**ORIGINAL PAPER-PRODUCTION ENGINEERING** 



# Interactions between chloride-based salts (CaCl2 and MgCl2), ionic liquids, pH, and titanium oxide nanoparticles under low and high salinity conditions, and synthetic resinous crude oil: dorud oilfield

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# Abstract

Unfortunately, oil reservoirs are complex considering the fluids (e.g., crude oil composition) and rock properties making it hard to propose a simple enhanced oil recovery (EOR) method for higher oil production. Besides, most of the investigations had focused on crude oil which is a complex mixture of thousands of components making it hard to extract any reliable conclusions with respect to the crude oil type. So, the current study is focused on the application of ionic liquids from different families of pyridinium and imidazolium, titanium oxide nanoparticles, and salts (MgCl<sub>2</sub> and CaCl<sub>2</sub>) in the presence of resinous synthetic oil for the first time. The obtained results using the central composite design (CCD) approach revealed the positive effect of resin fraction on the IFT reduction by 27% considering the initial value (34.9%). Using the CCD approach revealed that using pH = 7, MgCl<sub>2</sub> concentration = 21,000 ppm, CaCl<sub>2</sub> concentration = 21,000 ppm, resin fraction of 9wt%t and 500 ppm of [C<sub>12</sub>mim][Cl] concentration reduces the IFT to minimum value of 0.62 mN/m while the minimum IFT value for optimum conditions of solution includes [C<sub>12</sub>py][Cl] and TiO<sub>2</sub>-NPs (0–200 ppm) for better wettability alteration toward water-wet condition (27.3°) than [C<sub>12</sub>mim][Cl] (33.2°). Moreover, the IFT measurements revealed that the presence of TiO2-NPs is effective in reducing the IFT of the optimum formulations to 0.55 and 0.84 mN/m for [C<sub>12</sub>mim][Cl], and [C<sub>12</sub>py][Cl] are applicable for EOR purposes as new hybrid solutions.

**Keywords** Acidic crude oil  $\cdot$  TiO<sub>2</sub>-NPs  $\cdot$  Pyridinium  $\cdot$  Imidazolium  $\cdot$  Ionic liquid  $\cdot$  Interfacial tension  $\cdot$  Contact angle  $\cdot$  Design of experiments

Lis	t of symbols	L	Drop length (m)
D	Equatorial diameter (m)	$R$ and $R_{\rm m}$	Radius of the drop at equator (m)
d	Diameter at the distance D from the top of	R <sub>o</sub>	Radius of the drop at edge (m)
g H	the drop (m) Acceleration of gravity (m $s^{-2}$ ) Shape-dependent parameter (m)	Greek letters $\gamma$ $\Delta$ $\rho$	Interfacial tension (mN/m) Difference between two parameters Density (kg m <sup>-3</sup> )
	Mehrdad Pazhoohan Me.Pazhoohan@iau.ac.ir	ω Abbreviations	Rotational speed (rad/s)
1	Department of Civil Engineering, Dashtestan Branch, Islamic Azad University, Dashtestan, Iran	Al <sub>2</sub> O <sub>3</sub> ANOVA	Aluminum oxide Analysis of variance
2	Department of Management, Bahonar Technical and Engineering College of Shiraz, Fars Branch, Technical and Vocational University, Tehran, Iran	API <sup>o</sup> ASO ASTM	API gravity Asphaltenic synthetic oil American Society for Testing and
3	Incubation Centre of Arak Science and Technology Park, Fanavari Arena Exir Sabz Company, Arak 381314-3553, Iran	CA	Materials Contact angle
4	Arak Science and Technology Park, Fanavari Atiyeh Pouyandegan Exir Company, Arak, Iran	CaCl2	Calcium chloride

CCD	Central composite design
CMC	Critical micelle concentration
EDTA	Ethylenediaminetetraacetic
EOR	Enhanced oil recovery
Fe <sub>2</sub> O <sub>3</sub>	Iron oxide
Fe <sub>3</sub> O <sub>4</sub>	Iron(II,III) oxide
GC	Gas chromatography
IFT	Interfacial tension
ILs	Ionic liquids
MgCl2	Magnesium chloride
NPs	Nanoparticle
OOIP	Original oil in place
pН	Potential of hydrogen/power of hydrogen
ppm	Part per million
PSNP	Polysilicon NPs
RSO	Resinous synthetic oil
SiO2	Silicon oxide
SiO <sub>2</sub> -NPs	Silicon oxide nanoparticles
SLS	Sodium lauryl sulfate
TiO2	Titanium oxide
WNW-ESE	West-northwest-east-southeast
NE-SW	Northwest-southwest
wt%	Percentage by weight
ZrO2	Zirconium dioxide
[C <sub>12</sub> mim][Cl]	1-Dodecyl-3-methyl imidazolium chloride
[C12py][C1]	1-Dodecyl-3-methyl pyridinium chloride

# Introduction

Using enhanced oil recovery (EOR) processes increased over the past three decades due to the sources of energy limitations and the oil production reduction while the consumption increases daily facing the entire globe with energy crises. In detail, with the aid of the reservoir's natural pressure, only 10–15% of the original oil in place (OOIP) can be produced means the necessity of performing secondary and tertiary oil recovery processes to extract the trapped oil in the reservoir. In detail, it is possible to produce 10–15% in addition to the primary oil production through the secondary oil recovery processes. So, even after secondary oil recovery processes, more than 65–70% of the OOIP remained unrecovered which is a significant amount of wealth that remained trapped and unrecovered.

At this point, it is highly required to use new and innovative oil recovery processes commonly known as EOR methods such as gas injection, chemical injection, in situ combustion, modified-water injection (such as smart water and low-salinity water), microbial injection, and nanoparticles injection to extract the remained oil in the reservoir. Unfortunately, although several EOR approaches introduced and examined over the past years, the main shortcomings of the tested EOR methods are their limitation in activating activate a few mechanisms. Respecting these limitations, a combination of several EOR methods have been proposed as hybrid methods during the past decade to activate multiple mechanisms with the main concentration on the IFT reduction, wettability alteration, viscosity reduction, and swelling of crude oil (Cheraghian 2015; Abhishek et al. 2015).

In other words, considering the energy crises, and limitations of each EOR method, it is highly required to use hybrid methods (Cheraghian and Hendraningrat 2016). As a way out, hybrid methods were proposed based on the concomitant application of the low-salinity aqueous solution, surfactant solutions, nanoparticles (NPs), etc. (Bera and Belhaj 2016; Khalil et al. 2017; Li et al. 2021; Negin et al. 2016). Among the EOR methods, nanoparticle injection is one of the new approaches which can reduce the IFT, wettability of the rock surface toward water-wet status, reduce crude oil viscosity (Ju et al. 2006; Torsater et al. 2012; Zaid et al. 2013; Al-Anssari et al. 2016; Saien and Gorji 2017; 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).

Besides the aforementioned possible mechanism, it is also possible to produce nano-emulsion using NPs (Bobbo et al. 2012) for selective plugging the pores (Anganaei et al. 2014; Hashemi et al. 2013), thermal conductivity enhancement purposes (Aveyard et al. 2003; McElfresh et al. 2012) disjoining pressure manipulation (McElfresh et al. 2012; Zamani et al. 2012).

The other important feature of the NPs is their carrying capability which can transport the compartments to the narrow pathways and small pores where the oil droplets are trapped. In light of this capability, NPs are good candidates to be used as a carrier to deliver specific chemicals to a specific destination in the pore structures and networks (Rod-riguez et al. 2009). Considering these unique advantages of NPs, many researchers focused on the application of NPs in the EOR processes to recover more trapped oil by activating two main mechanisms of IFT reduction and wettability alteration besides the other mechanisms aforementioned (de Castro Dantas et al. 2017; Moradi et al. 2015; Suleimanov et al. 2011).

As an example, the effect of polysilicon NPs (PSNP) was investigated in changing the rock wetness since it is a vital mechanism especially if it moves toward strongly water-wet conditions (Onyekonwu and Ogolo 2010). Among the different possible NPs, it is well established that using silicabased NPs is a good approach to move the wettability of the rock surfaces toward strongly water-wet (highly required to produce more trapped oil under constant rate) (Cheraghian 2016; Hendraningrat et al. 2013b, c, d; Torsater et al. 2012).

The point is that although silica-based NPs are potential NPs for EOR purposes, there are other NPs examined by different researchers such as  $Al_2O_3$  and iron oxide (Fe<sub>2</sub>O<sub>3</sub>). In

detail, Mohammadi et al. (2014) performed several experiments to find if  $Al_2O_3$ -NPs are capable of producing higher oil from the sandstone rocks. Just a year after, Tarek (2015) investigated the idea of using a mixture of different NPs including  $Al_2O_3$ , iron oxide (Fe<sub>2</sub>O<sub>3</sub>), and SiO<sub>2</sub> to prepare a hybrid solution for tertiary oil recovery purposes which can activate different effective mechanisms and enlighten this fact that the NPs are potential to modify the thermal conductivity; but also they are potential to activate several effective mechanisms such as IFT reduction and wettability alteration (Cheraghian and Hendraningrat 2016; Sheng 2010).

Similar to the NPs considered new and innovative chemicals for EOR purposes, ionic liquids (ILs) which are a new class of surfactants that proposed due to their unique features. In detail, ILs are a new class of chemicals with numerous characteristics such as being highly stable under harsh salinity and temperature conditions (salinity and temperature) (Chen et al. 2014; Dharaskar Swapnil 2012; Domańska 2005; Lee and Kim 2013; Martins et al. 2014; Peng et al. 2011). These characteristics of ILs come from their unique and bulky structure since they are generally comprised of cationic and anionic sections making it possible to fabricate any specific-task IL regardless of the application.

In detail, it is possible to fabricate any desired IL for any specific purpose such as EOR processes with tailoring proper cationic and anionic sections (José-Alberto and Jorge 2011; Khupse and Kumar 2010). For example, different researchers have investigated the possible application of different ILs, especially from the imidazolium family for EOR purposes through reservoirs with harsh salinity (Hezave et al. 2013b; Smit et al. 1991).

The results reported by those researchers revealed that the dissolution of cationic ILs in the aqueous solution can neutralize the opposite charges that existed in the solution due to the dissolved salts providing the chance of easier accumulation of surfactant molecules in the interface which means lower IFT values. The point must be clarified that the results reported by Hezave et al. (2013a) demonstrated that this is not only the IFT reduction leading to higher oil recovery during the EOR processes, but also this is the concomitant effect of IFT reduction and wettability alteration causes more oil production (Rodríguez-Palmeiro et al. 2015).

The other point is that besides the chemical combination, there is a complicated and undeniable interaction between the crude oil type and the chemical combination concomitant with the operating conditions such as pH (Demirbas 2016; Demirbas and Taylan 2015; Muhammad et al. 2013).

In general, crude oil is comprised of saturates, aromatics, resin, and asphaltene fractions, and the last two fractions are the most essential because of their detergency nature which can act as natural surfactants (Demirbas et al. 2015; Lashkarbolooki et al. 2014). So, several investigations were focused on the possible interactions that exist between the

chemicals and these fractions acting as the natural surfactant and consequently affect the wettability and IFT (Andersen 1994; Lashkarbolooki et al. 2016; Mozaffari 2015; Mozaffari et al. 2021, 2015; Wu et al. 1998).

Considering the existed ample space for the interactions between a new class of IL-based surfactants from pyridinium and imidazolium families in the presence of NPs and since there is a small number of investigations dealing with specific fractions of crude oil, especially resin, and asphaltene fractions, performing this investigation is essential for EOR purposes. The point is that using specific fractions for IFT reduction and wettability alteration investigations is required since these fractions can act as natural surfactants and introduce interactions with other chemicals such as surfactants and alkalis. Moreover, most of the performed previous investigations used changing one factor at a time as the design of the experiment approach. In contrast, in the current investigation, central composter design (CCD) is used which provides the chance to investigate the possible interactions between several parameters on the IFT reduction and wettability alteration. To sum up, this investigation is essential since the impacts of several parameters including IL type, pH, salt type, and low and high salinity conditions in the absence and presence of metallic-based NPs of TiO2 on the wettability alteration and IFT reduction were examined for the first time. In this way, the present work is designed in a way to examine the application of synthetic resinous oil prepared from the resin fraction of heavy-acidic crude oil, pyridinium, and imidazolium-based ILs of [C12py][Cl], and [C<sub>12</sub>mim][Cl] and TiO<sub>2</sub>-NPs under different concentrations of 0-1000 ppm and 0-200 ppm, respectively, for IFT reduction and wettability alteration purposes at different pH values of 3-11 for the first time based on the best knowledge of the authors. Besides, instead of using formation brine which is a complex combination of different salts, two divalent salts of MgCl<sub>2</sub> and CaCl<sub>2</sub> with low and high salinity conditions (1000-41000 ppm) were selected as the target salts to prepare the sample brine.

The worth mentioning point is that using NPs for EOR purposes has risk which is the risk of NPs precipitation due to agglomerations or other phenomena that may lead to pore plugging which in severe cases can cause catastrophic outcomes which are entrapment of crude oil in the reservoir forever. In light of this limitation, it is highly required to investigate the stability of  $TiO_2$ -NPs in the presence and absence of ILs to ensure the long-term stability of the prepared solutions to unveil the possible risk of  $TiO_2$ -NPs precipitation.

The other point is that the current investigation mainly focuses on applying resinous synthetic oil with concentrations of 0-9 wt% dissolved in toluene. This range of concentration was selected since it can cover the resin concentration in different crude oils since it is merely passing 10 wt% in crude oils. Also, the obtained results can be used for the

resin fractions structurally similar to the examined resin fraction (considering the aromaticity). Moreover, the main goal of this selection is to characterize the impact of the used chemicals on the resin fraction which is one of the most essential fractions in crude oil. Generally, crude oil is a combination of thousands of compounds that can be categorized into four general fractions saturates, aromatics, resin, and asphaltene (SARA analysis). In this way, using a specific fraction to prepare the synthetic oils provides a better chance to differentiate between the impacts of chemicals on each fraction for more reliable conclusions. After that, by knowing the impact of chemicals on the different fractions, anyone can find the effect of examined chemicals on the crude oils using the SARA analysis. In other words, in the light of knowing each fraction's role in the efficiency of the used chemical, one can extract generalized conclusions without performing a large number of experiments. Unfortunately, this approach has a limitation that comes from the different structures of each fraction, especially resin and asphaltene fractions. However, the point is that it is possible to eliminate this limitation to some extent if researchers use some identification such as aromaticity to characterize the existing fractions in the crude oil.

# **Materials and methods**

## **Material and solutions**

The sample crude oil which is used to extract resin fraction was a heavy-acidic crude oil with asphaltene and resin contents of 6.3% and 9.8%, respectively, which was provided by one of the Iranian oil companies (density of 0.923 g cm<sup>-3</sup> @ ambient temperature (dorud oilfield)). This oilfield is the largest Iranian offshore oil field (25 km and 5 km long and wide, respectively) located in the Persian Gulf with 88 wells, 47 are production wells (Chehrazi et al. 2013a). The formation of this oilfield is a combination of Asmari, Surmeh, Yamama, and Manifa which the Asmari section has an APIº degree of 23-25 while the APIo of Surmeh, Yamma, and Manifa are 29.5, 35, and 31, respectively (Setudehnia 1978). The worth mentioning point is that the current oilfield has 2 gas injection wells, and 12 water injection wells which means that this oilfield is a good candidate for the waterbased EOR processes. On the other side, the maximum production of 139.74 thousand bpd of crude oil and condensate was the old record of this reservoir which will lose its economic production rate in 2041. Respecting the Dorood structure, it can be observed that this oilfield is an elongated anticline, plunging toward the NNE from Cretaceous and late Miocene times. In detail, two independent structural events from late Cretaceous times led to an NNE-SSW-orientated folds while the second structural event occurred in late Oligocene–Pliocene times which uplifted the structure (Bosold et al. 2005; Chehrazi et al. 2013b; Fard et al. 2006).

The point is that during the first period of structural modification, WNW–ESE which was perpendicular to the present-day fold axis was the main directional movement. On the other hand, the main stress direction during the second structural event was NE–SW, with a slight change to N020 (Berberian and King 1981; Beydoun 1991; Ghazban 2007; James and Wynd 1965; Setudehnia 1978).

The required salts of MgCl2 and CaCl2 were supplied from Sigma-Aldrich, the USA, with a minimum purity of 99.0%, and the TiO<sub>2</sub> nanoparticles (20–30 nm) were prepared from Borhan, Iran, with a minimum purity of 99%. Besides, the required ILs were synthesized using a standard procedure and materials using 1-methyl pyridinium, 1-chloro dodecane, and 1-chloro octane (Merck/Fluka, purity > 99.5%).

#### Interfacial tension measurement

The required IFT and contact angle values were measured via a pendant drop equipment works based on the pendant drop mechanism which is one of the most accurate methods of IFT and contact angle measurements (Yang et al. 2014). In this way, ambient condition pendant drop equipment was used in the present study (APEX Technologies Co., Arak. Iran).

A brief description of the used equipment and related theory is give n by Stauffer (1965).

$$\gamma = \frac{\Delta \rho g D^2}{\mu} \tag{1}$$

where  $\Delta \rho$ , g, and H are the difference between the bulk and drop phases, acceleration of gravity, and the shape-dependent parameter, respectively. Besides, the H value in Eq. 1 known as the shape factor is correlated to the S value which is the d/D. To calculate the S value, it is required to find the D and d diameters which are the equatorial diameter and the diameter at the distance D from the top of the drop, respectively. The equipment has three sections (a) an automatic dispensing system, (b) an image recording, and (c) a dispatching section, and online IFT and contacts angle calculation software. Using the first section, the required drop volume can be dispensed at the tip of the nozzle in an upward or downward direction depending on the difference between the bulk phase and drop phase using an automatic micro-metering injection system. In the second section, the camera and lens assembly capture the required images at different time intervals and dispatch them to the calculation software where the images are analyzed and the small diameter and large diameters are detected and calculated, and then converted to the IFT values. The point that must be defined is that the used software automatically detects the small and large diameters and then converts the calculated parameters to the IFT values.

#### **Contact angle measurement**

Knowing the wettability of a system is one of the most essential characteristics of several industries from enhanced oil recovery processes to medical. In this way, during the past decades, several methods have been proposed to measure the wettability of the systems one of the most essential methods is contact angle measurement. Among the different methods for measuring the contact angle values, using the sessile drop is the most widely used and accurate method which provides the chance of static CA measurement for the operator with an acceptable level of accuracy using online software. If the water CA is lower than 90°, the surface is said to be hydrophilic, and if the contact angle is higher than 90°, the surface is hydrophobic.

#### **Resin extraction procedure**

In this study, IP 143/90 (Petroleum, 1985) was used to extract the asphaltene fraction in the first stage and then the resin extraction was isolated from the de-asphalted crude oil. The point is that among the different fractions of the crude oil, resin, and asphaltene fractions is a natural surfactant that has significant effects on the IFT reduction during the chemical EOR methods. It is required to investigate the sole and combinative effect of these fractions in the presence of different chemicals. Besides the effects of these fractions on the possible IFT or wettability alteration, crude oil is a combination of thousands of chemicals makes it hard to extract any reliable and generalized conclusion if the crude oil is being studied for EOR purposes. Respecting these reasons, several investigations were performed to study the role of different chemicals in the presence of only resin and asphaltene fractions (Lashkarbolooki et al. 2014, 2016; Wu et al. 1998) leading to no generalized and consistent results. In brief, using the IP 143/90 for asphaltene isolation purposes, n-heptane with a ratio of 40:1 was applied in the first place. Then, the remaining molten and de-asphalted oil was contacted with a silica gel column (Merck, 35-70mesh ASTM) to extract the resin fraction using the column chromatography method (Soorghali et al. 2014). After that, saturates and aromatics were washed and eliminated from the extracted fraction using 70:30 n-heptane and toluene solution. At last, an acetone/dichloromethane/toluene mixture with a ratio of 40:30:30 was used to achieve the resin fraction (Yarranton et al. 2000).

Besides the isolation of resin and asphaltene fraction, these two fractions were elementally analyzed using a CHNSO analyzer (Thermo Flash EA 1112 series) to determine the C, H, N, S, and O contents. Based on the performed analysis, the resin fraction with the H/C ratio of 1.39 compared with the asphaltene H/C ratio of 1.17 revealed lower aromaticity characteristics which means a more branched structure of resin fraction than the asphaltene molecules. With respect to this finding, it seems that the resin molecules are more similar to the surfactant molecules than the asphaltene molecules.

#### Central composite design (CCD) approach

Using the design of the experiment approach to lower the required number of experiments is one of the most promising methods used during the past decades. These types of approaches are highly applicable, especially for systems dealing with large numbers of independent parameters and wide ranges of intervals. In other words, using the design of the experiment approach except changing one factor at a time substantially reduces the required number of experiments. Among the widely used and examined design of experiment approaches, central composite design (CCD) under response surface methodology is among the widely used methods. In this way, the CCD approach was used to examine the effect of different operating parameters such as pH, IL type and concentrations, salinity level (low and high salinity conditions) and salt type (CaCl<sub>2</sub> and MgCl<sub>2</sub>), and resin concentrations, while IFT was selected as a response. In more detail, a CCD approach was applied to optimize the variables to obtain the best responses. So, five levels of  $-\alpha$ , -1, 0, +1, and  $+\alpha$  were selected for each factor as the lowest, low, center, high, and highest levels, respectively. All experimental designs were executed randomly to minimize experimental errors precisely. Then, the analysis of variance ANOVA from Design Expert 7.0 software with a 95% confidence level was used to investigate the contribution of main factors and their interactions.

# **Results and discussions**

#### **Resin fraction and interfacial tension**

In the first stage of this investigation, the effect of resin fraction was investigated on the IFT reduction if it dissolves in the toluene. The performed CHNSO test (Thermo Flash EA 1112 series) revealed that the resin fraction has H/C ratio of about 1.39 while the asphaltene H/C ratio was 1.16 means the lower aromaticity of the resin fraction consequently leading to a more branched structure of resin. As a consequence of this type of structure, it seems that extracted resin fraction from the heavy-acidic crude oil introduces a more surfactant nature compared with the asphaltenic fraction. On the other side, since the main focus of the current investigation is the interactions between the chemicals and operating conditions with the resinous synthetic oil, no further analyses were performed on the asphaltene fraction in this study. In the first place, the effect of resin concentration was examined in the range of 1-9 wt% to find if this fraction can act as a surfactant. In this way, four IFT measurements using distilled water were performed with resin concentrations of 0, 1, 5, and 9wt%. The measurements revealed that the IFT was reduced from 34.9 mN/m (distilled water/toluene) to a minimum value of 25.3 mN/m for the resinous synthetic oil prepared by dissolution of resin in the toluene with a concentration of 9 wt%. According to these findings, it seems that the resin fraction can act as a natural surfactant in the light of its structure and heteroatoms of sulfur and oxygen existing in the resin structure.

A closer look (Fig. 1) revealed that as the pH value increased, the IFT was reduced due to the acidic nature of the resin fraction interacting with the solution contents which produced in situ surfactant, consequently empowering the surfactant-nature of the dissolved resin fraction in the toluene.

#### Effect of ionic liquids on interfacial tension

In the next stage of this investigation, the effects of two different ILs from pyridinium and imidazolium families concomitant with the different concentrations of  $MgCl_2$  and  $CaCl_2$  in the range of 1000–41000 ppm were examined (see Figs. 2, 3, 4, 5). The measurements of this section are divided into two subsets, one of them was performed using distilled water as the aqueous solution containing ILs as the surfactant, and the second set of experiments was performed using two different salts of  $MgCl_2$  and  $CaCl_2$  with different concentrations concomitant with the dissolved ILs. The depicted results in Fig. 2a–c revealed that increasing the ILs concentrations in the absence and presence of salts leads to a reduction in IFT due to the surfactant nature of the ILs. Besides, the overall observed trend revealed that using  $[C_{12}py][CI]$  leads to a better reduction in IFT compared with



Fig. 1 Effect of pH and resin concentration on the IFT of synthetic resinous oil and distilled water



Fig. 2 IFT variation, a 1 wt% resin, b 5 wt% resin, and c 9 wt% resin

the IFT reduction that occurred by  $[C_{12}mim][Cl]$  due to the higher acidic nature of the imidazolium compared with the pyridinium for all the examined pH values and resin fractions. However, using  $[C_{12}mim][Cl]$  revealed better functionality for IFT reduction in the solution with a pH value of 11 and resin fraction of 9 wt%. In detail, imidazolium cation is an acidic component with pKa=21-23 which comes from the H2 hydrogen of the imidazolium nucleus while pyridine is often used as an organic base in chemical reactions pKa=5. In light of this fact, it seems that since the acidic resin fraction is in contact with a basic surfactant neutralization of repulsive forces occurred leading to easier packing of the pyridinium-based ILs in the interface consequently leading to more IFT reduction compared with the imidazolium-based IL.

But in the case of an aqueous solution with a pH value of 11 and synthetic oil with a resin fraction of 9 wt%, the condition was completely different. The reason behind this observed shifting behavior can be attributed to the formation of complexes between the [C12py][Cl] and resin molecules producing overwhelming repulsive forces that move the IL molecules toward the bulk instead of packing them into the interface consequently leading to higher IFT values than the  $[C_{12}mim][Cl]/synthetic resinous oil system. The$ other point that can be extracted from the depicted results in Fig. 2 is that for both examined ILs and pH values, a sharp critical micelle concentration (CMC) value of 400 ppm was obtained since most of the IFT reduction occurred if the IL concentration increases from 0 to 400 ppm while further increase in the IL concentration from 400 to 1000 ppm led to a lower reduction in IFT values.

In the second series of experiments, the effects of ILs were examined on the IFT reduction under different pH values and in the presence of MgCl<sub>2</sub> and CaCl<sub>2</sub> (in the range of 500–50000 ppm) (see Fig. 3). The point is that in the current phase, central composite design (CCD) approach was used as the design of experiment method instead of changing one factor at a time method to reduce the number of required measurements since the number of experiments would be extensive if changing one factor at a time approach was used. In this way, the parameters including IL type (imidazolium-based and pyridinium-based), pH value (3–11), resin fraction (1–9 wt%), and MgCl<sub>2</sub> and CaCl<sub>2</sub> concentrations (1000–41000) were used as the independent parameters (see

Table 1). According to the intervals tabulated in Table 1 and 2, the IFT measurements were performed and used to find the optimum operating condition besides the possible interactions that exist between different parameters.

The point is that two different sets of experiments were performed based on the CCD approach for two ILs of  $[C_{12}mim][Cl]$  and  $[C_{12}py][Cl]$  while the other operating parameters of pH value, resin fractions in toluene, and salinities were the same. With a close look into the results obtained for  $[C_{12}mim][Cl]$ , one can conclude that the quadratic model can predict the IFT values for different conditions with an acceptable level of accuracy (see Table 3 and 4).

In general, a glance into the results tabulated in Table 3 revealed that the F value for the model is about 45.99 means that there is only a 0.01% chance that a large value for "Model F value" occurred due to the noise. Moreover, the "Prob > F" parameter (for the values lower than 0.05) is an indication which revealed that all of the examined parameters of pH, salt concentrations, IL concentration, and resin fraction are effective parameters their effect must be taken into account. Besides, a closer look into the results revealed that not only the individual parameters have a profound effect on the IFT but also the interactions that existed between the MgCl<sub>2</sub>/[C<sub>12</sub>mim] [Cl] and CaC<sub>12</sub>/[C<sub>12</sub>mim][Cl] are dominant among the other interactions. On the other side, if the "Prob > F" values are greater than 0.1 as tabulated in Table 3, it is an indication that those parameters are insignificant in the model.

In the next stage, the error analysis namely the <u>sequential</u> <u>model sum of squares</u> and <u>lack of fit tests</u> was performed to



Fig. 3 Packing of NPs in the crude oil/aqueous phase interface (Nowrouzi et al. 2019)

Table 1         The parameter intervals           using CCD approach for         [C12mim][C1]	Run	pH	MgCl <sub>2</sub> Concen- tration (ppm)	CaCl <sub>2</sub> Concen- tration (ppm)	[C <sub>12</sub> mim][Cl] Con- centration (ppm)	Resin Frac- tion (wt%)	IFT (mN/m)
[][]	1	5	31,000	11,000	750	3	2.8
	2	7	21,000	21,000	500	5	1.3
	3	7	21,000	2100	500	5	1.4
	4	9	11,000	11,000	250	7	9.2
	5	9	31,000	11,000	750	7	0.83
	6	5	11,000	3100	750	7	89
	7	7	21,000	41,000	500	5	0.93
	8	9	11,000	11,000	750	3	2.3
	9	5	11,000	11,000	250	3	10.5
	10	9	31,000	1100	750	3	1.8
	11	7	21,000	21,000	0	5	24.2
	12	5	31,000	11,000	250	3	8.9
	13	7	41,000	21,000	500	5	0.85
	14	9	11,000	31,000	250	3	7.7
	15	9	31,000	31,000	250	7	5
	16	5	31,000	11,000	250	7	7.5
	17	9	11,000	31,000	250	7	7.5
	18	7	21,000	21,000	500	5	1.3
	19	9	11,000	11,000	250	3	10.2
	20	9	11,000	11,000	750	7	1.1
	21	5	11,000	11,000	750	3	1.9
	22	5	31,000	31,000	250	3	6.7
	23	7	21,000	21,000	500	1	2.2
	24	7	21,000	21,000	500	5	1.5
	25	9	11,000	11,000	750	7	0.93
	26	7	21,000	21,000	500	9	0.62
	27	5	31,000	31,000	750	7	1.6
	28	5	31.000	31.000	750	7	1.4
	29	7	21.000	21.000	500	5	1.45
	30	11	21,000	21,000	500	5	0.8
	31	9	31,000	31,000	250	3	8
	32	9	11,000	11,000	750	3	1.4
	33	5	11,000	11,000	250	7	9.3
	34	7	21,000	21,000	500	5	3.3
	35	7	1000	1000	500	5	2.7
	36	9	31,000	31,000	750	7	0.85
	37	7	21,000	21,000	1000	5	3.6
	38	5	31,000	31,000	31,000	3	2.4
	39	9	31,000	31,000	50	7	6.8
	40	5	11.000	11.000	750	3	2.5
	41	7	21.000	21.000	500	5	1.36
	42	5	31.000	31.000	250	7	5.8
	43	5	11,000	11.000	750	7	1.1
	44	9	31,000	31,000	250	3	5.7
	45	7	21.000	21.000	500	5	1.4
	46	7	21,000	21.000	500	5	1.42
	47	, Q	31,000	31,000	750	3	1.12
	48	5	11.000	31,000	250	3	8.2
	49	3	21,000	21,000	50	5	1.76
		5	11,000	31,000	250	5 7	7.6
		5	11,000	51,000	250	1	7.0

Table 2The parameter intervalsusing CCD approach for  $[C_{12}py]$ [Cl]

Run	pН	MgCl <sub>2</sub> Concen- tration (ppm)	CaCl <sub>2</sub> Concen- tration (ppm)	[C <sub>12</sub> py][Cl] Con- centration (ppm)	Resin Frac- tion (wt%)	IFT (mN/m)
1	9	31,000	11,000	250	7	6.6
2	7	21,000	21,000	500	9	5.2
3	5	11,000	11,000	750	3	7.9
4	9	31,000	31,000	750	7	5.2
5	9	31,000	31,000	750	3	6.1
6	9	11,000	11,000	750	3	6.2
7	9	11,000	31,000	750	3	6.6
8	9	31,000	11,000	750	3	5.8
9	9	11,000	31,000	250	3	7.1
10	7	21,000	21,000	500	5	5.6
11	7	21.000	21.000	500	5	5.4
12	7	21.000	21.000	500	5	5.8
13	5	11,000	31,000	750	7	44
14	7	21,000	21,000	500	,	9
15	7	21,000	41,000	500	5	53
15	0	21,000	41,000	250	5	5.5
10	9	21,000	21,000	230	/ 5	5.0
1/	/ ~	21,000	21,000	300	3	5.4
18	5 -	31,000	11,000	/50	3	5.5
19	5	11,000	11,000	250	7	7.2
20	9	31,000	31,000	250	3	7.4
21	5	11,000	11,000	250	3	9.2
22	9	11,000	11,000	750	7	2.2
23	7	41,000	21,000	500	5	4.5
24	5	31,000	11,000	250	7	6.8
25	5	31,000	31,000	250	7	5.1
26	9	31,000	11,000	250	3	7.4
27	5	11,000	31,000	250	7	5.2
28	9	11,000	11,000	250	7	4.6
29	7	21,000	21,000	500	5	5.4
30	5	31,000	31,000	750	7	3.5
31	7	21,000	21,000	500	5	5.7
32	9	31,000	31,000	250	7	7.4
33	7	21,000	21,000	500	5	5.7
34	5	31,000	31,000	750	3	4.4
35	3	21,000	21,000	500	5	6.2
36	11	21,000	21,000	500	5	5.6
37	5	11,000	31,000	250	3	6.5
38	7	21.000	21.000	500	5	5.6
39	7	21.000	21.000	0	5	6.1
40	9	11.000	11.000	250	3	7.2
41	9	31,000	11,000	250 750	7	3.4
42	7	21,000	1000	500	5	6.6
43	, 5	31,000	11 000	250	3	7.2
44	5	31,000	31,000	250	3	49
45	5	11,000	11 000	750	7	ч.) 45
т.) Лб	5	11,000	31,000	750	, 3	т.J 6 Л
40 47	5	11,000	21,000	750	י ק	0. <del>4</del> 4 2
4/	9	1000	31,000	/30	1	4.2 5.7
4ð	/	1000	21,000	500	5	5.7
49	7	21,000	21,000	1000	5	3.2
50	5	31,000	11,000	750	7	3.9

Table 3	ANOVA for response
surface	quadratic model in the
presenc	e of [C <sub>12</sub> mim][Cl]

Source	Some of squares	df	Mean square	F value	P value prob > $F$	
Model	854.84	20	42.74	45.99	< 0.0001	Significant
A-pH	2.70	1	2.70	2.91	0.0987	
B-MgCl2 Conc	8.69	1	8.69	9.35	0.0048	
E-CaCL2-Conc	14.28	1	14.28	15.37	0.0005	
D-C12mim	194.91	1	194.91	532.53	< 0.0001	
E-Resin frac	8.15	1	8.15	8.77	0.0060	
AB	0.83	1	0.83	0.90	0.3519	
AC	9.112E-003	1	9.112E-003	9.805E-003	0.9218	
AD	3.200E-003	1	3.200E-003	3.443E-003	0.9536	
AE	0.20	1	0.20	0.21	0.6475	
BC	0.031	1	0.031	0.034	0.8558	
BD	8.67	1	8.67	9.33	0.0048	
BE	0.017	1	0.017	0.018	0.8930	
CD	5.48	1	5.48	5.89	0.0216	
CE	0.56	1	0.56	0.60	0.4432	
DE	7.813E-003	1	7.813E-003	8.406E-003	0.9276	
A <sup>2</sup>	0.070	1	0.070	0.075	0.7863	
B2	0.19	1	0.19	0.20	0.6542	
C2	0.84	1	0.84	0.91	0.3493	
D2	309.18	1	309.18	332.68	< 0.0001	
E2	6.384E-003	1	6.38E-003	6.870E-003	0.9345	
Residual	26.95	29	0.93			
Lack of fit	26.92	22	1.22	252.74	< 0.0001	Significant
Pure error	0.034	7	4.841E-003			
Cor total	881.79	49				

 Table 4
 Error analysis for the results and proposed model

Sequential Model Sum of Squares [Type I]								
Source	Sum of Squares	df	Mean Square	F Value	P value prob > $F$			
Mean vs Total	814.38	1	814.38					
Linear vs Mean	528.74	5	105.75	13.18	< 0.0001			
2FI vs Linear	15.81	10	1.58	0.16	0.9980			
Quadratic vs 2FI	310.29	5	62.06	66.77	< 0.0001	Suggested		
Cubic vs Quadra	26.86	15	.79	264.87	< 0.001	Aliased		
Residual	0.095	14	6.760E-003					
Total	1396.18	50	33.92					
Lack of fit								
Source	Sum of Squares	df	Mean Square	F Value	P value prob > $F$			
Linear	353.02	37	9.54	1970.87	< 0.0001			
2FI	337.21	27	12.49	2579.85	< 0.0001			
Quadratic	26.92	22	1.22	252.74	< 0.0001	Suggested		
Cubic	0.061	7	8.679E-003	1.79	0.2296	Aliased		
Pure Error	0.034	7	4.841E-003					

Sequential Model Sum of Squares [Type I]: select the highest order polynomial where the additional terms are significant and the model is not aliased

find the most accurate and proper models which directed the conclusions toward the quadratic model (see Table 4). In the last stage, the proposed quadratic model (see Eq. 2 for the fitting parameters of each constant) was analyzed to find the accuracy of this model.

$$IFT = 5.57 - 0.02A - 0.17B - 0.21C - 0.77D - 0.84E$$
  
- 0.49AB + 0.56AC - 0.063AD - 0.1AE + 0.013BC  
- 0.15BD + 0.39BE + 0.26CD + 0.26CE - 0.29DE  
+ 0.085AA - 0.11BB + 0.097CC - 0.23DD + 0.38EE (2)

Table 5 Statistical analysis results for the proposed model

SD	0.96	R-squared	0.9694
Mean	4.04	Adj R-squared	0.9484
C.V %	23.89	Pred R-squared	0.8729
PRESS	12.10	Adeq precision	32.89

Cor total

94.68

The obtained results revealed that considering the <u>stand-ard deviation</u> and <u>PredR-Squared</u> concomitant with <u>Adj</u> <u>R-Squared</u> which values are about 0.8729 and 0.9484, respectively, one can conclude that the proposed model is accurate enough to be used to predict the IFT values of the mixtures in different intervals in the examined ranges of the parameters. Besides, the <u>Adeq Precisions</u> which is the ratio of signal to noise ratio is an indication of the capability of the proposed model to navigate the designed space. In detail, since the "<u>Adeq Precision</u>" is well above the value of 4 (32.819), the proposed model is well-suited for predicting the IFT value of the mixture under different conditions (see Table 5).

In the next stage of this section, the effect of  $[C_{12}py][Cl]$ on the IFT in the presence of different salts under different operating conditions was examined using the CCD approach (Table 2 and 6). The obtained results revealed that similar to the results obtained for the solutions comprised of  $[C_{12}mim]$ [Cl], operating conditions including pH, CaCl<sub>2</sub>, and MgCl<sub>2</sub> concentrations, and resin fraction introduced a profound effect on the IFT value. The point is that although similar

Table 6	ANOVA for response
surface	quadratic model in the
presence	e of [C <sub>12</sub> py][Cl]

Source	Some of Squares	df	Mean Square	F Value	P value prob > $F$	
Model	93.22	20	4.66	92.28	< 0.0001	significant
A-pH	0.016	1	0.016	0.32	0.5779	
B-MgCl2 Conc	1.16	1	1.16	22.89	< 0.0001	
E-CaCL2-Conc	1.68	1	1.68	33.28	< 0.0001	
D-C12py	24.03	1	24.03	475.65	< 0.0001	
E-Resin frac	28.22	1	28.22	558.78	< 0.0001	
AB	7.61	1	7.61	150.56	< 0.0001	
AC	10.13	1	10.13	200.45	< 0.0001	
AD	0.13	1	0.13	2.47	0.1265	
AE	0.32	1	0.32	6.34	0.0176	
BC	5.000E-003	1	5.000E-003	0.099	0.7553	
BD	0.72	1	0.72	14.25	0.0007	
BE	4.81	1	4.81	95.13	< 0.0001	
CD	2.21	1	2.21	43.65	< 0.0001	
CE	2.20	1	2.20	43.65	< 0.0001	
DE	2.64	1	2.64	52.37	< 0.0001	
$A^2$	0.23	1	0.23	4.58	0.0409	
B2	0.42	1	0.42	8.38	0.0071	
C2	0.30	1	0.30	6.02	0.0204	
D2	1.66	1	1.66	32.79	< 0.0001	
E2	4.74	1	4.74	93.91	< 0.0001	
Residual	1.46	29	0.051			
Lack of fit	1.29	22	0.059	2.35	0.1248	Not significan
Pure error	0.17	7	0.025			

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to the results obtained for [C<sub>12</sub>mim][Cl], the interactions between [C<sub>12</sub>py][Cl] and CaCl<sub>2</sub> and MgCl<sub>2</sub> are significant, all the interactions between pH/CaCl<sub>2</sub>, pH/MgCl<sub>2</sub>, MgCl<sub>2</sub>/ Resin fraction, CaCl<sub>2</sub>/Resin fraction, and [C<sub>12</sub>py][Cl]/resin fraction are significant and undeniable. In this way, it seems that in contrast to the results obtained for [C<sub>12</sub>mim][Cl], the presence of  $[C_{12}py][Cl]$  in the mixture solution has a significant effect on all of the examined parameters. This observed trend can be correlated to the fact that imidazolium cation is an acidic component with pKa = 21-23 which comes from the H<sub>2</sub> hydrogen of the imidazolium nucleus while pyridine is often used as an organic base in chemical reactions pKa = 5. In light of this fact, it seems that since the resin fraction has an acidic nature and is contacted with a basic surfactant neutralization of repulsive forces existed between the molecules occurs leading to easier packing of the pyridinium-based ILs in the interface consequently leading to more IFT reduction compared with the imidazoliumbased IL.

The analysis of the obtained results through the modeling stage revealed that similar to the results obtained for the solutions including  $[C_{12}mim][Cl]$ , the best model in the quadratic model can accurately model the IFT values of the mixtures including  $[C_{12}py][Cl]$  (see Table 7). Besides, further analysis revealed that not only the "sequential model sum of squares" revealed that the quadratic model is the best, but also the "lack of fit tests" confirmed the capability of the quadratic model (see Table 7). Moreover, the calculated "*Adeq precision*" value which is about 47.339 is a good indication for the capability of the proposed model for the IFT prediction since the "*Adeq precision*" value must be above 4 to indicate the potential of the proposed model for accurate performance (see Table 8).

As a final point regarding the proposed quadratic model, one can use the fitting parameters tabulated in Table 10 to reproduce the measured IFT values for the different operating conditions and solutions prepared by the dissolution of different chemicals (see Eq. 3).

$$IFT = 1.41 - 0.26A - 0.47B - 0.6C - 3.52D - 0.45E$$
  
- 0.16AB - 0.017AC + 0.01AD + 0.79AE + 0.031BC  
- 0.52BD - 0.023BE + 0.41CD + 0.13CE - 0.016DE  
- 0.047AA + 0.077BB + 0.16CC + 3.11DD - 0.014EE (3)

The worth mentioning point is that a glance into the operating parameters and measured IFT values for both data sets determined using the CCD approach revealed that Run#22

Table 8 Statistical analysis results for the proposed model

SD	0.22	R-squared	0.9845
Mean	5.75	Adj R-squared	0.9739
C.V %	3.91	Pred R-squared	0.9457
PRESS	5.15	Adeq precision	47.339

Sequential Model Sum of Squares [Type I]							
Source	Sum of squares	Df	Mean square	F value	P value prob > $F$		
Mean vs total	1654.28	1	1654.28				
Linear vs mean	55.10	5	11.02	12.25	< 0.0001		
2FI vs linear	30.75	10	3.08	11.85	< 0.0001		
Quadratic vs 2FI	7.36	5	1.47	29.13	< 0.0001	Suggested	
Cubic vs Quadra	1.25	15	0.083	5.37	< 0.0016	Aliased	
Residual	0.22	14	0.015				
Total	1748.96	50	34.98				
Lack of fit							
Source	Sum of squares	Df	Mean square	F value	P value prob > $F$		
Linear	39.41	37	1.07	42.60	< 0.0001		
2FI	8.65	27	0.32	2.81	0.0010		
Quadratic	.29	22	0.059	2.35	0.1248	Suggested	
Cubic	0.042	7	5.971E-003	0.24	0.9608	Aliased	
Pure Error	0.17	7	0.025				

**Table 7** Error analysis for the results and proposed model (for the solutions including  $[C_{12}py][Cl]$ )

Sequential Model Sum of Squares [Type I]: select the highest order polynomial where the additional terms are significant and the model is not aliased

and Run#26 led to the lowest IFT values of 2.2 and 0.62 mN/m. In this way, these two solutions were selected and used to find the effect of these two solutions on the wettability alteration considering the initial condition of the rock wettability which was strongly oil-wet with a contact angle of about  $125.3^{\circ}$ . The measurements revealed that the application of this aqueous solution in the presence of synthetic resinous oil with different concentrations of 1, 3, 5, 7, and 9 wt% led to the reduction in contact angle revealed the movement of the rock wettability toward water-wet conditions (see Table 11).

# Effect of optimum formulation on wettability alteration

The measurements revealed that for both examined optimum formulations of  $[C_{12}mim][Cl]$  and  $[C_{12}py][Cl]$  in contact with the synthetic resinous oil prepared using different resin fractions, as the resin fraction increases from 1 to 9 wt%, a reduction in contact angle from 67.3° to 51.2° for  $[C_{12}mimi]$ [Cl] and from 62.3° to 42.2° for  $[C_{12}py][Cl]$ . A closer look into the tabulated results in Table 9 revealed a better functionality of  $[C_{12}py][Cl]$  for changing the wettability of the rock surface toward water-wet conditions. However, an increase in the resin fraction has a moderate effect on the movement of the rock wettability toward strongly water-wet conditions.

# Aqueous solution stability at the presence of TiO<sub>2</sub>-NPs

In the second stage of this investigation, the stability of the aqueous solution containing  $TiO_2$ -NPs was investigated since precipitation of NPs in the reservoir is an undeniable risk that must be reduced to its minimum level or even eliminated precipitation and pore plugging. In this way,

**Table 9** the effect of optimum chemical formulation on the wettability alteration of the rock surface as a function of different resin fraction concentration in the synthetic oil (initial condition =  $125.3^{\circ}$ )

Run	Optimum formulation	Resin frac- tion wt%	Contact angle
1	Run#26 ([C <sub>12</sub> mim][Cl])	1	67.3
2	Run#26 ([C12mim][Cl])	3	56.7
3	Run#26 ([C12mim][Cl])	5	54.3
4	Run#26 ([C12mim][Cl])	7	50.2
5	Run#26 ([C12mim][Cl])	9	51.2
6	Run#22 ([C12py][Cl])	1	62.3
7	Run#22 ([C12py][Cl])	3	56.2
8	Run#22 ([C12py][Cl])	5	51.2
9	Run#22 ([C12py][C1])	7	46.3
10	Run#22 ([C <sub>12</sub> py][Cl])	9	42.2

compatibility tests must be performed to find the concentration and pH value leading to the most stable aqueous solution containing TiO2-NPs for a long period and at least one month. In this way, considering the optimum chemical formulation for each IL (led to the lowest IFT values), the compatibility tests were performed by changing the TiO<sub>2</sub>-NPs concentration between 0 and 200 ppm. All of the prepared solutions revealed long-term stability (more than four weeks) in the presence of ILs regardless of the IL type while the aqueous solutions prepared without ILs experienced precipitation after 5 h of solution preparation. As a consequence of these observations, it seems that the application of IL is a crucial parameter to stabilize the TiO<sub>2</sub>-NPs for a long period. Respecting these facts, using the optimum formulation along with the TiO<sub>2</sub>-NPs has the minimum risk of precipitation due to the results obtained during the compatibility test stage.

The point that must be clarified is that the maximum concentration of  $\text{TiO}_2$ -NPs was selected at 200 ppm since as the concentration of  $\text{TiO}_2$ -NPs was increased to values higher than 200 ppm, the transparency of the solution faded which put the operator in trouble to measure the IFT in contact with the dark solution of the synthetic oil.

#### Effect of TiO<sub>2</sub>-NPs on the IFT

In the next phase of this investigation, the synergistic effect of  $\text{TiO}_2$ -NPs was investigated by measuring the IFT value between the aqueous solution/synthetic resinous oil by ranging the TiO<sub>2</sub>-NPs concentration between 0–200 ppm, and the chemical formulations were kept constant as obtained for Run#22 and Run#26. The worth mentioning point is that although the chemical formulations obtained for Run#26 and Run#22 are in contact with specific fractions of resin dissolved in toluene (9 wt% for [C<sub>12</sub>mim][Cl] and 7 wt% for [C<sub>12</sub>py][Cl], respectively), the IFT measurements of this section were performed using different resin fractions in the range of 1–9 wt% (see Table 10 and 11).

The measured IFT values revealed that an increase in the  $TiO_2$ -NPs concentration led to a reduction in the IFT from the maximum value of 2.2 to 0.62 mN/m for  $[C_{12}mim][CI]$  and from 6.8 to 0.84 mN/m for  $[C_{12}py][CI]$  which all of this minimum IFT values was obtained if the  $TiO_2$ -NPs concentration was increased to 200 ppm. The point is that for all of the  $TiO_2$ -NPs concentrations and different resin fractions dissolved in toluene, the IFT values were measurable except the solutions were prepared by 100 ppm and 200 ppm of  $TiO_2$ -NPs and resin fractions of 9 wt% which led to IFT values lower than 0.4 mN/m made it impossible to measure the IFT values for those solutions using pendant drop method (see Table 12). Similar results were obtained for the effect of  $TiO_2$ -NPs concentration by Nowrouzi et al. (2019)

Table 10 The effect of TiO<sub>2</sub>-NPs on the IFT reduction of the solution includes [C12mim][Cl] in the contact with the resinous synthetic oil

Resin fraction	TiO <sub>2</sub> -NPs Concentration (ppm)	IFT (mN/m)	
1	0	2.2	
1	100	1.33	
1	200	0.87	
3	0	1.9	
3	100	1.34	
3	200	0.98	
5	0	1.3	
5	100	0.94	
5	200	0.76	
7	0	1.05	
7	100	0.81	
7	200	0.55	
9	0	0.62	
9	100	Immeasurable	
9	200	Immeasurable	

Table 11 The effect of TiO<sub>2</sub>-NPs on the IFT reduction of the solution includes [C12py][Cl] in the contact with the resinous synthetic oil

Resin fraction	TiO2-NPs Concentration (ppm)	IFT (mN/m)
1	0	6.8
1	100	4.5
1	200	3.1
3	0	4.1
3	100	2.8
3	200	1.78
5	0	2.9
5	100	2.1
5	200	1.42
7	0	2.2
7	100	1.29
7	200	0.79
9	0	1.87
9	100	1.11
9	200	0.84

who examined the impact of TiO2-NPs on the IFT reduction using different concentrations of 500 and 1000 ppm in the formation brine and diluted formation brine which were carbonated using CO<sub>2</sub> dissolution.

In detail, they reported that the presence of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-NPs, MgO-NPs, and TiO<sub>2</sub>-NPs are so effective for IFT reduction, especially  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-NPs. For example, under similar conditions of 1000 ppm of NPs, the salinity of 10-times diluted water (10 times), and under pressure and temperature

<b>Table 12</b> The effect of $TiO_2$ - NPs on the CA for the solution includes [ $C_{12}$ mim][Cl] in the contact with the resinous	Resin frac- tion	TiO <sub>2</sub> -NPs Concentration (ppm)	CA	
synthetic oil	1	0	67.3°	
	1	100	56.3 °	
	1	200	45.2 °	
	3	0	56.7 °	
	3	100	50.2 °	
	3	200	41.1 <sup>o</sup>	
	5	0	54.3 °	
	5	100	46.5 °	
	5	200	38.2 °	
	7	0	50.2 °	
	7	100	43.5 °	
	7	200	35.6 °	
	9	0	51.2 °	
	9	100	42.5 °	
	9	200	33.2 °	

of 13.79 MPa, and 40 °C, respectively, the IFT values were γ-Al<sub>2</sub>O<sub>3</sub>, MgO, and TiO<sub>2</sub> are 2.85, 3.31, and 6.43 mN/m, respectively. Although they examined the effect of NPs in the presence of carbonated water, the mechanism which is correlated to the NPs are the same since NPs can produce a monolayer depending on the type and size of NPs which can boost the packing of different molecules and ions at the interface leading to lower IFT values. In brief, based on the theory and mechanism proposed by Li et al. (2013) and Dahle (2013) it is reported that NPs can produce a layer between nanofluid and crude oil in the interface that reduces the IFT between the immersed phases. The functionality of this formed layer is usually considered similar to the layer that the surfactant molecules can produce. The noteworthy point is that although the effect of surfactant concentration on the IFT is mostly in a linear trend, the impact of NPs concentration is not similar to the surfactant molecules (Dahle 2013; Hendraningrat et al. 2013a).

As described in Fig. 3 (Nowrouzi et al. 2019), the formation of nanofilms on the interface of the drop/bulk in the presence of ions moves the NPs toward a more harmonic and tidy pattern in the interface, especially if the number of NPs are less than the ions. As a consequence of this tidiness, the entropy of the whole suspension increases by increasing the freedom for nanoparticles leading to higher pressure on the volume (Chengara et al. 2004). The point is that the NPs form a thin film consisting of the interface which is the consequence of structural disjoining pressure with the source of the Brownian motion and electrostatic repulsion between NPs. In this regard, Aveyard et al. reported that the formation of this nanofilm is highly dependent on the NPs concentration and size, salinity, temperature, and interfacial

properties. For example, as the amount NPs concentration increases or the size of NPs reduces in the nanofluid, the film progression increases on the interface. The other possible reason behind the effect of NPs on the IFT is the fact that NPs are not generally amphiphiles but an increase in surface pressure is measured on their adsorption due to a decrease in the IFT caused by the appropriate wettability of the nanoparticles at the interface of oil and water (Binks 2002) [82].

In this way, the ILs with bulky structures can reduce the interfacial tension in the first stage. After that, in light of this reduction in IFT, the NPs easily move toward the interface to form a progressed thin film layer of NPs which is essential to modify the IFT and wettability alteration. Besides, the bulky structure of the ILs provides a proper chance for the NPs to be packed in the IL structure for easier packing and arrangement in the interface. As a consequence of this higher amount of packed NPs in the interfaces, a thinner film of NPs would be formed in the interface leading to lower IFT values and probably better wettability alteration toward the strongly water-wet condition. Moreover, the presence of IL can reduce the repulsive forces between the NPs means a higher amount of NPs can be packed in the interface leading to lower IFT values.

#### Wettability alteration

In the last stage of this investigation, the effect of optimum formulations was examined on the CA of the thin sections prepared from the carbonate rocks which were aged under the temperature of 80 °C and pressure of 1000 psi for 1 month to restore them to the oil-wet condition (similar to the reservoir condition) (see Table 12 and 13).

**Table 13** The effect of  $TiO_2$ -NPs on the CA for the solution includes  $[C_{12}py][Cl]$  in the contact with the resinous synthetic oil

Resin frac- tion	TiO <sub>2</sub> -NPs Concentration (ppm)	CA
1	0	62.3 °
1	100	52.1 °
1	200	43.8 °
3	0	56.2 °
3	100	46.5 °
3	200	39.8 °
5	0	51.2 °
5	100	41.6 °
5	200	34.4 °
7	0	46.3 °
7	100	37.5 °
7	200	30.1 °
9	0	42.2 °
9	100	34.2 °
9	200	27.3 °

A close look into the results tabulated in Table 12 and 13 revealed that increasing the concentration of TiO<sub>2</sub>-NPs in both aqueous solutions of [C<sub>12</sub>mim][Cl] and [C<sub>12</sub>py][Cl] leads to a considerable reduction in the CA which means the strongly water-wet conditions. This observed effect on the CA variation is correlated to the effects of ILs, and TiO<sub>2</sub>-NPs can synergistically move the rock wettability toward strong water-wet conditions. In detail, the penetration of surfactant molecules into the oil film existing on the rock surface can change the rock wettability to more water-wet status. As a consequence of this penetration, the surfactant molecules stick to the rock surface rendering the rock surface toward more water-wet conditions. In detail, the presence of surfactants in the aqueous solution can manipulate the key interactions responsible for the wettability alteration such as the electrostatic force, the hydrophobic force, and the attractive force between the surfactant and polar components of the crude oil and rock morphology. In general, the wettability alteration of an oil-wet carbonate rock surface depends upon the type of surfactant, oil composition, the concentration of surfactant, and brine salinity. The other point which can manipulate the efficiency of the surfactant for wettability alteration is the presence of salts in the aqueous solutions. In detail, salts can also accelerate the diffusion of surface-active constituents from the bulk solution to the interface and, thus, enhance the adsorption of the surfactant at the interface, resulting in the decrease of the rock surface from intermediate-wet to water-wet increasing the oil recovery rate.

Regarding the effect of NPs on the wettability alteration, a similar trend was observed by 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 conditions. In detail, they reported the wettability alteration in the presence of silica NPs due to changes in the solid/fluid interface caused by the 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  $39^{\circ}$  to  $26^{\circ}$ (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. Also, Morrow reported considerable wettability changes for quartz surfaces were due to the 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).

Moreover, Ershadi et al. (2015) utilized hybrid carbon/ silica nanotubes to change the rock wettability of surfaces toward a water-wet state. It was reported by Ershadi et al. (2015) that the value for the CA increases, and that explains the capability of this hybrid combination of nanoparticles to render the rock surface more water-wet while their investigation revealed the dual effects of the used NPs on the modification of both wetness change and IFT. The reduction of interfacial tension, IFT is the most effective mechanism that might enhance oil production. According to the findings, it is possible to categorize the possible mechanisms regarding NPs into three different classes, and one of the most important ones besides disjoining pressure and density difference



Fig. 4 Ordering of nanoparticle in the wedge-film resulting in structural disjoining pressure gradient at the wedge vertex (Salehi et al. 2010)

**Fig. 5** Effect of chemicals on the wettability alteration

is changing wetness. The application of NPs can directly produce a gradient between reservoir fluids and injecting fluid by manipulating the density of the fluid can consequently affect the movement of oil film on the surface of rocks and replace it with water film which means changing the oil-wet condition (Al-Anssari et al. 2016; Maghzi et al. 2011; Wang et al. 2005).

Besides, Wasan et al. (2011) performed a visual-video microscopy-based investigation to examine solid surface modification with the assistance of immiscible liquid spreading on a solid surface occurring to Brownian motion. Their findings revealed that the NPs arrangement leads to the formation of a wedge film between the oil and solid substrates (see Figs. 4 and 5. At this point, a pressure gradient appears between the thin layer and the bulk of fluid and is boosted as the NPs concentration enhances. As a consequence of this pressure gradient, it would be possible to manipulate by affecting the film tension toward the vertex of the wedge, consequently influencing the surface wettability (Kondiparty et al. 2011; Wasan et al. 2011).

Besides the other NPs, Aghajanzadeh et al. (2019) have investigated the effect of silica-nanoparticles on the changing wetness of rock surfaces. They have reported that according to the obtained results the concentrations of NPs enhance the changing wetness was shifted from oil-wet to water-wet. Moreover, the results of spontaneous imbibition examinations revealed an increase of about 15% higher oil recovery using nanofluid compared with the case only formation brine was utilized. Finally, they examined the effect of NPs presence in the injected solution during the core flooding experiments and found that not only the relative permeability curve



was modified and moved toward the right side of the curve also the water relative permeability was reduced to 0.23 mD from its initial value of 0.43 mD at the residual oil saturation due to wetness change toward water wet status from strongly oil-wet (Aghajanzadeh et al. 2019).

On the other hand, an innovative application of nanoparticles with anionic surfactants was performed by Ershadi et al. (2015) illustrating the possible effect of surfactant existence that might reduce the IFT values. As well as maybe, accelerate the penetration of NPs to enhance their impact on the rock surface wettability, moreover, the reduced IFT and the wetness change strengthen one another, and that definitely will enhance the oil production by producing more trapped oil from the reservoirs (Resasco et al. 2015). Furthermore, Karimi et al. (2012) utilized Zirconium oxide (ZrO<sub>2</sub>) to alter the rock wetness surfaces. In addition, it was found that the adsorption of these NPs might modify the surface toward neutral wet, as well as it was reported that measuring the air/water CA values demonstrated the change in wettability from oil-wet to neutral wetting states. In addition, it was found the energy-dispersive X-ray, EDX, and the analysis of the samples aged in a solution containing NPs of ZrO<sub>2</sub> revealed that the surfaces are composed of Ca and Zr as constituent materials, which means zirconium, was adsorbed onto the surface [8]. One of the other innovative investigations is related to the production of a new family of NPs, e.g., Fe<sub>3</sub>O<sub>4</sub> NPs coated nanoparticle Ethylenediaminetetraacetic (EDTA) as a hydrophilic polymer or Sodium Lauryl Sulfate (SLS) as an anionic surfactant by the dip-coating method recently proposed by Shalbafan et al (2019). In this method, a nanoparticle can effectively change the wettability of rock surfaces from oil-wet to water-wet conditions by activating the disjointing pressure mechanism.

The last point is that the experiments performed by Hendraningrat and Torsæter (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 revealing 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 (Hendraningrat and Torsæter 2014) and those obtained in the current investigation, it seems that combining the SiO<sub>2</sub>-NPs with ILs as the chemical surfactant and stabilizer can provide a more efficient chemical formulation for oil recovery purposes.

# Conclusions

The application of 1-dodecyl 3-methyl pyridinium chloride  $([C_{12}py][Cl])$  and 1-dodecyl 3-methyl imidazolium chloride  $([C_{12}mim][Cl])$  as novel surfactants (0–1000 pm) in the absence and presence of titanium oxide nanoparticles  $(TiO_2-NPs)$  (0–200 ppm) besides pH (3–11) and divalent salts namely magnesium chloride and calcium chloride in the range of 1000–41000 ppm are investigated. Besides, instead of using crude oil comprised of many components, synthetic resinous oil was used for interfacial tension (IFT) and wettability alteration measurements using the central composite design (CCD) and changing one factor at a time to reduce the required number of experiments. Respecting this approach, the following results were obtained:

- The presence of resin acts as the natural surfactant reducing the interfacial tension to minimum value of 25.3 mN/m in the absence of different chemicals.
- In the absence of salts, pH, and  $TiO_2$ -NPs,  $[C_{12}py][Cl]$  leading to lower IFT values than  $[C_{12}mim][Cl]$  due to the acidic nature of the resin fraction and basic nature of  $[C_{12}py][Cl]$  leading to the positive interaction in the interface which can effectively reduce the IFT.
- The minimum IFT value was obtained for pH = 7, MgCl<sub>2</sub> concentration = 21,000 ppm, CaCl<sub>2</sub> concentration = 21,000 ppm, resin fraction of 9 wt% and 500 ppm of [C<sub>12</sub>mim][Cl] concentration.
- The positive interaction that existed between the different operating parameters put the  $[C_{12}mim][Cl]$  in a better situation for IFT reduction than the  $[C_{12}py][Cl]$  although in the absence of different chemicals,  $[C_{12}py][Cl]$  leading to better functionality.
- Combining the TiO<sub>2</sub>-NPs with the optimum chemical formulations for [C<sub>12</sub>mim][Cl] and [C<sub>12</sub>py][Cl] shifted the wettability toward strongly water-wet condition.
- The CA values are reduced to values of 33.2° and 27.3° for [C<sub>12</sub>mim][Cl] and [C<sub>12</sub>py][Cl] with TiO<sub>2</sub> concentration of 200 ppm and resin fraction of 9wt%.
- The IFT measurements revealed that the presence of  $TiO_2$ -NPs not only moved the wettability toward strongly water-wet condition, but also the IFT of both chemical formulations for ILs experienced a reduction to minimum values of 0.55 mN/m and 0.84 mN/m for [C<sub>12</sub>mim][Cl] and [C<sub>12</sub>py][Cl].

As the last point, although the obtained results revealed the efficiency of the obtained optimum formulation on the IFT reduction and wettability alteration toward desired conditions, the practical applications of these optimum formulations must be examined using other experiments. For example, it seems highly applicable if the obtained optimum formulations are used in the core flooding experiments and adsorption tests analysis which can be the next phase of similar investigations currently performed. These two experiments and tests are necessary since they can provide better insight regarding the required amount of chemicals used in the optimum formulations (cost evaluation) and the possible tertiary oil recovery in the field scale (feasibility and capability). Moreover, the impact of these formulations must be examined in the presence of reservoir heterogeneities since the rock interactions with fluids have a significant effect on the efficiency of the optimum formulation.

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