consequently, liberating oil from carbonate rocks is difficult.

Monfared et al. [175] used a mechanistic method to study the wettability alteration of sandstone surfaces by SiO_2 nanofluid. Nanoparticles can influence the wettability of minerals. The mineral surface charge (Ca^{2+} and HCO_3^{2-}) changes when immersed in deionised water. Moreover, when SiO_2 nanoparticles are in contact with water, the negative surface charge of the nanoparticles increases because of the occurrence of other negative charges [176]. The negative particles of the nanofluid approach the mineral surface and change the mineral charges, causing a significant change in the wettability [175].

Many minerals are classified as carbonate minerals. The structure of carbonate is significantly different from that of sandstone and several carbonates have high hydraulic conductivity fractures covered with low-permeability matrix blocks [177,178]; therefore, significantly less oil is recovered from carbonate minerals than sandstone. Most in situ oils remain in a porous medium; consequently, wettability alteration would be helpful in the oil recovery process [179].

2.1.7 Effect of the mixture of polymers/surfactants and nanoparticles on wettability

Polymer flooding is the process by which polymers are injected into the reservoir to recover the reserve oil. Polymers exhibit several advantageous properties, for example, they can improve the mobility ratio, which increases the oil mobility, resulting in greater oil recovery. However, polymer flooding has inherent disadvantages such as a high operating cost. Recently, nanoparticles/nanofluids have been widely used with polymers during the EOR process, which has decreased the operating costs and significantly increased the oil recovery [153].

Gbadamosi et al. studied the synergistic effect of Al_2O_3 nanoparticles and polymers (PAM, HPAM) on mineral wettability and oil recovery (Fig. 7). When the oil-wet surface was treated with HPAM, the contact angle

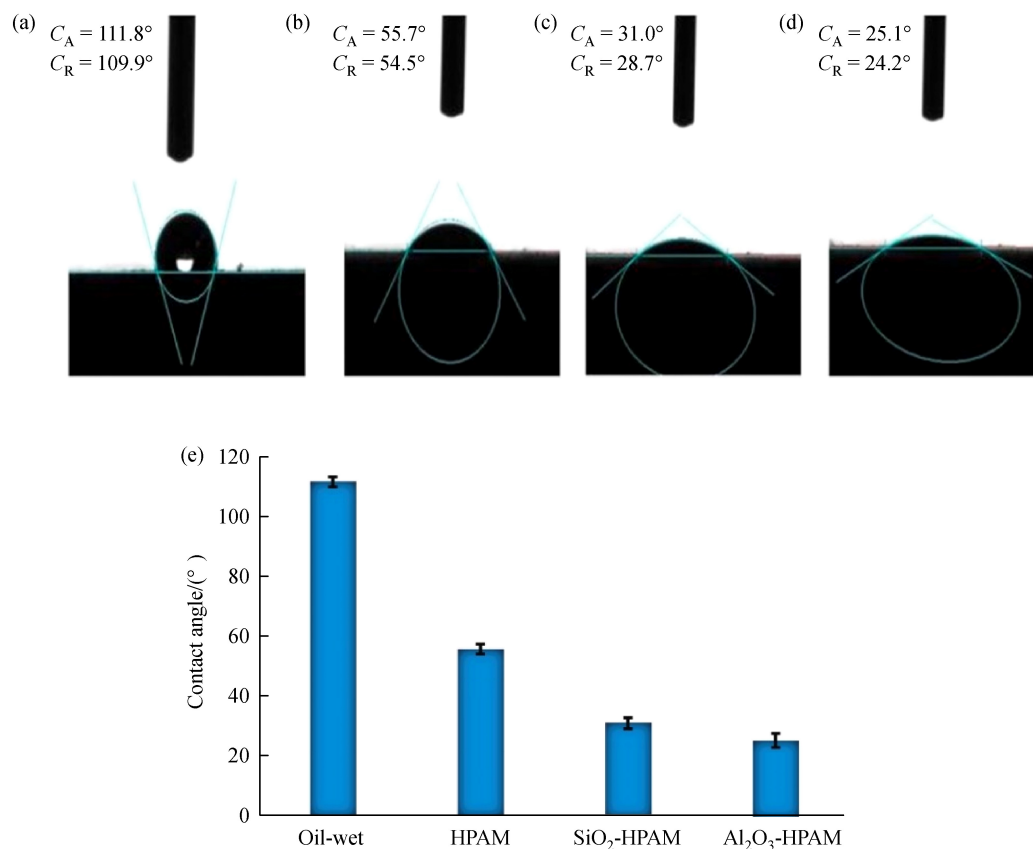


Fig. 7 Contact angle of (a) oil-wet surface, (b) HPAM, (c) SiO₂-HPAM, (d) Al₂O₃-HPAM and (e) total measurements. Reprinted with permission from ref. [156], copyright 2019, Elsevier.

decreased to 55.7°. This is because the surface changed from the oil-wet to water-wet state. The pulling and stripping effects were the primary reasons for the alteration of surface wettability by the polymers. The polymer-nanoparticle wettability alteration was due to the adsorption of nanoparticles on the rock surface.

Zhou et al. used a surfactant to modify the SiO₂ nanoparticles; then, the surface-modified nanoparticles were used to enhance oil recovery under the complex reservoir conditions (high temperature/salinity) [65].

Yekeen et al. studied the synergistic effects of nanoparticles and surfactants on the wettability alteration of rocks (Fig. 8). The nanoparticles/surfactant showed a synergistic effect in decreasing rock wettability when compared to the utilisation of only nanofluids. For different surfactants, nanoparticles/surfactants have different effects on mineral wettability.

2.1.8 Micro-mechanism of wettability alteration

A previous study showed the effect of nanofluids on the alteration of mineral wettability. However, the results were macroscopic. The detailed micro-mechanism is as follows.

Nanoparticles can be effectively adsorbed on the surface of minerals, which makes the oil-wet mineral surface

hydrophilic. The SEM (Fig. 9) and atomic force microscopy (Fig. 10) results show that nanoparticles can be adsorbed onto oil-wet mineral surfaces, thereby altering the mineral surface morphology [180]. Oil covers the oil-wet mineral surfaces that have not been treated with nanofluids. However, after nanofluid treatment, nanoparticles cover the mineral surface. As nanoparticles exhibit the property of hydrophilicity, the surface becomes more hydrophilic.

In addition to the adsorption of nanoparticles on the mineral surface, the mineral surface free energy decreases after treatment using nanofluids [181]. The mineral surface free energy is related to the surface roughness and surface chemical properties. When the mineral surface roughness increases, the surface free energy decreases. As the surface free energy decreases, the mineral hydrophilicity is correspondingly enhanced.

To explore the effect of nanoparticles on energy alteration, the effects of nanoparticles on electrostatic interaction energy, van der Waals attraction energy, hydration (structural) energy, and total interaction energy were studied [182]. The interaction energy in nanofluids is higher than that in deionised water, as shown in Fig. 11. The repulsive force between the rock and the oil in nanofluids is higher than that in deionised water. The

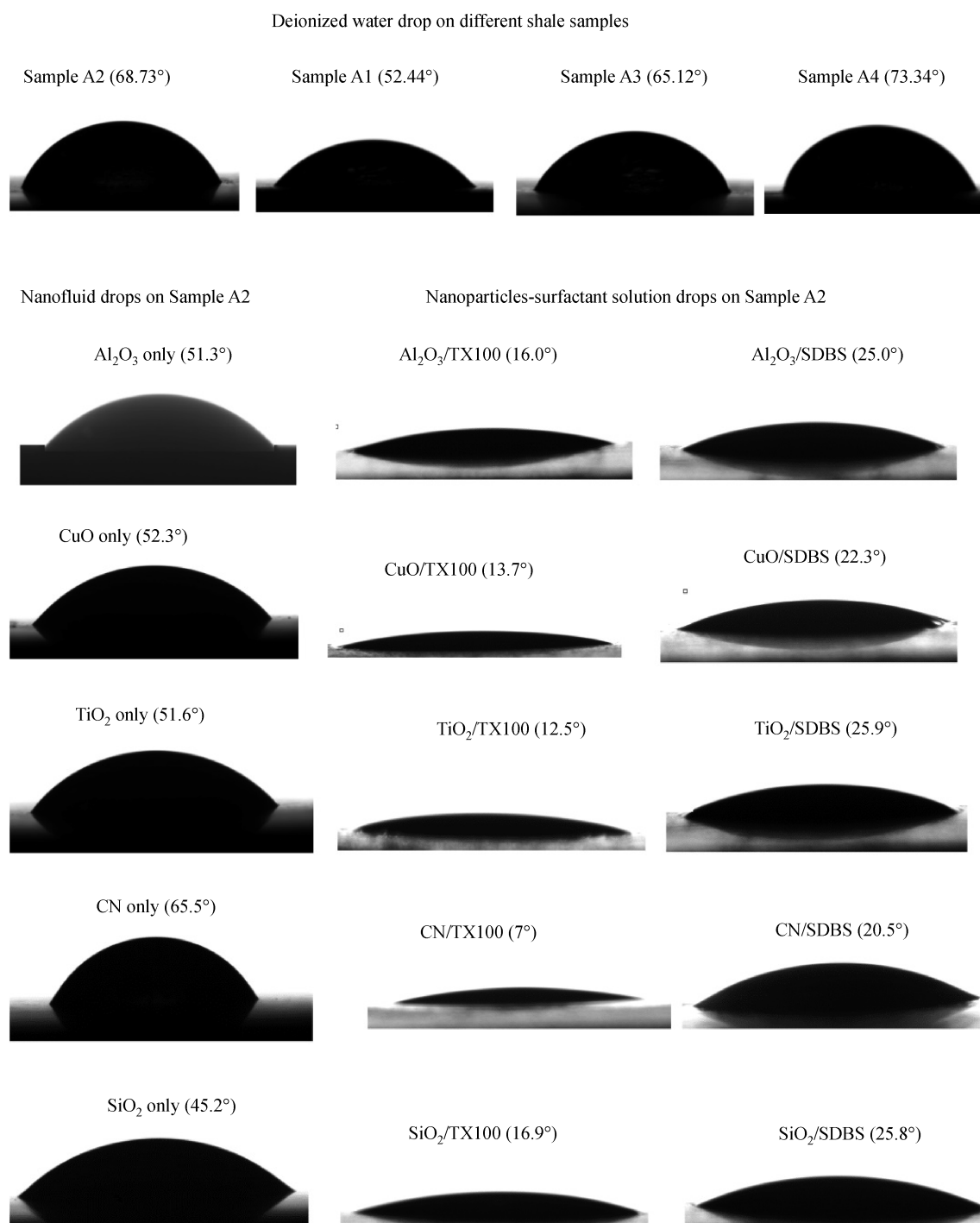


Fig. 8 Contact angle of nanoparticles, nanoparticle/surfactant mixture. Reprinted with permission from ref. [148], copyright 2020, Elsevier.

contact angle is inversely proportional to the maximum interaction energy, which represents the energy barrier against the oil attached to the rock. When the potential energy barrier increases, the stability of the water film on the rock increases, which decreases the contact angle. When the salinity increases, the water film stability decreases, and the electrostatic interaction energy in the total interaction energy decreases. Nanofluids can effectively enhance the water film stability, which results in a

more hydrophilic mineral surface. Moreover, the effect of nanofluids on wettability alteration becomes more obvious under low-salinity conditions.

2.2 Heavy oil molecule/water micromechanics: interfacial tension alteration

Interfacial tension is the force of attraction between molecules at the interface of two fluids. The oil/water

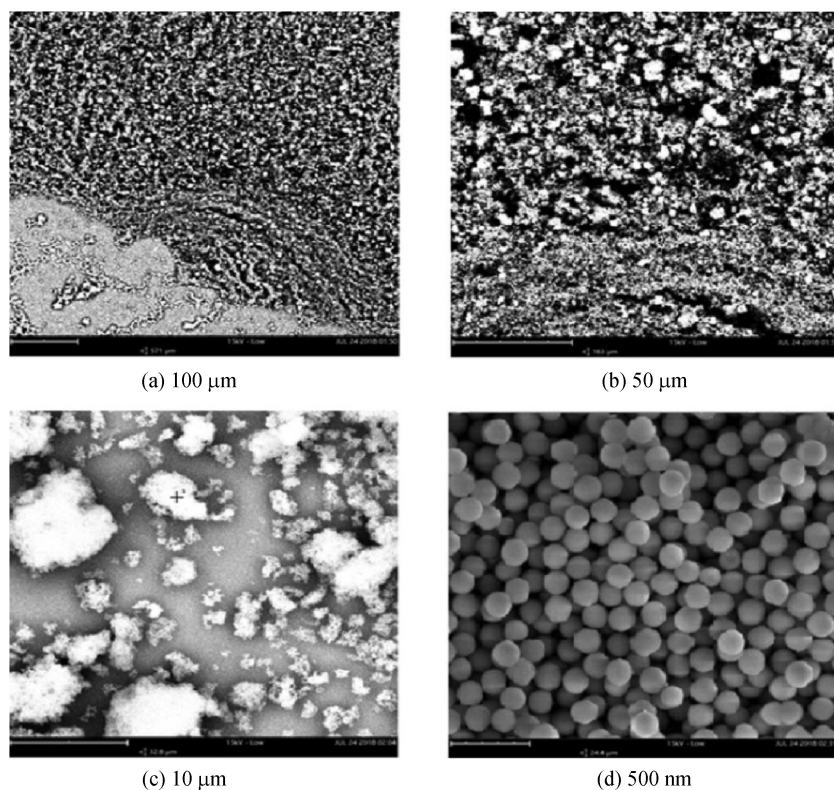


Fig. 9 SEM images after treatment with 0.1% SiO₂ nanofluid: (a) lowest magnification at 100 μm to (d) highest possible magnification at 500 nm. Reprinted with permission from ref. [180], copyright 2020, Elsevier.

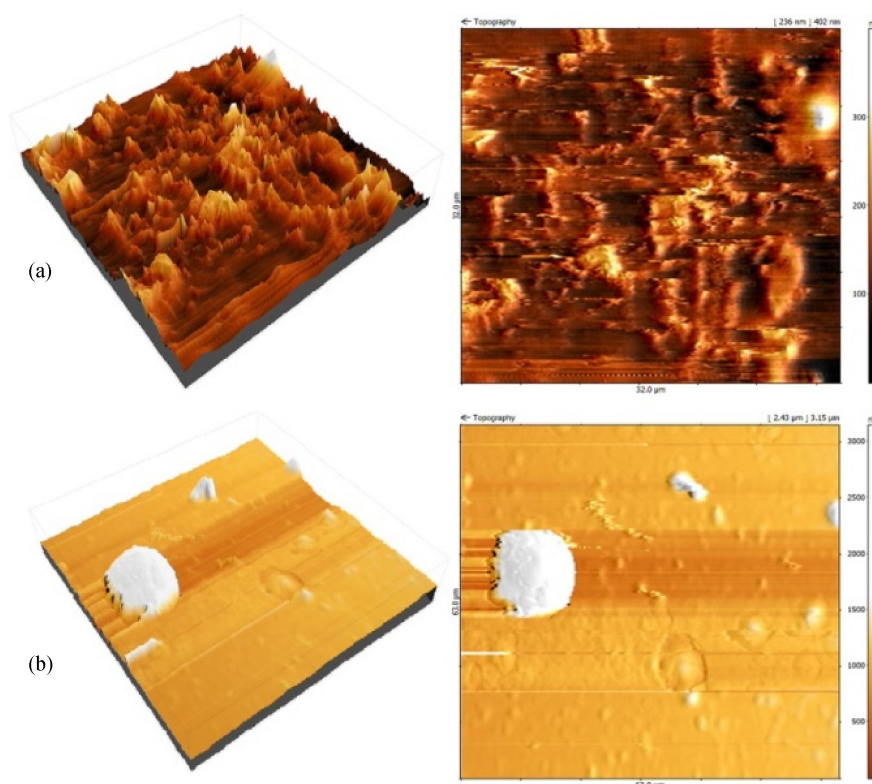


Fig. 10 Topographical images of quartz surfaces aged with (a) stearic acid ($10^{-2} \text{ mol} \cdot \text{L}^{-1}$) and (b) 0.1% SiO₂ nanofluid. Reprinted with permission from ref. [180], copyright 2020, Elsevier.

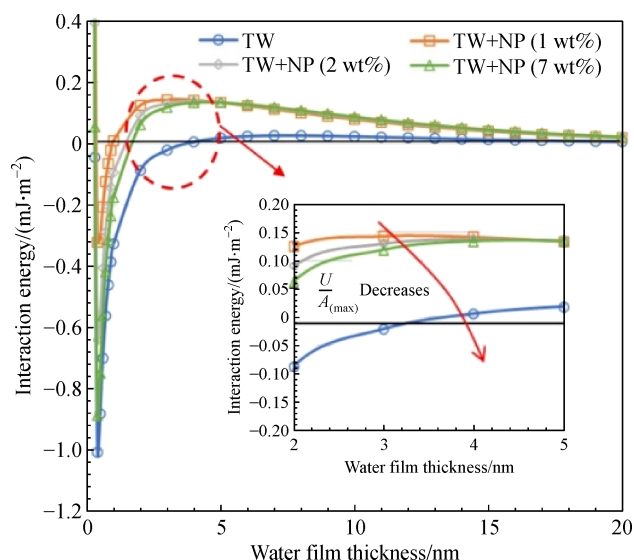


Fig. 11 Total interaction energy per unit area versus water film thickness for the rock surface-aqueous phase-oil systems when A_H (oil) = 4.5×10^{-20} J. The aqueous phases are tap water (TW) and TW + nanoparticle with different carbon nanoparticles. Reprinted with permission from ref. [182], copyright 2021, Elsevier.

interfacial tension influences oil recovery during the EOR process [183,184]. The effect of nanofluids on the oil/water interfacial tension was contradictory, as shown in Table 2.

2.2.1 Role of nanofluids in oil/water interfacial tension

Most nanoparticles can be adsorbed on the oil/water interface, resulting in a decrease in the oil/water interfacial tension [103]. However, certain studies indicated that nanoparticles could increase the oil/water interfacial tension under specific conditions [198], and their conclusions were significantly different from the traditional conclusions. Moreover, certain studies have also indicated that nanoparticles alone have no effect on the oil/water interfacial tension [186,195,215,216]. These studies indicated that the effects of nanofluids on the oil/water interfacial tension were contradictory and nonuniform.

Wu et al. synthesised SiO_2 -based amphiphilic Janus nanofluid by grafting hydrophobic chains onto SiO_2 nanoparticles, and the interfacial tension and oil recovery were studied [103]. The oil/water interfacial tension was reduced to $2.28 \text{ mN} \cdot \text{m}^{-1}$ when the Janus nanoparticles were 0.05 wt%, as shown in Fig. 12, and the oil recovery increased by 15.74% when the Janus nanofluid concentration was $100 \text{ mg} \cdot \text{L}^{-1}$. Joonaki et al. identified that Al_2O_3 , Fe_2O_3 , and SiO_2 nanofluids could decrease the oil/water interfacial tension [64]. Soleimani et al. synthesised ZnO nanoparticles through a chemical route, which could decrease the oil/water interfacial tension and increase oil recovery [154].

However, Saïen et al. indicated that the effect of

nanoparticle on the oil/water interfacial tension was related to the hydrophilicity and hydrophobicity of the nanoparticles [198]. The toluene/water interfacial tension caused by hydrophobic Al_2O_3 nanoparticles was lower than that caused by hydrophilic Al_2O_3 nanoparticles under the same conditions. The interfacial tension decreased when the hydrophobic Al_2O_3 nanoparticle concentration increased; conversely, the interfacial tension increased when the hydrophilic Al_2O_3 nanoparticle concentration increased. The reason for this occurrence can be explained as follows: hydrophilic Al_2O_3 nanoparticles are hydrated in water, resulting in an increase in the repulsive force between nanoparticles; this causes the water molecules to stay in the bulk region; consequently, a larger amount of work is required to create a novel interface surface, which results in a higher interfacial tension.

Certain researchers indicated that nanofluids have no effect on the oil/water interfacial tension [186,215]. Vignati et al. used hexamethyldisilazane to treat the SiO_2 surface; then, the effects of the surface-treated and surface-untreated SiO_2 nanoparticles on iso-octane/octanol-water interfacial tension were measured, which indicated that the nanoparticle concentration and SiO_2 hydrophobicity had no effect on the oil/water interfacial tension [215]. Saleh et al. indicated that bare SiO_2 nanoparticles do not influence the trichloroethylene/heptane-water interfacial tension [186].

The effect of the nanoparticle species on the oil/water interface is shown in Fig. 13 [208]. Biswal and Singh studied the role of 0.1 wt% SiO_2 , TiO_2 , and ZnO nanoparticles on oil/water (hexane/heptane/decane/toluene, water) interfacial tension [208]. Figure 13 shows that the interfacial tension caused by different nanoparticles demonstrated different trends.

It was observed that temperature influences the oil/water interfacial tension. Certain studies concluded that the oil/water interfacial tension decreased with increasing temperature. However, other studies have verified the existence of an optimum temperature.

Wen et al. studied the effects of nanoparticles and ions on the interfacial tension by molecular dynamic simulation [217]. The research focused on the role of ions and nanoparticles in the interfacial tension. When the temperature increased, more nanoparticles were adsorbed on the oil/water interface, resulting in a reduction in the oil/water interfacial tension. Yekken et al. [214] studied the effect of nanoparticle ($\text{Al}_2\text{O}_3/\text{ZrO}_2/\text{SiO}_2/\text{CN}$)-surfactant (CTAB/SDBS/TX-100/SDS) mixtures on the decane/water interfacial tension at different temperatures, as shown in Fig. 14. The oil/water interfacial tension decreased with the increase in temperature, because the rate at which the surfactant and nanoparticles moved from the bulk solutions to the oil/water interface increased when the temperature increased.

Saïen et al. studied the effect of magnetite nanoparticles and SDS on the *n*-hexane/water interfacial tension at

Table 2 Variation in oil/water interfacial tension caused by different concentrations of nanofluids, oil phase, and temperature

Ref.	Nanofluids type	Dispersion phase	Nanofluids concentration	Oil phase	Temperature	Interfacial tension without nanoparticle/(mN·m ⁻¹)	Interfacial tension with nanoparticle/(mN·m ⁻¹)
[185]	Hydrophilic SiO ₂	Alkyl/polyoxyethylene	—	Medium	—	31	1.7
[186]	PSS-SiO ₂	—	1–5 mg·L ⁻¹	Trichloroethylene	Ambient temperature	22.5	14.5
[187]	SiO ₂ Aerosil 200	CTAB	0.01–5	Paraffin oil	25 °C	52	5
[188]	Colloidal SiO ₂	SDS, TX-100, C ₁₂ E ₄	—	Trichloroethylene	22.5 °C + 0.5 °C	40	2
[189]	TiO ₂	Deionised water	0.1 wt%	Mineral oil	25 °C–55 °C	52	36
[190]	Colloidal SiO ₂	CTAB	1 wt%	Hexane	20 °C	72.5	21
[191]	Bi ₂ Te ₃	Deionised water	0.318 wt%	Gas-liquid	—	72	48
[192]	Gold	Deionised water	0.0218 wt%	Gas-liquid	—	72.38 ± 0.41	67.53 ± 0.66
[193]	Nonferrous metal	Sulfanole	0.001 wt%	7 cp	25 °C	10.9	1.09
[194]	Laponite/silver/ Fe ₂ O ₃	1% PVP	2 wt%	—	—	73.6	40.97
[195]	SiO ₂	Lecithin/tween 60	1%	Vegetable oil	25 °C	11	6
[196]	SiO ₂	5 wt% NaCl	3 g·L ⁻¹	Light oil	Ambient temperature	26.5	1.95
				Heavy oil		28.3	7.3
[197]	SiO ₂	Ethanol	0.4	—	Ambient temperature	26.3	1.7
[198]	Hydrophilic Al ₂ O ₃	Saturated base fluid	1–10 ⁻⁵ to 5–10 ⁻⁴	Toluene	293.2 K–323.2 K	37.1	55.7
	Hydrophobic Al ₂ O ₃						14.4
[199]	Hydrophilic SiO ₂	500 ppm SDS	1000 ppm	Kerosene	Ambient temperature	7.43	6.10
	hydrophobic SiO ₂	6000 ppm SDS				2.85	4.24
		500 ppm SDS				7.43	3.71
		6000 ppm SDS				2.85	4.64
[200]	SiO ₂	Brine	10%	Crude oil	25 °C ± 1 °C	16 ± 2	1.4 ± 0.3
[201]	ZrO ₂	Deionised water	1 g·L ⁻¹	<i>n</i> -Heptane	23 °C ± 0.5 °C	51.4	36.8
[202]	Magnetite	SDS	0–5 × 10 ⁻⁴	<i>n</i> -Hexane	288.2 K–308.2 K	51.4	41.5
[64]	Fe ₂ O ₃	Synthetic brine, propanol	0.3	Degassed reservoir oil	25 °C	38.5	2.25
	Al ₂ O ₃						2.75
	SiO ₂						1.45
[203]	SiO ₂	0.5 wt% SDS	0–2 wt% brine	Crude oil	60 °C	21.7	4.2/6.3
[139]	SiO ₂	Brine	0.05	Degassed light crude oil	22 °C	19.2	16.9
					35 °C	12.57	15.60
					50 °C	12.14	12.80
[80]	Al ₂ O ₃	3 wt% NaCl, 1 wt% PVP	0.05	Degassed crude oil	—	19.2	12.8
	SiO ₂						17.5

Ref.	Nanofluids type	Dispersion phase	Nanofluids concentration	Oil phase	Temperature	(Continued)	
						Interfacial tension without nanoparticle/(mN·m ⁻¹)	Interfacial tension with nanoparticle/(mN·m ⁻¹)
[204]	SiO ₂	Deionised water	0.1	Oil	Ambient temperature	13.62	10.69
[205]	ZrO ₂	2000 ppm SDS 3000 ppm C ₁₂ TAB	100 ppm	Heavy crude oil	25 °C	16	3.1
[206]	SiO ₂	5% NaCl	0–6 g·L ⁻¹	Crude oil	Ambient temperature	18.4	5.4
[207]	SiO ₂	SDS	1 × 10 ⁻⁴	<i>n</i> -Hexane	293.2 K	26.5	38.4
[208]	SiO ₂ /TiO ₂ /ZnO	Tween 20	0.1 wt%	Four oils	25 °C	48.9	31.2
[145]	Hydrophilic SiO ₂	PAM SDS-PAM	0.5–2 wt%	Crude oil	30 °C–90 °C	–	–
						18.03	10.22
[144]	SiO ₂	Brine	Polyethylene glycol 8000	Oil	Ambient temperature	4.9	1.12
						43	8.8
[209]	SiO ₂	CTAB	0.5–2.0 wt%	<i>n</i> -Heptane	25 °C	39	41
[210]	SiO ₂	2-Poly(2-methacryloyloxyethyl phosphorylcholine)	0.1–0.2	<i>n</i> -Decane	Ambient temperature	47	35
[211]	SiO ₂	Oly ₂ (DMAEMA)	0.1	Bitumen oil	Ambient temperature	27	14
[154]	ZnO	SDS	0.05–0.5	–	–	34.52	30.74
[212]	SiO ₂	CTAB	–	Kerosene	298.2 K	48.7	7.5
[152]	Fe ₃ O ₄	Seawater	0.01–0.03 wt%	Crude oil	25 °C	30	17.29
						26.32	14.80
						22.49	14.47
[96]	PK-Fe ₃ O ₄	Deionised water	0.2 wt%	Bitumen (10%)	Ambient temperature	14.40	8.59
[153]	SiO ₂	Xanthan gum	0.1–0.5	Crude oil	30 °C	17.8	8.54 (0.5 wt%)
						14.64	6.46 (0.3 wt%)
[213]	CuO	Deionised water	0–8 wt%	–	25 °C	72	38
[168]	NiO/SiO ₂	Deionised water	12–30 wt%	Sorush oil	–	29.02	1.28/ <1
[157]	SiO ₂ /Al ₂ O ₃	Brine	–	Heavy mineral oil	27 °C	27.5	9.3/11.5
[214]	Al ₂ O ₃ /ZrO ₂ /SiO ₂ /CN	CTAB/SDBS/TX-100/SDS	0.1–2 wt%	<i>n</i> -Decane	303 K/323 K/353 K	47.53	2.98
[103]	SiO ₂ -C ₁₂ JNPs	Brine	0.05 wt%	Crude oil	50 °C	28	2.28
[92]	Hydrophilic SiO ₂	SOS/EHAC, brine	–	<i>n</i> -Decane	25 °C to 65 °C	11.8	7.8
[165]	SiO ₂	Brine (LSW)	–	Crude oil	70 °C	6.20	2.31
[163]	SiO ₂	Brine (LSW)	0.05 wt%	Crude oil	70 °C	6.20	2.31

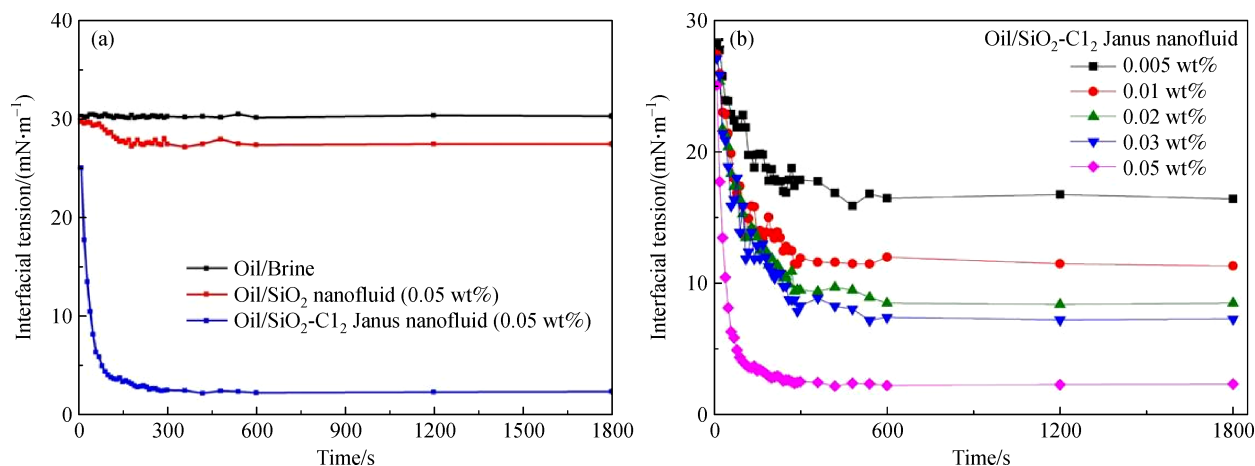


Fig. 12 (a) Dynamic oil/water interfacial tension of different systems; (b) dynamic oil/water interfacial tension of different concentrations of Janus nanofluids. Reprinted with permission from ref. [103], copyright 2020, Elsevier.

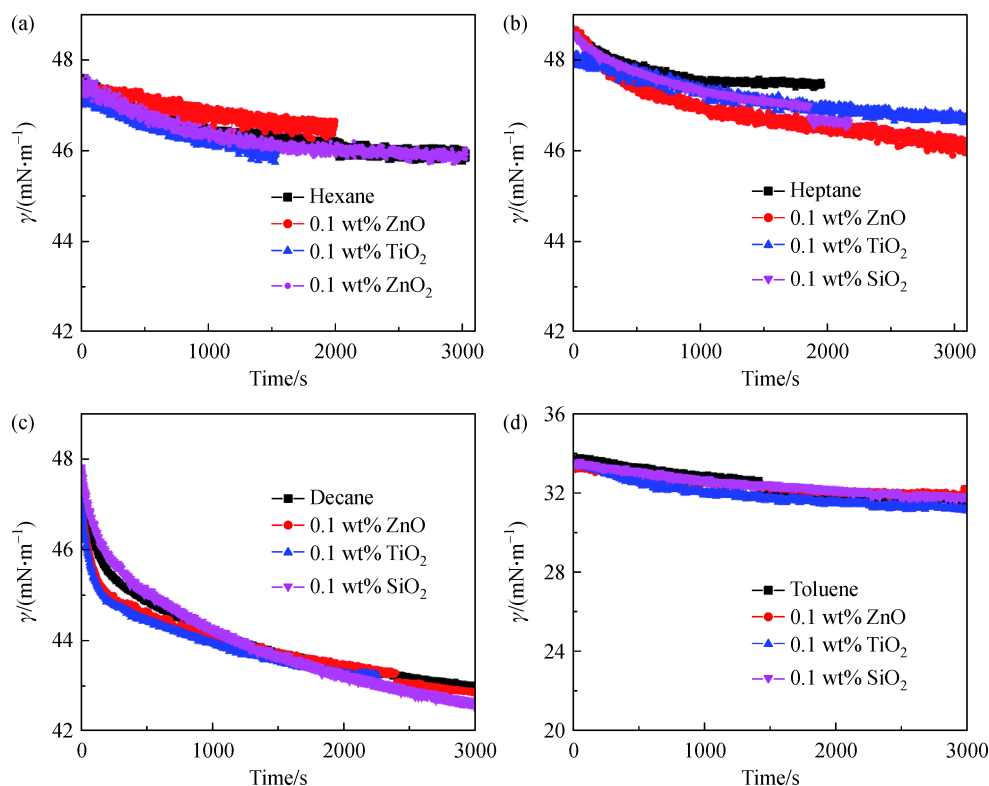


Fig. 13 Interfacial tension of different oil/water systems: (a) *n*-hexane, (b) *n*-decane, (c) *n*-heptane, and (d) toluene, in the absence of nanoparticles and in the presence of 0.1 wt% of ZnO, TiO₂, and SiO₂ nanoparticles. Standard deviations are less than 1%. Reprinted with permission from ref. [208], copyright 2016, the Royal Society of Chemistry.

different temperatures, as shown in Fig. 15. Figure 15 shows that the oil/water interfacial tension decreased with increasing temperature at a constant concentration of nanoparticles and SDS.

Ivanova et al. studied the effect of temperature on oil/water interfacial tension in a nanoparticle-surfactant system [92]; however, their results were different from

the results presented by Yekeen et al. [214] and Saïen et al. [198]. As shown in Fig. 16, the oil/water interface showed a 'V' pattern with increasing temperature for different salinities. Specifically, the oil/water interfacial tension decreased from 25 °C to 35 °C at different salinities owing to the closely packed surfactant layer formed at the interface due to the counterion screening effect. The

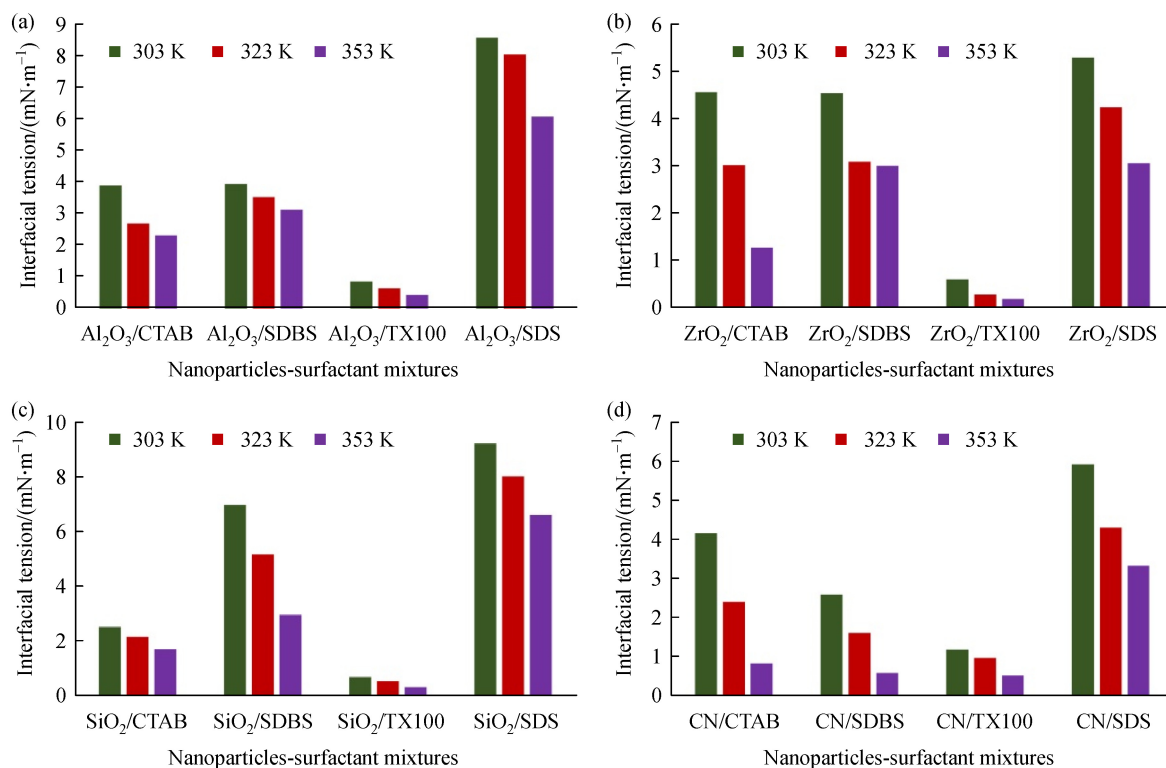


Fig. 14 Influence of temperature (303 K, 323 K, and 353 K) on the adsorption of (a) Al₂O₃-surfactant mixtures, (b) ZrO₂-surfactant mixtures, (c) SiO₂-surfactant mixtures, and (d) CNT-surfactant mixtures at decane/water interface. Reprinted with permission from ref. [214], copyright 2019, Royal Society of Chemistry.

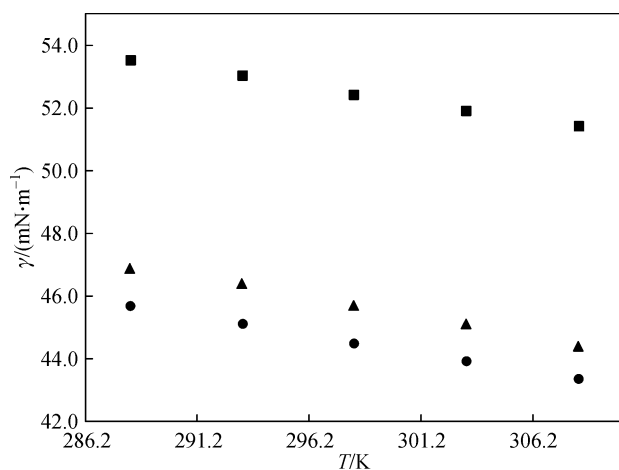


Fig. 15 Variation in interfacial tension versus temperatures: ■, only nanoparticles with a mass fraction of 1.00×10^{-4} ; ▲, only SDS with a concentration of 0.80×10^{-4} mol·dm⁻³; ●, mixture of nanoparticles with a mass fraction of 1.00×10^{-4} and SDS with a concentration of 0.80×10^{-4} mol·dm⁻³. Reprinted with permission from ref. [202], copyright 2014, Royal Society of Chemistry.

interfacial tension increased marginally from 35 °C to 65 °C; however, when the temperature increased, the oil/water interfacial tension decreased.

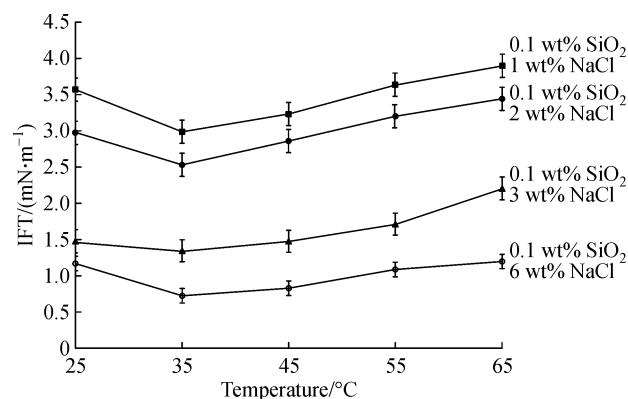


Fig. 16 Interfacial tension of *n*-decane/nanosurfactant formulations of 0.1 wt% sodium octylsulfonate and 0.1 wt% nanoparticles in different salinities as a function of temperature. Reprinted with permission from ref. [92], copyright 2020, Wiley.

2.2.2 Synergistic effect of nanofluids and surfactants on interfacial tension

Recent research indicates that nanoparticles and surfactants have a synergistic effect on the reduction of interfacial tension [218]. However, the conclusions are nonuniform, and the synergistic effect of nanofluids and

surfactants on the reduction in interfacial tension has not been verified by all researchers.

Saien and Bahrami studied the effect of modified SiO₂ nanoparticles and an anionic surfactant (SDS) on the *n*-hexane/water interfacial tension [207]. The results indicate that nanoparticles and anionic surfactants could synergistically decrease interfacial tension, which was due to the higher adsorption of nanoparticles onto the oil/water interface with anionic surfactants. The synergistic effect of magnetite nanoparticles with SDS [202] and cationic surfactant (CTAB) [212] on the reduction in oil/water interfacial tension was also obvious.

Although most studies indicated that nanoparticles and surfactants have synergistic effects on the reduction of the oil/water interfacial tension, the use of only nanoparticles can also decrease the oil/water interfacial tension; however, certain studies have indicated that nanoparticles have no effect on interfacial tension. Moghadam and Azizian studied the individual role of ZnO nanoparticles and the synergistic effect with CTAB on interfacial tension [216]. ZnO nanoparticles have no effect on interfacial tension, but ZnO nanoparticles and CTAB surfactant have a synergistic effect on the reduction of interfacial tension, which was because ZnO nanoparticles and CTAB surfactant could be adsorbed onto the oil/water interface.

Conversely, several recent studies have also indicated that nanoparticles and surfactants have no synergistic effect on interfacial tension, and nanoparticles would increase the oil/water interfacial tension when compared to using only the surfactant. Biswal and Singh [208] investigated the role of a non-ionic surfactant (Tween 20) on the oil/water interfacial tension with/without nanoparticles, as shown in Fig. 17. Figure 17 shows that the oil/water interfacial tension increased with different nanoparticles when compared to the case where only Tween 20 was used (without nanoparticles). Nanoparticles hindered the movement of Tween 20 molecules from the bulk to the

interface. This can be explained as follows: surfactants are adsorbed on the nanoparticle surface, where they would stay in the bulk phase; consequently, their tendency to move to the oil/water interface decreases, which causes the oil/water interfacial tension to increase. Thus, nanoparticles reduced the effect of Tween 20 in decreasing the oil/water interfacial tension, i.e., the excess concentration of Tween 20 at the oil/water interface decreased in the presence of nanoparticles.

Molecular dynamics simulation should be performed to analyse the synergistic effect of nanofluids and surfactants in decreasing the oil/water interfacial tension. The current experimental research on the synergistic effect presents contradictory conclusions, and molecular dynamics simulation can be used explain the process from the molecular scale.

In recent years, several studies have focused on the N-EOR using molecular dynamic simulation method [219–226]. Liang et al. [225] studied the effects of three species of modified nanoparticles (hydrophilic, hydrophobic, mixture of hydrophilic and hydrophobic) on detaching SiO₂ surface-adsorbed oil drips. The results indicated that the grafted nanoparticles could achieve greater oil liberation from the mineral surface when compared to water, and the mixture of hydrophilic and hydrophobic nanoparticles showed the optimal effect on oil detachment. Wang and Wu [221] studied the effect of charged nanoparticles on oil-drop detachment, and the results indicated that the oil drops could be completely detached from the mineral surface when the charge of nanoparticles increased to a threshold value. Moreover, the research showed that the surface wettability of nanoparticles influenced oil-drop detachment, and the charged hydrophobic nanoparticles showed the optimal effect. Li et al. [223] studied the effect of hydrophilic/hydrophobic modification of the nanoparticle surface on oil/water interfacial tension, and the results indicated that both hydrophilic and hydrophobic modifica-

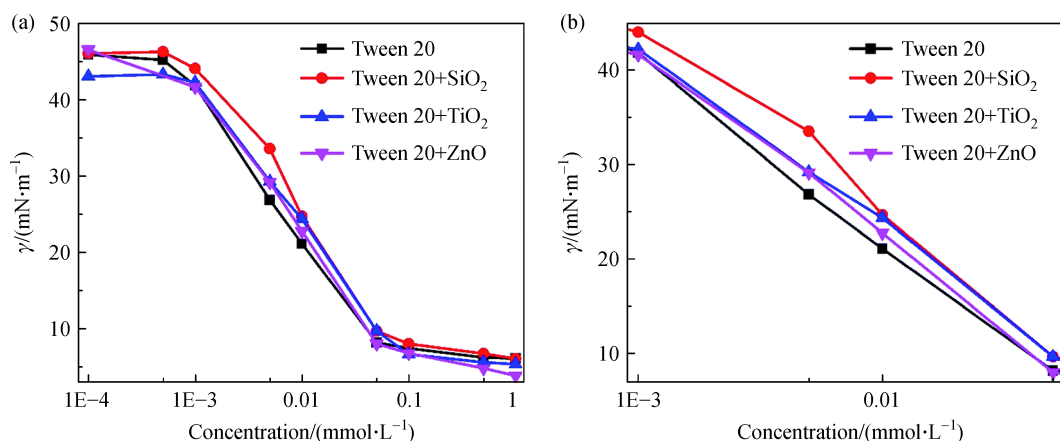


Fig. 17 (a) Equilibrium interfacial tension of Tween 20 surfactants in presence of 0.1 wt% of different nanoparticles, i.e., SiO₂, TiO₂, and ZnO at *n*-hexane/water interface; (b) interfacial tension data at the concentration range of 0.001–0.05 mmol·L⁻¹ (standard deviations are less than 1%). Reprinted with permission from ref. [208], copyright 2016, Royal Society of Chemistry.

tion of nanoparticles can reduce the oil/water interfacial tension; however, the interfacial tension value was not the determining factor. The strong interactions of the nanoparticles-oil phase, nanoparticles-minerals surface, oil-minerals surface, and oil-water influenced oil recovery. Yekshaveh et al. [224] indicated that SiO_2 nanoparticles can alter calcite wettability, and the optimal nanoparticle concentration influences oil recovery. Moreover, when the charge of nanoparticles increases, the aqueous viscosity of the nanofluids also increases, and this increase in solution viscosity helps in detaching the oil.

2.3 Heavy oil molecules/particle/surface micromechanics: structural disjoining pressure

Structural disjoining pressure is the pressure at the wedge film [227–234]. As shown in Fig. 18, the structural disjoining pressure promotes the nanofluids to move towards the boundary layer, which liberates the oil drops from the solid surface. The structural disjoining pressure is influenced by temperature, nanoparticle size, nanofluid salinity, volume fraction, particle size, and polydispersity [228,235,236].

Zhang et al. used the model fractured porous media to study the nanofluid's structural disjoining pressure on EOR [238]. The research conducted by Nikolov et al. indicates that nanoparticle layering exists between the oil droplets and minerals, which aids in the liberation of the oil from the minerals [230].

Kondiparty et al. experimentally analysed the spread of nanofluids on solids [239]. In this experiment, SiO_2 nanoparticles (19 nm) with different concentrations (5%, 10%, and 20%) were dispersed in deionised water, and the nanofluids were used to displace the oil drops from a glass

surface. The results indicated that the rate of movement of the nanofluid film was related to the nanoparticle concentration and oil-drop volume. The nanofluid film is composed of nanofluids, which promotes the liberation of oil from minerals. When the nanoparticle concentration was increased, the inner contact line rate increased. When the drop volume decreased, the inner contact line movement rate decreased. The increase in the inner contact line rate reflects the increase in the capillary pressure. The inner contact line is a unique property of nanofluids. Liu et al. proposed a novel theory to prove the structural disjoining pressure; then, they used this model to verify the dynamic spreading of nanofluids on solids [240]. It can be noted that the nanoparticles decrease in size at higher concentrations, which helps in increasing the inner contact line rate. Although structural disjoining pressure has been widely used to explain the N-EOR mechanism, this theory was only verified using light oil. No research has been conducted to observe the structural disjoining pressure of nanofluid-enhanced heavy oil.

2.4 Micromechanics of heavy oil molecules: viscosity reduction

It is well known that oil viscosity influences oil recovery during the EOR process. Oil recovery increases significantly when the viscosity of heavy oil is decreased. Nanoparticles can decrease heavy oil viscosity, and the details of the research are presented subsequently.

Patel et al. studied the effects of nanoparticles and temperature on the viscosity of heavy oil [241]. CuO , Fe_2O_3 , and NiO (0.05, 0.1, 0.5 wt%, respectively) were used to decrease the heavy oil viscosity at different temperatures. The nanoparticles could achieve a 50%–70%

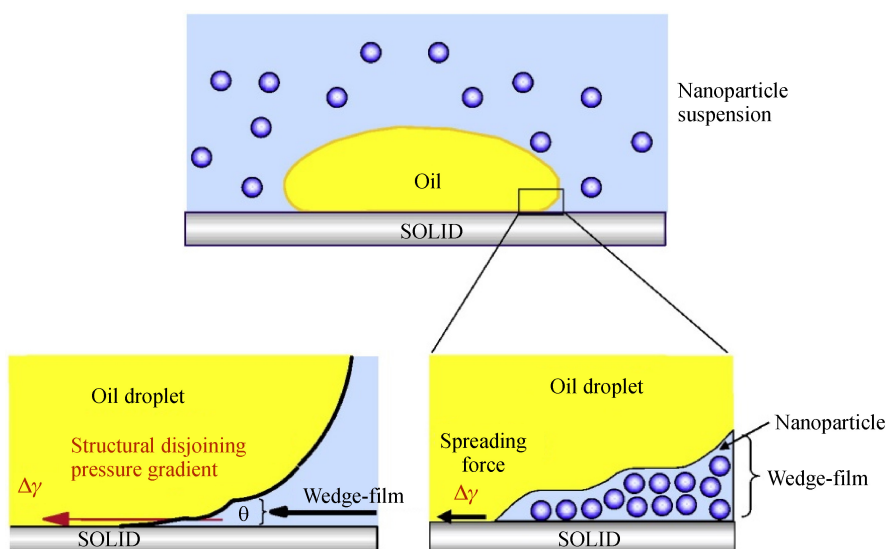


Fig. 18 Structural disjoining pressure diagram in a nanoparticle suspension. Reprinted with permission from ref. [237], copyright 2011, Elsevier.

viscosity reduction owing to the molecular-level interactions between the nanoparticles and heavy oil component. The heavy oil viscosity is influenced by the nanoparticle species, concentration, and temperature. The optimal nanoparticles for heavy oil reduction are based on the nanoparticle species and temperature. Taborda et al. studied the viscosity reduction of heavy crude oils by adding nanoparticles [242]. They identified that nanoparticles (SiO_2 , Fe_3O_4 , Al_2O_3) could decrease the viscosity of heavy/extra-heavy crude oils. When the SiO_2 nanoparticles (7 nm) were $1000 \text{ mg} \cdot \text{L}^{-1}$ at shear rates below 10 s^{-1} , the heavy oil viscosity was the lowest, and the viscosity decreased by 52%. Franco-Ariza et al. investigated the effect of nanofluids on heavy oil mobility, and asphaltenes could adsorb onto nanoparticles [243]. Asphaltenes can be adsorbed onto the nanoparticle surface, which helps in decreasing the oil viscosity.

Parejas et al. studied the temperature, nanoparticles type and concentration on decrease the heavy oil viscosity [244]. Liu et al. used nanoparticles (TiO_2 and CuO), ethyl cellulose and the quaternary ammonium salt of heptadecenyl hydroxyethyl imidazoline (QASHI) to decrease the bitumen viscosity [245]. The bitumen viscosity decreased with the addition of TiO_2/CuO nanoparticles, and the viscosity was influenced by the nanoparticle species, size, shear rate, and temperature. The decrease in the viscosity occurred owing to the adsorption of asphaltenes on the nanoparticles, which resulted in a decrease in the asphaltene content in heavy oil, leading to a reduction in oil viscosity. Moreover, the surfactant (QASHI) also causes a decrease in the bitumen viscosity. Nanoparticles and surfactants have a synergistic effect on the reduction of bitumen viscosity (Fig. 19) as surfactants can decrease the resin and asphaltene aggregates. Different nanoparticles have different effects on the reduction of heavy oil viscosity, as shown in Fig. 20.

Although several studies have indicated that nanoparticles can decrease the oil viscosity, there is a lack of an in-depth mechanism to analyse this reduction. The phenomenon of asphaltene adsorption on the nanoparticle surface was only inferred from the reduction in viscosity, and was not verified directly through experiments. There is significantly limited research on the effect of nanofluids on the reduction of oil viscosity; moreover, the properties of nanoparticles and nanofluids have several differences, which must also be considered for further analysis.

3 Nanofluid-assisted EOR method

3.1 Nanofoam technology

Gases such as CO_2 , N_2 , CH_4 , H_2S [246,247] can be injected into the subsurface reservoirs to push oil out of the pores [248]; this method has been widely used in the EOR process [249]. The gas injection method can solve the

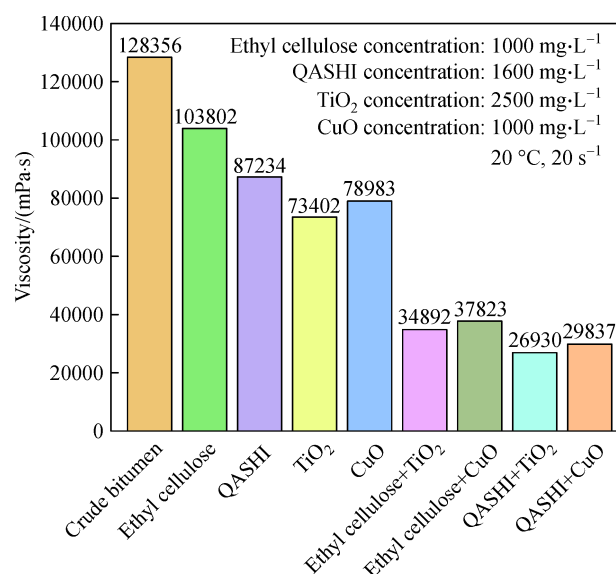


Fig. 19 Synergistic effect of nanoparticles and surfactants. Reprinted with permission from ref. [245], copyright 2020, Royal Society of Chemistry.

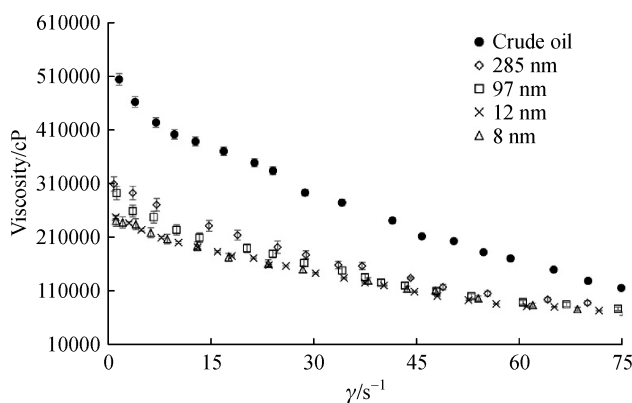


Fig. 20 Viscosity of heavy oil in the absence and presence of S8, S8A, S8B, A135, and F97 nanoparticles at $1000 \text{ mg} \cdot \text{L}^{-1}$, 298 K , with a shear rate ranging between 0 and 75 s^{-1} . Reprinted with permission from ref. [242], copyright 2017, American Chemical Society.

problems related to capillary and viscosity forces, and the gas can effectively sweep the residual oils [249,250]. Among these gases, CO_2 is widely used in the EOR process because it is non-flammable and nontoxic [251]. However, during the gas injection process, gas channelling problems exist [252], which results in a lower sweep efficiency and limited gas injection efficiency [253,254].

The foam flooding method was proposed for EOR as it can inhibit gas displacement caused by viscous fingering [246]. To overcome these drawbacks, a co-injection of gas and surfactant solution was used to produce foam to reduce the gas mobility and improve the oil-sweep efficiency [255]. However, foams are thermodynamically unstable

(kinetically stable); this instability became more obvious under large-scale application or in extreme conditions, and the application is subject to multiple limitations [256,257]. Several factors influence the foam flooding process, such as surfactant species, reservoir species, temperature, aqueous-phase environment (salinity, pH), properties of the oil, pressure, wettability, and surface adsorption [249].

The reservoir oil can decrease the foam stability because oil drops can spread through the gas/liquid interface in the foam lamellae. However, if the residual oils create a stable film in the surfactant, the foam stability can be increased [249]. In addition, many methods have been used to cooperate with surfactants to overcome the breakable property of surfactant-stabilising foams, which can cause a reduction in the surfactant adsorption and improve foam stability. In recent years, stable nanoparticle-surfactant foam systems have been widely used for EOR [258]. The superior performance of these systems can be attributed to the small size of the nanoparticles [259], which can result in their easy movement through rock pores; consequently, nanoparticles could remain stable under reservoir conditions (high temperature, high salinity) [250].

Nanoparticles can be adsorbed on oil/water interfaces, and their roles are similar to those of surfactants [260]. Rafati et al. indicated that emulsified oils were adversely affected by foam stability, even when the system included surfactants [261]. Mobility influenced the foam flooding process, and the results indicated that surfactant solutions could decrease the oil and gas mobility in porous media [262]. It was observed that nanoparticles alone can effectively enhance foam stability, because they could modify the oil/water and oil/solid interfaces; consequently, they could easily pass through the pore-throat structure [263].

Many studies have focused on the synergistic effects of nanomaterials and surfactants on stabilising the foams [263,264]. Manan et al. [248] used SiO_2 , Al_2O_3 , TiO_2 , and CuO nanoparticles to stabilise alpha olefin sulfonate foams at different concentrations, and all the aforementioned nanoparticles could improve foam stability, of which Al_2O_3 nanoparticles showed the optimal effect. Yekeen et al. [265] showed that nano $\text{Al}_2\text{O}_3/\text{SiO}_2$ -SDS could make the foam thicker than only SDS. Li et al. [266] showed that a CTAB- SiO_2 aqueous system could increase the SiO_2 nanoparticles surface hydrophilicity, which could increase the half-life of the foam. Different nanoparticles (SiO_2 , Al_2O_3 , TiO_2 , CuO , ZrO_2 , and CaCO_3) and surfactants demonstrated obvious synergistic effects on the stabilising foam. Rafati et al. [267] showed that CaCO_3 , BaSO_4 , and SrSO_4 could improve the thermodynamic stability of foam.

Surfactants can be adsorbed onto the surface of nanoparticles, which increases the surface hydrophobicity of the nanoparticles; consequently, the nanoparticles can move easily in the gas/liquid interface. Surfactants can also be adsorbed on the gas/liquid surface dynamically, that is,

surfactants are desorbed at the same time. In contrast to surfactants, nanoparticles are irreversibly adsorbed onto the gas/liquid interface, and foam coalescence becomes slow, which makes the foam more stable [268].

Bashir et al. [249] studied the effect of nanoparticles and polymers on foam stability, and the results indicated that high nanoparticle and polymer concentrations were beneficial for foam stability, and this effect was observed in high-temperature and high-salinity conditions. Nanoparticles and surfactants/polymers show an obvious synergistic effect in stabilising foams [269]. On one hand, surfactants/polymers molecules are adsorbed onto the nanoparticle surface owing to electrostatic repulsion, van der Waals forces, and supplementary steric repulsive forces, and the adsorption effect improves the dispersion stability of nanoparticles in the aqueous phase. On the other hand, nanoparticles and surfactants can control the interface properties, and the polymer can control the foam structure. Therefore, polymers can increase the foam viscosity; then, the nanoparticle settling rate decreases and the foam becomes more stable [257].

Nanoparticle surface modification can enhance foam stability, which improves foam flooding efficiency [250]. Yekeen et al. [265] indicated that when the surface hydrophobicity of nanoparticles was increased, the foam stability was enhanced. Singh and Mohanty [270] indicated that when polyethylene glycol was used to modify SiO_2 nanoparticles, the foam stability increased, resulting in an increase in the oil recovery. Rahmani [253] used CH_3 -coated SiO_2 nanoparticles to stabilise CO_2 foams, and the results showed that when SiO_2 nanoparticles were coated with CH_3 , the hydrophobicity was improved, and the foam stability was enhanced. Rezvani et al. [271] indicated that nanocomposites ($\text{Fe}_3\text{O}_4/\text{SiO}_2$, $\text{Fe}_3\text{O}_4/\text{TiO}_2$, $\text{Fe}_3\text{O}_4/\text{chitosan}$) showed a better effect on the reduction in oil/water interfacial tension and foam stability when compared to the unmodified Fe_3O_4 nanoparticles.

In conclusion, nanoparticles could increase the stability of the foam, and the reasons are as follows: 1) A large amount of adhesion energy exists between the nanoparticles and thin liquid films such as foam films, which prevents the foams from coalescing with each other. 2) Because nanoparticles can adsorb and aggregate between the bubbles in thin liquid films, nanoparticles can increase the lamellae thickness, which helps in improving the foam stability. 3) Nanoparticles can decrease the liquid drainage from foam lamellae as well as the gas/liquid interfacial tension and gas/liquid interface capillary pressure, resulting in an increase in the foam stability.

3.2 Nanoemulsions for EOR

In recent years, several researchers have focused on emulsions in the EOR process [105,272–275]. Certain researchers used emulsions to store heavy oil; then, the

demulsification process was used to obtain the oil. Asphaltene can stabilise emulsions, and certain methods have been used to break emulsions [276,277]. Nanoparticles can stabilise emulsions because nanoparticles can be adsorbed on the oil/water interface. These films prevent droplet coalescence, resulting in more stable emulsions.

During N-EOR processes, Pickering emulsions that are stabilised by nanoparticles have been extensively studied. Temperature, aqueous-phase environment, and nanoparticle properties influence the stability of oil/water emulsions. The formation of emulsions can help the nanofluids to flow through low-permeability zones, which increases the entrapped oil. The wettability of nanoparticles also influences the stability of emulsions. When the contact angle of nanoparticles varies significantly from 90° , the adsorption of nanoparticles increases, resulting in more stable Pickering emulsions. When the nanoparticles are hydrophilic, they are easily dispersed in the aqueous phase, resulting in the occurrence of oil-in-water emulsions. However, hydrophobic nanoparticles are easily dispersed in the oil phase, resulting in the occurrence of water-in-oil emulsions. The emulsion type is influenced by the oil polarity, hydrophilic/hydrophobic nature of the nanoparticles, and the amount of oil or water phase. The wettability of the nanoparticles also influences the properties of emulsions, which can be altered by physical and chemical modifications.

Sharma et al. studied the effect of nanoparticles on stabilising oil/water emulsions with polymers, which were then used to enhance oil recovery [278]. The stabilisation of Pickering emulsions was influenced by nanoparticles, surfactants, and polymers. The results indicated that the polymer and Pickering emulsions could increase the oil recovery by 1%–6%, and the nanoparticles could stabilise the emulsions; moreover, it was also observed that the Pickering emulsions were effective in the EOR process.

3.3 Reduction of the injected fluid mobility ratio

Injected fluid mobility is the relative permeability of the injected fluids to its viscosity, which influences oil recovery. When the viscosity of the injected fluid is higher than that of oil, the mobility control is good, and the oil recovery benefits from the superior mobility control. When the mobility control is poor, the oil recovery decreases because of viscosity fingering. Good mobility control can be achieved by several mechanisms.

To obtain an optimal mobility control, the viscosity of the injected phase should increase in the emulsion form. Nanofluids can increase the viscosity of injected liquids, and several researchers have focused on this direction of research. Nanoparticles can increase the viscosity of the foams or emulsions because they are adsorbed onto the oil/water interface, thereby resulting in good mobility control. This results in an increase in oil recovery.

4 Multiscale multiphase pore/core displacement experiment

In recent years, several researchers have focused on multiscale, multiphase pore (core) displacement experiments in N-EOR processes, and the behaviour of nanofluids during the multiphase displacement process has been extensively studied.

The nanofluid flow and transport influence the oil recovery and oil properties during the N-EOR process. Different parameters, such as porosity of the structure, evolution, electrochemical change, change in bacterial effects, diffusivity, and permeability changes, can influence the properties of porous media. The nanofluids that are transported into the porous media are influenced by the properties of the aqueous solution, oil phase, and porous media. During multiphase displacement, the interaction forces influence the nanoparticle and oil phase behaviours, where the interaction forces include electrostatic, structural, and van der Waals forces.

Apart from the interaction forces, wettability is still a key parameter which influences multiphase flow efficiency, relative permeability, capillary pressure, and residual oil. The wettability index influences fluid distribution and the oil phase, which influences oil recovery. The wettability of the porous media was identified to influence the multiphase flow characteristics, sweep efficiency, and residual oil distribution. Reservoir wettability influenced oil recovery during the multiscale, multiphase pore displacement process, where the sandstone rocks were in the water-wet state and the carbonate rocks were in the oil-wet state. Immiscible multiscale, multiphase displacement can be divided into imbibition and drainage. When the non-wetting phase is injected into the pore, the process can be classified as the drainage process; the opposite process is termed as the imbibition process. During the multiphase flow process, the wetting phase forms films around the rocks and pores, and the non-wetting phase remained in the centre and formed continuous pores. To study the multiphase flow displacement mechanisms, experimental work (micro-computed tomography, micro-CT) can be used, which can aid in building the pore geometry and fluid distribution model.

From previous studies, it was noted that, although nanofluids could effectively alter mineral wettability and oil/water interfacial tension, the nanoparticle transportation property performed an important role during the multiphase core displacement process. Nanoparticles can be transported into porous media, and the process is influenced by the nanoparticle concentration, injection rate, salinity, and temperature. When nanoparticles are transported into the porous media, surface deposition, mono-particle pore-throat plugging, and multi-particle pore-throat plugging influence the transportation efficiency. Surface deposition indicates the adsorption of

nanoparticles on the rock surface; this process is influenced by salinity, pH, and other factors, which influence the electrostatic attraction and electrostatic repulsion. In mono-particle and multi-particle pore-throat plugging processes, large mono-particles or multi-particles plug the pore throat, respectively, which influences oil recovery. When the oil and water phases are injected into bead packs, the bead packs influenced the residual saturations and fluid distribution, which performed an important role during the multiphase core displacement process.

When compared to other nanoparticles, transition-metal nanoparticles can effectively transfer the reservoir rock surface. Nanoparticle dispersion stability influences nanoparticle transportation in porous media. When nanoparticles are aggregated together, the nanoparticle size increases significantly. Different nanoparticles had different charges; for instance, SiO_2 nanoparticles have a negative charge, whereas Al_2O_3 nanoparticles have a positive charge. Nanoparticles are adsorbed onto the rock surface, which influences the nanoparticle utilisation. When nanoparticle surfaces are modified by other functional groups, surfactants can stabilise the nanofluids.

Cheng et al. [279] used the micro-CT method to investigate the remaining oil characteristics on a pore scale, and the remaining oil flow behaviour in porous media was investigated. They studied the size distribution of the remaining oils at different flow rates through an *in situ* micro-CT method. Moreover, they explored the changes in the morphology of the remaining oils, behaviour of the microscopic remaining oils in the pores, and EOR mechanism at different flow rates. During the multiscale, multiphase core displacement process, the rock properties (permeability, porosity, compressibility), fluid properties (density, viscosity), and rock-fluid interactions (capillarity and wettability) were observed to influence oil recovery, in different multiphase fluid processes. Among other parameters, the capillary pressure, relative permeability, oil saturation, water saturation, and other parameters influenced the permeability effect.

5 Multiphase flow fluid–solid coupling simulation

In recent years, several researchers have proposed numerical models to study multiphase flow in a fluid–solid coupling model and analyse the relationship between capillary pressure, relative permeability, and water saturation [280]. Moreover, a mathematical model could be used to explain nanoparticle transport in heterogeneous media. Nanoparticles can be retained in the porous media, which influences oil recovery, and the mechanism can be divided into surface deposition, mono-particle plugging, and multi-particle plugging. Therefore, a model to explain the damage should be proposed. Various simulation software programs were used to simulate the EOR process, and gas,

brine, and chemicals were injected, which could increase oil recovery. These simulations explained the N-EOR process and multiphase fluid flow (porous media).

Ali et al. [280] studied the behaviour of nanofluids during a two-phase flow process using micro-CT and molecular dynamic simulation. The results showed that nanofluids could effectively alter the sandstone wettability in brine solution. In this study, nanofluids (in brine) were used to enhance oil recovery from the porous sandstone structure; then, *in situ* micro-CT was used to observe the behaviour of oil drops, and the capillary pressure, relative permeability, viscosity, and density were measured. The simulation results showed that the BiFeO_3 nanofluid could effectively alter the wettability of the porous medium when compared to other nanofluids, and BiFeO_3 nanofluids showed higher relative permeability and capillary pressure. Abdelfatah et al. [281] built a corresponding mathematical model, and the model was used to characterise nanoparticle transport in porous media.

6 Opportunities and challenges

Currently, nanofluids are widely used in the EOR process, and the corresponding mechanisms have been reviewed. However, there are some opportunities and challenges in the N-EOR process: 1) Nanoparticles can easily aggregate under reservoir conditions (high temperature, pressure, and salinity). The instability of nanofluids limits their industrial applications. Therefore, researchers should study high-stability nanofluids using novel methods. The synthesis of nontoxic nanoparticles should be focused on, and highly efficient nanoparticles should be developed. 2) Nanoparticles of different species cause environmental pollution, and certain specific nanoparticles are harmful to the human body, which are easily inhaled into the lungs. Therefore, research on biological hazards should be conducted. Moreover, the cost of nanofluids should be evaluated before industrialisation. Limitations in recycling nanoparticles has limited its industrialisation. 3) The analysis of N-EOR theory is limited, and mathematical simulations of N-EOR should be performed, which can solve the challenges in the N-EOR mechanism. For surfactant/polymers-based N-EOR process, mathematical models can help researchers understand the oil recovery mechanisms, and the different mechanisms can be connected together. 4) The adsorption of nanofluids on minerals should be explained. This adsorption is influenced by the rock type, temperature, and salinity; however, these mechanisms are unclear. 5) Although nanofluids have been widely used to enhance oil recovery at the experimental scale, no field trial of N-EOR has been published. At the field scale, nanoparticles would be transported in a porous media; however, research on nanoparticle transport in porous media is limited. The research should focus on the transport of nanoparticles/surfactants/polymers in porous media, the molecular

dynamic simulation and mathematical modelling of nano-particle transport through porous media should be studied; such a research will be helpful for industrialisation.

7 Summary and conclusions

In this review, N-EOR mechanisms were systematically studied, and future research directions for these mechanisms were proposed. The detailed summary and conclusions are as follows: 1) Nanofluids perform an important role in heavy oil molecules/particle/surface systems. Nanofluids can alter the wettability of minerals (particle/surface micromechanics), oil/water interfacial tension (heavy oil molecules/water micromechanics), structural disjoining pressure (heavy oil molecules/particle/surface micromechanics), and viscosity reduction (micromechanics of heavy oil molecules). 2) Nanofluids can alter minerals wettability as they are adsorbed onto the minerals. When the minerals become water-wet, the oil recovery increases. The wettability of the minerals is influenced by the nanofluid concentration, nanoparticle size, temperature, and surfactant concentration. Nanofluids can be adsorbed onto the oil/water interface, which alters the oil/water interfacial tension and enhances oil recovery. However, the role of nanoparticles in oil/water interfacial tension is unclear; certain studies have indicated that nanoparticles can decrease the oil/water interfacial tension, while other results have indicated that nanoparticles increase or have no effect on the oil/water interfacial tension. The viscosity reduction is due to the asphaltene adsorbed onto the minerals; when the asphaltene content decreases, the oil viscosity decreases, and oil recovery is increased. 3) Structural disjoining pressure is another theory in the N-EOR process, where the structural disjoining pressure liberates the oil from minerals; this can significantly increase oil recovery. The experimental and theoretical analysis of structural disjoining pressure has indicated these results. 4) Nanofluids also perform an important role during the multiscale, multiphase core displacement experiment, which have been indicated through simulations.

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