Effect of SiO₂ nanoparticles + 1-dodecyl-3-methyl imidazolium chloride on the IFT and wettability alteration at the presence of asphaltenic-synthetic oil

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Abstract
Using nanoparticles (NPs) in different industries such as enhanced oil recovery processes increased during the past decade due to its significant effects on the wettability alteration and IFT reduction to some extent. On the other side, ionic liquids (ILs) are proposed a new class of solvents that introduce considerable advantages in different areas of sciences. In this way, a hybrid method based on the NPs and ILs is proposed in the current investigation. So, silicon dioxide (SiO₂) as one of the most effective NPs on the wettability alteration and 1-dodecyl-3-methyl imidazolium chloride ([C₁₂mim][Cl]) as a new class of surfactants are used to find their effects on the interfacial tension (IFT) reduction and wettability alteration at the presence of asphaltenic synthetic oil for the first time. In this way, the stability of SiO₂-NPs at the presence of and absence of IL is examined which revealed stability of SiO₂-NPs for more than one month at the presence of IL while fast precipitation was observed if no IL existed in the solution. After that, the effect of IL and SiO₂-NPs on the IFT reduction and wettability alteration is investigated by changing the concentration of these chemicals between 0 and 2000 ppm and ranging the asphaltene content between 2 and 10%wt. The results revealed that for all of the examined concentrations of IL and asphaltene fraction, reduction in IFT is inevitable as the concentration increases. Besides, the results demonstrate that there is a threshold value for asphaltene content (6%wt) in which for the values below or higher than this threshold, the effect of IL on the IFT reduction reduces leading to the vanishing of a sharp reduction in IFT and determining a distinguished critical micelle concentration (CMC). According to findings, for asphaltenic synthetic oil (ASO) with 6%wt asphaltene content CMC value of 250 ppm is obvious while for the other ASO, no obvious and distinguished CMC values exist. Moreover, the results reveal that the IFT reduces to the value of 0.48 mN/m as the IL concentration increases to 2000 ppm while the asphaltene content is kept constant at 6%wt. Further IFT measurements demonstrate the negligible effect of SiO₂-NPs on the IFT reduction while the concomitant existence of SiO₂-NPs and IL with the concentration of 1000 ppm moves the wettability of the rock surface toward strongly water-wet with contact angle (CA) of 33.1°. The worth mentioning point is that the entire amount of reduction in the CA from 156.3° (initial condition) to 33.1° at the presence of hybrid solution is not completely due to the presence of SiO₂-NPs and it is the cumulative effect of IL and SiO₂-NPs presence. Finally, several core flooding experiments are performed using different chemical formulations which reveal that using a hybrid solution of SiO₂-NPs + IL with a concentration of 1000 ppm for each chemical increases the tertiary oil recovery to 15.2%wt based on OOIP for the ASO/formation brine with asphaltene content of 10%wt.

Keywords Asphaltene · Synthetic oil · SiO₂-NPs · Ionic liquid · Wettability alteration · IFT reduction · Tertiary oil recovery

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Introduction

In the light of its unique characteristics nanoparticles (NPs) were widely used in EOR industries for IFT reduction, (Ju et al. 2006; Torsater et al. 2012; Zaid et al. 2013), changing the wettability of rock surface toward water-wet condition (Al-Anssari et al. 2016; Saien and Gorji 2017), viscosity modification and even enhancing the swelling factor of the crude oil (Ehtesabi et al. 2015; El-Diasty and Ragab 2013; Kazemzadeh et al. 2015; Mohammadi et al. 2017; Taborda et al. 2016, 2017; Wei et al. 2007), producing nano-emulsion (Bobbo et al. 2012), selective pore plugging (Anganaei et al. 2014; Hashemi et al. 2013), and disjoining pressure (Aveyard et al. 2003; McElfresh et al. 2012), or even increasing the thermal conductivity of the rocks using metal-based NPs. Using NPs is of great interest since they can activate multiple mechanisms including wettability alteration, IFT reduction, and disjoining pressure which means better sweep efficiency (McElfresh et al. 2012; Zamani et al. 2012). The other important features of NPs is their transportation capability through the porous media comes from their small sizes which keep them dispersed in the reservoir fluids and make it easy their movements through the pore networks (Rodriguez Pin et al. 2009). According to these unique features, application of NPs for IFT reduction, wettability alteration, etc., were proposed and examined through the EOR industries (de Castro Dantas et al. 2017; Moradi et al. 2015; Suleimanov et al. 2011).

For example, Onyekonwu and Ogolo (Onyekonwu and Ogolo 2010) investigated the potential of polysilicon NPs (PSNP) such as lipophobic and hydrophilic (LHPN), and hydrophilic and lipophobic (LHPN) through EOR processes considering the wettability alteration as the main effective mechanism. Also, Hendraningrat et al. (Cheraghian and Hendraningrat 2016; Hendraningrat et al. 2013a, 2013b, 2013c; Torsater et al. 2012) claimed that using silica-based NPs have considerable influence on the rock surface wettability which can modify the oil recovery factor. Moreover, Mohammadi et al. (2014) selected the aluminum oxide nanoparticles (Al$_2$O$_3$-NPs) as an EOR agent for the sandstone reservoir. After that, Tarek (2015) examined a method which was using a combination of different types of NPs instead of using individual type of NPs. In detail, Tarek reported that using a mixed solution of different NPs such as Al$_2$O$_3$, iron oxide (Fe$_2$O$_3$) and SiO$_2$ is more efficient than the solution includes comprised only one type of NPs.

According to these findings and fast growth of using NPs in the different industries, a new NPs-based approach was appeared after 2000, which is the NPs chemical effects for EOR purposes instead of their application through thermal-based technique (Cheraghian and Hendraningrat 2016; Sheng 2010). In this way, the current investigation is designed to find the probable application of SiO$_2$-NPs for tertiary oil recovery purposes by examining its effect on the wettability alteration, IFT reduction and tertiary oil recovery through core flooding experiments. The point is that, unfortunately, using NPs suffers a major drawback which is the fast precipitation of NPs in most of the cases at the absence of chemical stabilizer which are usually chemical surfactants. In this way, selection of proper surfactant is the other important aspect of using NPs for successful EOR purposes. Among the different possible surfactants, using IL-based surfactants from imidazolium or pyridinium families are of great interest during the past decade due to their unique features, especially their stability at the harsh salinity and thermal condition.

In general, ILs are a new substitution of conventional chemicals since they can provide unique characteristics such as lower melting and glass transition temperature (Dharaskar Swapnil 2012; Domańska 2005), are cost-effective and commercially available (Chen et al. 2014), are non-flammable, and have a wide range of solubility and miscibility (Lee and Kim 2013; Martins et al. 2014; Peng et al. 2011), especially for the researchers who are seeking for green solvents. Since these chemicals are comprised of two different sections (cationic and anionic groups), it is possible to tailor any type of IL with a specific characteristic that makes them a good candidate for different industries. In detail, ILs are molecules that can be tuned for any specific application such as EOR by changing the numbers of anions and cations combination (José-Alberto and Jorge 2011; Khupse and Kumar 2010).

For example, Smit et al. (1991) and Hezave et al. (2013c) reported similar outcomes regarding the surface activity of ILs especially if they are utilized in aqueous solution with high salinity. In detail, they have claimed that as the cationic IL are dissolved in saline water, neutralize the positive charges of cationic ILs can be neutralized by negatively charged ions resulting in the accumulation of ILs molecules at the oil–water interface leading to low IFT values. But the point that must be considered is that the IFT reduction using ILs is not low enough to consider the IFT reductions a significant mechanism for oil recovery since they can only reduce the IFT up to 100 $10^{-4}$ mN/m (in special cases $10^{-2}$ mN/m$^{-1}$) (Hezave et al. 2013a). So it seems that individual application of ILs is not satisfactory for oil recovery purposes (Rodríguez-Palmeiro et al. 2015).

In this way, a hybrid solution including SiO$_2$-NPs and [C$_{12}$mim][Cl] is proposed to find its effect on the ASO prepared by different wt% of asphaltene fraction using IFT and CA measurements along with the performed core flooding experiments. For this purpose, the IL and SiO$_2$-NPs concentrations were ranged between 0 and 2000 ppm while the asphaltene content in ASO was changed between 2 and
10%wt. The worth mentioning point is that most of the investigations regarding the effect of different EOR methods on the oil recovery were performed using crude oil from different reservoirs with different characteristics while each crude oil comprised of thousands of compounds. So, it is hard to extract any generalized correlation between the measurements (IFT, wettability, or tertiary oil recovery) and crude oil type. On the other hand, crude oils are mostly comprised of four main constituents including aromatics, saturates, asphaltenes, and resin fractions. So, it seems that using only one fraction during the IFT and wettability measurements or core flooding experiments can help the petroleum men and researchers to find a more generalized correlation between the operating conditions, concentrations, types of chemicals, etc., tertiary oil recovery. Among the different fractions, asphaltene is one of the most important constituents since they can act as the surface active agents and even can introduce more operational problems. In detail, asphaltene is one of the main compartments of each crude oil not only has direct influence on the different aspect of crude oil industries. In detail, asphaltenes which are the heaviest and most complex fraction of heavy oil have a high desire to be aggregated, causing severe problems in the production and transportation of heavy oil. Asphaltenes are also shown to play a key role in stabilization of water-in-crude oil (W/CO) emulsions and significantly impact the rheological properties of crude oil (Mozaffari 2015; Mozaffari et al. 2021, 2015).

In this way, the current investigation was focused on the application of asphaltenic synthetic oil as the sample oil for the first time concomitant with the SiO$_2$ and [C$_{12}$mim][Cl] as a new class of chemical formulation for EOR purposes (see Fig. 1).

**Materials and methods**

**Material and solutions**

They used crude oil is the oil utilized in the previous study performed by the coauthors with a density of 0.908 g·cm$^{-3}$ @ 15 °C. This crude oil was the heavy acidic type which was kindly provided by Offshore Oil Company, Iran. The analysis revealed that he used crude oil comprises 11.1% and 13.3% asphaltene and resin and the rest of the fractions were N. paraffins, I. paraffins, olefinic, naphthenes, aromatics saturates (C$_{15}$ < C$_{20}$), aromatics (C$_{15}$ < C < C$_{20}$), unknowns (C < C$_{20}$), and C$_{20+}$. The required salts and SiO$_2$ nanoparticles (20–30 nm) were prepared from Finenano, Iran, with a minimum purity of 99%.

Besides, the required IL, namely [C$_{12}$mim][Cl], was synthesized using 1-methylimidazole, 1-chlorododecyl (Merck/Fluka, purity > 99.5%). A brief description of the used method for synthesizing is previously reported elsewhere (Hezave et al. 2013b, 2013c) After synthesizing, the
accuracy of the used synthesis method was examined using FTIR for \([\text{C}_{12}\text{mim}] [\text{Cl}]\) as given in Fig. 2. In addition, the FTIR of the synthesized \([\text{C}_{12}\text{mim}] [\text{Cl}]\) are compared with those synthesized by Bennet et al. (1997) to reliably check if the mentioned synthesized method was accurate or not.

**Extraction of asphaltene and resin**

Since the main focus of the current investigation was the effect of SiO2 and IL on the wettability alteration and IFT reduction of synthetic crude oil, the asphaltene fraction was extracted from the heavy acidic crude oil using standard methods. In detail, each crude oil is a mixture of several thousands of compartments known as resin, asphaltene, saturates, and aromatics. Respecting this fact, it is rather impossible to analyze crude oil based on each individual element (Demirbas and Taylan 2015).

In this way, it is more common to examine each fraction of crude oil instead of examining each element on different aspects of oil industries such as their effects on the IFT reduction or wettability alteration during EOR processes (Demirbas 2016; Muhammad et al. 2013). According to reports, resin and asphaltene fractions are the most important and active fractions since they can act as natural surfactants although resin fractions are mostly considered as a stabilizer of asphaltene particles.

In general, resin fractions comprises of polar and heteroatoms such as nitrogen, oxygen, or sulfur (Demirbas et al. 2015) similar to the asphaltene but with some differences. The H/C ratio for resin fractions is about 1.2 and 1.7 which is higher than the H/C ratio of asphaltene fractions which is about 0.9 and 1.2. Respecting these differences, different extraction methods for resin and asphaltene fractions were reported although one of the most widely used and well-known methods is (IP 143/90) which is utilized in the present study for isolation of asphaltene fraction. Unfortunately, although these fractions have vital roles through aqueous interactions, their influences are not well established (Lashkarbolooki et al. 2014).

According to the results obtained from the spectroscopic analysis, asphaltene and resin fractions comprise of ester, hydroxyl groups, acid, long paraffinic chains with naphthenic rings, and carbonyl functions makes these fractions active as surfactants (Lashkarbolooki et al. 2016; Wu et al. 1998), although they are different considering aromaticity, size, physical appearance, and polarity. The used isolation procedure for asphaltene extraction was performed based on IP 143/90 procedure, known as the standard method for asphaltene and resin extraction (using n-heptane as solvent) (Petroleum 1985).

In brief, an aliquot of the petroleum cut (between 0.5 and 5 g) was carefully weighed and magnetically stirred with 40 ml hot n-heptane for 5 min to ensure the dissolution of the crude oil inside the n-heptane. N-Heptane is a common solvent for the separation of asphaltene fractions because asphaltene properties do not vary significantly with the carbon number of the solvent for n-heptane and higher-carbon-number alkanes (Andersen 1994).

After that, the solution was transferred into a larger glass flask and more n-heptane at room temperature was added to the primary solution. At this point, the resultant solution was shaken to observe the flocculation of the asphaltene particles. The resultant solution was filtered using a 0.45-pm Millipore filter which is suitable to be used under vacuum pressure for rapid separation and filtration process. The filtrate is the de-asphalted solution that can be used for further processing to isolate the resin fraction which is not the main target of this investigation. After isolating the asphaltene fraction, this fraction was analyzed which revealed that the weight percent of heteroatoms including S, O, and N in the isolated fraction is about 11.01%.

**IFT and CA measurement**

In this study, pendant drop equipment (Fanavari Atiyeh Poyandegan Exir Co., Arak. Iran) (see Fig. 3) was used to measure the IFT and CA values of different solutions.
The pendant drop method is a proper, simple, and accurate method for IFT and CA measurements (Yang et al. 2014).

The system is mainly comprised of three dependent sections including image capturing and processing unit, automatic injection system, and visual measuring chamber provide the condition for a drop to be contacted to the bulk phase at the tip of a nozzle. After injecting the drop at the tip of the nozzle, it is possible to use the drop shape analysis approach (Eq. 1) to find the large and small diameters and then calculate the IFT value (Stauffer 1965).

\[
\gamma = \frac{\Delta \rho g D^2}{H}
\]  

where \(\Delta \rho\), \(g\), and \(H\) are the difference between the bulk and drop phases, acceleration of gravity, and the shape-dependent parameter. The \(H\) value is depending on the shape factor value, i.e., \(S = d/D\), where \(D\) is the equatorial diameter and \(d\) is the diameter at the distance \(D\) from the top of the drop. Also, the software is developed in a way that it is possible to calculate the contact angle of the drop at the captive or non-captive condition by injecting the oil drop on the top of the
Results and discussion

Stability of SiO$_2$ particles

In the first stage of this investigation, the stability of SiO$_2$ particles in three different concentrations of 500, 1000, and 2000 ppm was investigated since any precipitation and agglomeration of nanoparticles may introduce destructive effects on the reservoir condition consequently entrapping the oil drops in the reservoir forever. The observations revealed that for all of the examined solutions prepared by formation brine and the aforementioned concentrations of NPs, the precipitation is evitable although the required time was different for each solution.

In this way, the stability of the SiO$_2$-NPs was investigated in the presence of IL-based surfactant namely 1-dodecyl-3-methyl imidazolium chloride in the range of 100, 200, 500, 1000, and 2000 ppm. The examined stability of NPs at the presence of [C$_{12}$mim][Cl] revealed that using IL concentration more than 500 ppm dissolved in the formation brine leading to a stable solution for more than one month. Respecting these findings, one can conclude that using IL with a concentration of 500 ppm is the best concentrating considering the economic issues. Although at the current stage, the optimum concentration is 500 ppm, this is the results of the next sections dictate which concentration is the proper and optimum IL concentration for efficient tertiary oil recovery.

Effect of [C$_{12}$mim][Cl] on the IFT

In this stage, the effect of IL dissolution in the formation of brine on the IFT reduction is going to be examined in the presence of synthetic asphaltenic oil with different concentrations of 2, 6, and 10 wt.%. In this way, in the first stage of IFT measurement, the IFT value of Heavy acidic crude oil and the synthetic asphaltenic oil (prepared by dissolving asphaltene in toluene) with different concentrations were measured in the absence of IL to see the effect of asphaltene on the IFT reduction. The measurements revealed that the IFT values for acidic heavy crude oil/formation brine (22.5 mN/m) (Behrang et al. 2021) were reduced to 21.8, 20.2, and 18.3 mN/m for synthetic oil prepared by 2, 6, and 10 wt.% of asphaltene dissolved in toluene.

According to these findings, it can be concluded that the presence of asphaltenes has a slight effect on IFT reduction which comes from its nature which is a natural surfactant due to its structure and existence of heteroatoms in its structure.

In the next stage of this section, the effect of IL was investigated on the IFT reduction of ASO/formation brine by changing the concentration between 50 and 2000 ppm to find the critical micelle concentration (CMC) and IFT variation trend (see Fig. 4).

A glance into Fig. 4 revealed that an increase in the asphaltene content from 2%wt to 6%wt leading to a reduction in IFT while further increase in the asphaltene content has a reverse effect on the IFT reduction. This observed trend can be related to the asphaltene molecules structure which can act as a cage to entrap the IL modules. In detail, both asphaltene and IL molecules are large and bulky molecules that can suck the molecules to their structure and stabilize their surface charge consequently reducing the repulsive forces and forming more stable complexes. As a consequence of forming more stable complexes, it is possible to have a stable film of asphaltene and IL molecules at the interface which can reduce the IFT in the desired manner. According to this hypothesis, it seems that increasing the asphaltene content from 2%wt to 6%wt can provide more stable film at the interface leading to a reduction in IFT and appearance of a sharp CMC value of about 250 ppm while further increase in the asphaltene concentration leading to an undesired increase in the IFT value and vanishing the sharp CMC value. Based on these findings, it can be concluded that although an increase in the asphaltene content from 2%wt to 6%wt was helpful for IFT reduction, further increase in asphaltene content is detrimental which leads to an increase in the IFT. The reason behind this reversed trend can be related to the fact that as the asphaltene concentration increases, the number of bulky and large molecules at the interface increases. On the other side, a higher number of IL molecules can be trapped and absorbed into the asphaltene structure which can enhance the repulsive forces. As a consequence of this phenomenon, there is a higher chance for the asphaltene and IL molecules to leave the interface to
form a more stable medium which means a lower number of asphaltene and IL molecules at the interface and higher IFT values.

Besides the overall observed trend for IFT variation, the CMC value is another important point that must be carefully being studied. In detail, as the surfactant concentration increases, the surfactant molecules can be adsorbed at the surface till it is fully overlaid, leading to the minimum surface tension value. At this point, further dissolution of surfactant in the aqueous solution leads to micelles formation in the volume phase above the transition concentration generally known as CMC. Knowing the CMC values is important since knowledge of this parameter indicates the point where the higher concentration of surfactant has no meaningful effect on the IFT which directly can be utilized as the limiting concentration for meaningful use.

In this way, the measured IFT values revealed that there is no sharp variation (CMC value) for 2 and 10%wt of asphaltene synthetic oil while for 6%wt of asphaltene synthetic oil the CMC value of 250 ppm is evident. So, it seems that there is a threshold value for asphaltene concentration which is below and higher than these values no obvious CMC value can be observed because of the negative impact of asphaltene and IL molecules on the formation of stable film at the interface. The worth mentioning point is that although the measurements revealed that the CMC value is about 250 ppm, the optimum concentration for IL was considered 1000 ppm for the rest of the experiments since in the real cases (at the presence of rock surface), adsorption of IL on the rock surface is inevitable which means that concentrations higher than 250 ppm are required for field applications.

In the last stage of this section, the IFT between SiO₂-NPs and ASO with different asphaltene contents of 2, 6, and 10%wt was measured at the presence of 1000 ppm of IL. The measured IFT values revealed that the presence of SiO₂-NPs in the solution has a slight effect on the IFT which can be neglected. So, the probable effect of SiO₂-NPs on the tertiary oil recovery comes from its influence on the wettability alteration.

**Effect of SiO₂-NPs on the CA**

In the current section, CA measurement was used to find the effect of SiO₂-NPs on the wettability alteration by changing the NPs concentration in the range of 0–2000 ppm. In normal cases, it is possible to find the direct effect of chemicals on the wettability alteration using different methods such as CA or Amott wettability index measurements. But in the current case, it is impossible to find the sole effect of NPs on the wettability alteration due to the fast precipitation of NPs makes it impossible to investigate the effect of these particles on the wettability alteration. In this way, two-step procedures must be used to find the effect of NPs on the wettability alteration the first step is the measurement of the effect of IL on the wettability alteration followed by the second stage which is the wettability alteration measurement for the solution comprises of both IL (as the stabilizer agent) and SiO₂-NPs. At this point, it is possible to consider the difference between the first and second steps as the sole effect of NPs on the wettability alteration, although this simplified calculation has inaccuracies due to antagonism or synergisms that existed between the NPs and IL. In other words, although using the difference between the first and second steps as the effect of NPs on the wettability alteration has intrinsic inaccuracies, it is the most available way to find a rough estimation on the effect of NPs on the wettability alteration.

Respecting the explained procedure and considering the optimum IL concentration of 1000 ppm selected in the previous section, the CA measurements were performed. In the first step, the effect of 1000 ppm of IL on the wettability alteration and CA variation was measured in the absence of NPs. The results revealed that the wettability of the aged thin section (using ASO with 6%wt asphaltene content) with CA of 156.3° (strongly oil-wet) was changed to a neutral condition with CA of about 88.2°. The worth mentioning point is that comparing the CA of the crude oil/formation brine/rock surface with the CA measured for synthetic crude oil (ASO with a concentration of 6%wt) revealed that CA was increased from 125° to 133° to 156.3° which means the higher capability of asphaltene fraction for wettability alteration toward oil-wet conditions compared with the crude oil. In the second stage, the CA of three solutions including 500, 1000, and 2000 ppm of NPs while the concentration of IL was kept constant at 1000 ppm were measured to find the probable effect of NPs on the wettability alteration. The measured CA values revealed that as the NPs concentration was increased from 500 to 2000 ppm, the Ca was reduced from 65.3° to 33.1° which is a strongly water-wet condition. (see Fig. 5).

The worth mentioning point is that similar trend was observed by Hendraningrat and Torsæter (Hendraningrat and Torsæter 2014) who examined the effect of silica-based nanoparticles on the IFT reduction, wettability alteration and tertiary oil recovery efficiency.

They reported that using silica-based NPs can change the wettability toward water wet condition. In detail, they reported the wettability alteration in the presence of silica NPs due to changes in the solid/fluid interface caused by adsorption of hydrophilic NPs. They also reported that the degree of water-wetness increased in both water- and oil-wet systems as shown by the smaller contact angle of the aqueous phase. They observed that once the hydrophilic NPs are introduced into the synthetic seawater (SSW), the NPs reduce the contact angle from 39° to 26° (a 33% reduction), which indicates that NPs have rendered the quartz
plate toward a more SWW system. In an oil-wet system, the presence of hydrophilic NPs in an SSW system tends to change the quartz plate to a weakly oil-wet system from 131° to 112° (a 15% reduction). Hence, the surface quartz wettability was modified and will favor the aqueous phase. Morrow1 reported that large changes in the wettability of a quartz surface can be achieved by adsorption of a monolayer of polar molecules. However, the use of a quartz plate has limitations in using a rock surface as a single mineral (quartz), as reported by Morrow (1990).

Core flooding experiments

In the last section, nine different core flooding experiments were performed to find the effect of proposed chemical formulations (see Table 1). The worth mentioning point is that for the core flooding experiments with NPs, 1000 ppm of NPs was used as the optimum concentration of NPs due to two reasons. The first reason is that using a high concentration of NPs is expensive making the practical application of NPs so limited. On the other hand, the measured CAs for NPs solutions with concentrations of 1000 and 2000 ppm revealed a slight difference between the measured CAs (42.3° for 1000 ppm of NPs and 33.1° for 2000 ppm of NPs). According to these facts, the optimum formulation for tertiary oil recovery experiments was selected as 1000 ppm of IL and 1000 ppm of SiO2-NPs although 500 of SiO2-NPs were also examined for better comparison.

In the first step of core flooding experiments, an aqueous solution with only 1000 ppm of IL was injected as the chemical formulation to find the individual effect of IL on the tertiary oil recovery. This experiment is required since the SiO2-NPs solution injection must be performed by 1000 ppm IL to avoid any precipitation. In this way, it is required to know

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Figure 5: The effect of SiO2 NPs on the CA change. a aged with crude oil (125.6°), b aged with 6 wt.% asphaltenic crude oil (156.3°), c 1000 ppm IL (88.2°), d 1000 ppm + 500 ppm SiO2-NPs (51.2°), e 1000 ppm + 1000 ppm SiO2-NPs (51.2°), and f 1000 ppm + 2000 ppm SiO2-NPs (33.1°).
the individual effect of an aqueous solution of 1000 ppm of IL on the oil recovery and the effect of SiO\textsubscript{2}-NPs + 1000 ppm of IL to quantify the individual effect of SiO\textsubscript{2}-NPs on the tertiary oil recovery. In other words, the presence of IL in the aqueous solution can enhance the oil recovery due to IFT reduction and wettability alteration while the SiO\textsubscript{2}-NPs can increase the oil recovery only by changing the wettability alteration. The results revealed that injection of aqueous solution (Run#1) with IL concentration of 1000 ppm leading to tertiary oil recovery of about 10.1% based on OOIP. This obtained oil recovery can be correlated to the effect of IL on both wettability alteration and IFT reduction. In the next step, the SiO\textsubscript{2}-NPs solutions with concentrations of 500 ppm to 2000 ppm while the concentration of IL kept constant at 1000 ppm were performed. The results revealed that the addition of SiO\textsubscript{2}-NPs has a direct increasing effect on the tertiary oil recovery from 13.8 to 21.2% based on OOIP which can be considered as the effect of SiO\textsubscript{2}-NPs on the wettability alteration. The other possible effect of SiO\textsubscript{2}-NPs besides its effect on the wettability alteration can be its adsorption on the rock surface consequently preventing the adsorption of IL on the rock surface leading to better efficiency of IL exited in the solution.

In other words, one can conclude that the difference between tertiary oil recovery of Run#1 and Runs#2, 3, and 4 is not purely related to the effect of SiO\textsubscript{2}-NPs on the wettability alteration and maybe it is related to the better efficiency of exited IL in the solution which its adsorption reduced. Unfortunately, since it is impossible to inject SiO\textsubscript{2}-NPs at different concentrations in the absence of IL, it is uncertain to conclude the differences between the aforementioned runs are purely related to the effect of used SiO\textsubscript{2}-NPs. The noteworthy point is that the investigation performed by Hendraningrat and Torsæter (2014) revealed that using the optimal nano-EOR condition reduced the residual oil saturation and increased the displacement efficiency in all wettability systems. They also reported that increasing the temperature can enhance the efficiency of the displacement mechanism. Finally, they performed an extended post-flush nano-flooding which revealed the possibility of producing more oil from the core plugs with maximum incremental oil recovered up to 4.9% of OOIP. According to the findings of Hendraningrat and Torsæter (2014) and those obtained in the current investigation, it seems that combining the SiO2-NPs with ILs as the chemical surfactant and stabilizer can provide more efficient chemical formulation for oil recovery purposes.

**Conclusions**

The present work is focused on the concomitant application of [C\textsubscript{12}mim][Cl] as an efficient surfactant and SiO\textsubscript{2}-NPs for IFT reduction, wettability alteration, and tertiary oil recovery processes.
recovery purposes. In this way, the NPs and IL concentrations were ranged between 0 and 2000 ppm to find the effect of these chemicals on the IFT reduction and wettability alteration in the first step after investigating the stability of the NPs in the absence and presence of IL. After that, several core flooding experiments were performed to find the effect of different chemical formulations on the tertiary oil recovery. The performed experiment revealed that:

- An increase in the IL concentration from 0 to 2000 ppm, leading to a reduction in IFT for all of the examined ASO with different asphaltene contents of 2, 6, and 10% wt with a sharp reduction in IFT (CMC value) for ASO with asphaltene content of 6% wt about 250 ppm.
- Addition of IL at all of the examined intervals to the SiO2-NPs solution provides stable conditions for NPs for more than one month which is suitable for field application.
- Although IL introduced a considerable effect on the IFT reduction, using SiO2-NPs has no meaningful effect on the IFT reduction which means that the presence of SiO2-NPs may lead to higher oil recovery only by changing the wettability of the rock surface.
- The measured CAs revealed the significant effect of IL on the wettability alteration which moves the rock surface toward neutral wet (88.2°) while the addition of SiO2-NPs moves the rock surface toward a strongly water-wet condition (33.1°).
- The performed core flooding experiments revealed the considerable effect of the proposed hybrid solution (SiO2-NPs + IL) for tertiary oil recovery purposes. In detail, the results revealed that the tertiary oil recovery was increased to 15.2% based on the OOIP for the hybrid solution of 1000 ppm SiO2-NPs and 1000 ppm of [C12mim][Cl].

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Declarations

Conflict of interest  The authors confirmed that there is no conflict of interest.

Ethical Approval  It is not extracted from one study and it is published from a series of studies performed regarding the EOR concerns.

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