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Akram
Al-Asadi

PhD Thesis

Nanofluids based on ionic liquids for enhanced oil recovery

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DOCTORAL THESIS

NANOFLUIDS BASED ON IONIC LIQUIDS FOR ENHANCED OIL RECOVERY

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Nanofluids based on ionic liquids for enhanced oil recovery

Dª. Ana María Soto Campos and Dª. Eva Rodil Rodríguez

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In Santiago de Compostela, 23 of February 2023

Dª. Ana María Soto Campos

Dª. Eva Rodil Rodríguez

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Abstract in English

During the ecological transition the full exploitation of, in principle, exhausted oil reservoirs is required to maintain current standards of living. The main objective of this thesis was the design of formulations containing surface-active ionic liquids and nanoparticles as the basis of an improved enhanced oil recovery (EOR) method. A state-of-the-art study regarding the use of nanoparticles as a method of EOR was carried out. This review provided the basis of the experimental work conducted. Two formulations were designed containing aluminum oxide nanoparticles and 1-dodecylpyridinium chloride or 1-dodecyl-3-methylimidazolium chloride, for carbonate reservoirs containing low and high salt concentration, respectively. Low chemicals adsorption and good oil recovery performance were achieved. The main conclusion of this thesis is that the cutting-edge EOR method proposed here must be further explored.

Contents

APPENDICES:

1. OBJECTIVES

Crude oil and its derived products still play a fundamental role in our lives. The uses and benefits of crude oil are numerous and current living standards would not be possible without it. Due to its non-renewable character and its environmental impact, we will undoubtedly be obliged to find substitutes. A transition from liquid hydrocarbons to renewable sources of energy is currently becoming a reality. However, obtaining bio-based materials without risking feed or forestry stocks is nowadays far from being possible. To make this ecological transition, time will be required. The full exploitation of in principle exhausted oil reservoirs, taking advantage of the already existing infrastructures and without new industrial investment, is a necessity to get this required time without compromising our welfare during the change.

After primary (natural output) and secondary (mainly pumping with water) recovery, approximately 60-80% of the oil still remains in a reservoir. Enhanced oil recovery (EOR) methods aim to improve production. Among these methods, two are currently highlighted as promising: the use of nanoparticles and the use of surface-active ionic liquids (SAILs). Considerable improvement in oil recovery is usually attributed to wettability alteration effects caused by the nanoparticles, that induce the detachment of the oil from the rock surface. SAILs are able to significantly reduce water-oil IFT, enhancing the mobility of the oil retained in the pores of the rocks, and can be tailor made for any given reservoir. However, despite the fact that the combination of methods for oil recovery produces a synergistic effect that multiplies the possibilities of the individual methods, the combination of these techniques had not been tested prior to this thesis.

The main objective of this thesis is the design of formulations containing SAILs and nanoparticles as the basis of an improved EOR method. To accomplish this goal, several specific objectives are defined.

The first specific objective is to carry out a state-of-the-art study regarding the use of nanoparticles as a method of EOR. Many questions need to be answered in this review. Is the use of nanoparticles really promising for the application? What are the most commonly applied nanoparticles? Are they stable by themselves in aqueous formulations or are other chemicals required? Are the same nanoparticles proposed for sandstone and carbonate reservoirs? Does the use of surfactants or polymers improve the performance of the nanoparticles alone? Unlike previous reviews that focused on the physicochemical mechanisms involved in recovery, this work aims to provide a critical analysis of the possibilities of nano-EOR according to the performance of the proposed formulations. To that aim, results achieved in core-flooding tests with proposed formulations will be critically analysed. This objective will be accomplished, in Chapter 3, with the publication of the paper entitled: "Nanoparticles in Chemical EOR: A Review on Flooding Tests" (Nanomaterials 12, 2022, 4142).

The second specific objective is to find an optimal formulation with the SAIL 1-dodecylpyridinium chloride and Al_2O_3 nanoparticles, both chemicals individually considered promising for the application in previous studies but never applied together. As stability of formulations is one of the major challenges in the application of nanoparticles in EOR, the work will start with the study of the formulation's stability at different SAIL and nanoparticle concentrations in either the absence or presence of salt. The need for stabilisers will be considered. Physical properties (density and viscosity) of aqueous solutions will be determined, not only because of their interest in this application but also in any other study involving these mixtures. A formulation will be optimised looking for a minimum water-oil IFT. Its applicability in sandstone and carbonate rocks will be assessed through adsorption studies. Wettability alteration will be considered as a possible EOR mechanism. Finally, core-flooding tests will be carried out with the optimised formulation containing the SAIL and the nanoparticles, but also with the individual compounds to confirm the increment in recovery due to the use of the combination of chemicals. This objective will be accomplished, in Chapter 3, with the publication of the paper entitled: "Nanofluid based on 1-

dodecylpyridinium chloride for enhanced oil recovery” (Petroleum Science, 20, 2023, 600-610).

The last objective focuses on analysing the influence of the SAIL’s cation on the performance of the formulation for the application. To that aim, the SAIL 1-dodecyl-3-methylimidazolium chloride is selected to be combined with the same nanoparticles (Al_2O_3). A similar study to the previous one will be carried out, considering stability, IFT, adsorption, wettability and core-flooding studies. This objective will be accomplished, in Chapter 3, with the publication of the paper entitled: “Enhanced oil recovery with nanofluids based on aluminium oxide and 1-dodecyl-3-methylimidazolium chloride ionic liquid” (Journal of Molecular Liquids, 363, 2022, 119798).

2. INTRODUCTION

Due to the significant social, industrial, and economic development that is taking place worldwide, there is an increase in the global demand for fossil fuels [1-2]. Energy needs are rising daily, and renewables haven't yet demonstrated that they can satisfy the total energy requirements [3]. Moreover, the replacement of all the products derived from the petrochemical industry by renewable materials is currently far from being a reality. Oil is and will be necessary to maintain our standards of living during the ecological transition. However, fresh findings of conventional oil reservoirs are now becoming less frequent, and investment in the search for oil as well as the development of new infrastructures for extraction does not make economic sense. However, it is known that after the application of current extraction technologies, approximately 60-80% of the oil still remains in the reservoir [3-7]. So finding new ways to extract that oil from the existing resources is essential. This has inspired researchers and petroleum experts to develop innovative recovery methods to extract more oil from, in principle, exhausted reserves.

Since the beginning of this century, nanotechnology has gained significant attention due to its utility in many varied applications. The National Nanotechnology Initiative defines the term as the management of matter having a dimension between 10 and 100 nm [8]. Quantum mechanical effects are important at this scale, and materials exhibit distinct or improved properties in this size range, such as an increased surface area [9-11]. In numerous fields including medicine, civil engineering, food science, and the oil and gas sectors, nanotechnology has been tested and successfully applied [11-13]. Oil recovery is considered one of the most promising and extensively investigated research areas, due to the ability of nanoparticles to easily penetrate through the pore throats of the rocks and alter reservoir characteristics to favour oil recovery [14-16].

2.1 Oil recovery stages

Three distinct stages (primary, secondary, and tertiary or enhanced recovery) of oil recovery are defined as follows [17]:

- Primary recovery is achieved under the natural driving mechanisms present in the reservoir. In other words, extraction is accomplished without requirement of external injection of any fluid or heat. Formation gas, gas cap, gravity drainage, rock and fluid expansion, and water, are the primary oil reservoir driving mechanisms.
- Secondary recovery occurs when there is a decline in the production of oil. To maintain pressure and efficiency of volumetric sweep, an external injection of fluids that do not mix with the oil, usually water and/or CO_2 gas, is applied to increase the natural energy of the reservoirs.
- Tertiary or enhanced oil recovery (EOR) denotes the recovery after the secondary stage. It is accomplished by external injection of particular fluids, such as miscible gases or chemicals, and/or thermal energy [17]. In chemical EOR, favourable conditions for oil recovery are obtained due to the interaction of injected fluids with oil and reservoir rocks. Wettability alteration, reduction of the IFT, lowering of the oil viscosity, oil swelling, favourable phase behaviour, and/or mobility modification is the desired result of such interaction [14].

After primary and secondary recovery processes, from one-third to even more than two-thirds of the oil are usually still trapped in reservoirs. This depends on the rock and fluid characteristics of the reservoirs (rock type, permeability -capacity of the medium to transmit fluids-, oil viscosity, etc...) and the driving mechanisms involved. Approximately 35% is considered to be the current factor of average global oil recovery [18]. The world's oil reserves would increase by nearly one trillion barrels if the recovery factor could be raised from the current amount of 35% to 45% [19]. It is worth mentioning that besides EOR methods, Improved Oil Recovery (IOR) methods, such as cement plug treatment or fracking, are applied in oil recovery [17]. However, these methods accelerate but do not improve oil extraction, and sometimes involve serious environmental damages. For this reason, research on efficient EOR methods is still of high interest.

2.2 Oil recovery mechanisms

The difficulties faced in oil recovery are mainly due to two factors. At the pore scale, the crude is trapped by capillary forces. Thus, EOR methods must improve displacement efficiency. At the oil field scale, there exist low permeability areas in which the fluid injected during the secondary extraction does not penetrate, because it follows preferential channels or because the geometry of the layout of the well is not favourable. The sweep efficiency must be improved to overcome these issues.

2.2.1 Microscopic displacement

Depending on the wettability of the rocks, a portion of crude oil in water flooding (the process of immiscible displacement) is trapped as stringers, isolated drops, or pendula rings (see Figure 2.1). When such a condition is reached, the permeability of the oil inside the reservoir is very low. Moreover, the injection fluid flows around the retained (or trapped) oil, losing its capacity for effective displacement [14]. The oil cannot transfer to the flowing streams due to capillary forces restricting (or preventing) the deformation and passage of oil through constrictions in the porous channels. This microscopic displacement is affected by: the pore structure's geometry, fluid-fluid interactions (including phase behaviour, bulk viscosity ratio, differential density, and IFT), interactions between fluids and rocks (including adsorption, ion exchange, and wettability), gravity, and the applied pressure gradient [20].

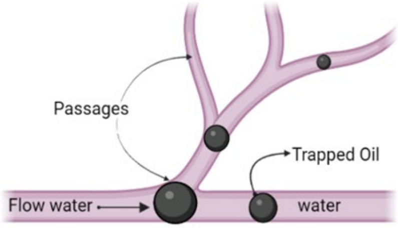

Figure 2.1: Blocking scheme for an oil droplet trapped in porous passages

Capillary and viscous forces govern the trapped phase, affecting the effectiveness of microscopic displacement.

2.2.1.1 Capillary forces

In order to increase or reduce the recovery efficiency of the displacement process, capillary forces play a significant role in the release or trapping of residual oil in pore spaces. The system's wetting properties, pore size and geometry, and surface and interfacial tensions between the rocks and fluids in the reservoir all work together to create capillary forces [21].

Surface and IFT

Condensed matter - solids and liquids - possesses surface tension because of the cohesive interactions among its constituent molecules. Molecules at the surface of a condensed phase under a vapour or gas have higher energy than more deeply located molecules because they are engaged in fewer attractive interactions with neighbouring condensed-phase molecules. Surface tension is defined as surface free energy per unit area. Liquids adopt bulk configurations of minimum surface area because in doing so they minimise their surface free energy. When a liquid comes into contact with a solid or with another liquid with which it is immiscible, the interfacial molecules of each phase may lower their energy through attractive interactions with the those of the other, resulting in an interfacial surface energy density, or IFT, that is intermediate between the surface tensions of the separate phases.

When immiscible phases (water and oil) coexist in a porous medium, surface energy related to the fluid interfaces influences the saturations, distributions and displacement of the phases [14]. Solutes that reduce the surface tension of a solvent have positive surface activity, and those that do so to a significant extent are known as surface active agents, or surfactants for short. This type of chemical is frequently used to favour oil displacement [22, 23].

Wettability

The distribution of fluids in a porous media depends not only on fluid-fluid but also on fluid-solid interactions. The ability of one fluid to spread out or attach to a rock surface when another fluid is present is known as wettability. When two immiscible phases, such as water and oil, are in contact with a solid phase, one of them is more strongly attracted to the solid and it is called the wetting phase [14].

If the reservoir rocks tend to be in contact with water, then they are considered to be water-wet. In this scenario, water exists in the reservoir's tiniest porous medium as a wetting (spreading) phase and predominately covers, as a film, the rock surface. The oil occupies the centre of larger pores, acting as a non-wetting (non-spreading) phase, forming globules surrounded by water. When the rocks are preferentially in contact with oil, they are oil-wet - oil occupies the small pores and contacts the majority of rock surface [24]. There are two basic subcategories of rock wettability: uniform wettability and non-uniform wettability. Strongly oil-wet to strongly water-wet conditions can both have uniform wettability. The rock exhibits neutral or intermediate wettability if it does not strongly prefer to be in contact with either oil or water [25].

The distribution of fluids within the media, relative permeability, and fluid saturation are all impacted by the wettability of porous media. Thus, oil recovery and productivity drastically depend on this parameter. Wettability alteration is based on changing the wetting state of reservoir rocks, to be more water-wet, as a method of EOR [25-27].

Capillary pressure

Because the interfaces are in tension, a pressure difference exists across the interface. It is called capillary pressure. In the context of oil recovery, the capillary pressure is the pressure difference between the non-wetting and wetting phases. Capillary pressures in a reservoir determine the saturation distribution, and hence the total in-situ volumes of fluids (oil/water/gas), and they are related to the fluid/fluid IFT, the relative wettability of the fluids, and the size of the pores.

Capillary pressure curves are usually determined for drainage (displacement of the wetting phase by the non-wetting phase) and imbibition (displacement of the non-wetting phase by the wetting phase) processes. Those data are useful to evaluate pore size distributions, predict fluid saturations, and assessing the relative importance of capillary and viscous forces during fluid flow in porous media [28].

2.2.1.2 Viscous forces

For a laminar flow of a fluid, dynamic viscosity is the ratio of the shear stress to the velocity gradient perpendicular to the plane of shear. It is a measure of the resistance to motion of a fluid due to the forces of cohesion between molecules. The viscosity, especially in the case of heavy oils, is a critical property in oil recovery. The velocity of flow and the viscosity of fluid are the dominant governing factors of viscous forces in porous media and are directly related to the pressure drop [28].

2.2.1.3 Alteration of viscous/capillary force ratio

The mobilisation of trapped phases inside the reservoir pores requires the alteration of the capillary number which is a ratio of the viscous-to-capillary forces. The mathematical expression for this dimensionless number varies slightly according to the different authors [17] but its physical meaning remains the same. The most common equation is:

$$N_C = \frac{F_v}{F_c} = \frac{v\mu}{\sigma cos} \tag{1}$$

where F_v and F_c are viscous and capillary forces, respectively; v is the velocity of the displacing fluid in the pore; μ is the viscosity; σ is the IFT between displacing and displaced fluid; and θ is the contact angle between the wetting phase and the oil.

A capillary number higher than 10^{-3} is required to achieve a good oil recovery. Thus, EOR methods attempt to raise this number. The increase of velocity means an increase of injection pressure, more energy cost and risk of rock fracture, so there is little room for modification. In chemical EOR, polymers are frequently used to increase the viscosity of the displacing fluid (again higher viscosity of the injection fluid means higher energy requirements). Surfactants are used to reduce the water/oil IFT and also can help to change wettability. Nanoparticles can improve the stability of surfactants and polymers, as well as multiply their performance, due to synergistic effects in their effectiveness.

2.2.2 Macroscopic displacement

The sweep efficiency controls how much of a reservoir is contacted by a displacement process. It depends on: the properties of displacing and displaced fluids, the properties and geological characteristics of the reservoir, and the geometry of the injection and production well pattern [14].

The efficiency of a displacement process can be analysed through the mobility ratio:

$$M = \frac{\lambda_D}{\lambda_d} \tag{2}$$

where D and d are the displacing and displaced fluid, respectively; and λ is the mobility of the fluid calculated as:

$$\lambda_i = \frac{k_i}{\mu_i} \tag{3}$$

i being the fluid (displacing or displaced); k is the effective permeability; and μ is the viscosity.

Conventionally, a mobility ratio $M \leq 1$ is considered favourable and $M > 1$ unfavourable [17]. The viscosity is a key parameter to get a suitable mobility ratio. The viscosity of the displacing fluid should be similar to that of the displaced fluid, polymers are frequently used to that aim. Thus, the formation of undesirable fingering (Figure 2.2) that produces a non-uniform flow and low sweep efficiency is avoided.

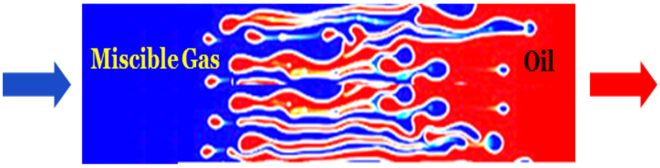

Figure 2.2: Viscous fingering in oil displacement

2.3 Enhanced oil recovery methods

As previously indicated, after primary and secondary oil recovery, one third or more of the original oil in place still remains in the reservoir. When secondary recovery ceases, EOR methods must be applied to extract that oil. Based on the mechanisms of oil recovery presented in section 2.2, many EOR methods have been designed. They aim to reduce the capillary forces that trap the oil in the pores of the rocks, to thin the oil or improve its mobility, or to alter the mobility of the displacing fluid. Most of them have been tested at laboratory scale, but some have also been evaluated at the field scale [29]. These methods can be divided into three categories: thermal, gas, and improved water flooding or chemical EOR:

a) Thermal methods involve heating of the oil field, thus reducing the viscosity of the crude and therefore facilitating its flow towards the well. Two main groups can be distinguished: processes in which a hot fluid such as steam is injected in the well, and processes in which the heat is generated within the well, e.g. by combustion. The risks and costs of these methods are high.

b) Methods of displacement by means of miscible fluids. A gas (natural gas, CO_2, or nitrogen) or alcohol is injected into the oil field at elevated pressures, to completely solubilise within the crude, reducing the problems of capillarity and increasing its mobility. These methods, specially with gases, face serious problems of adverse mobility ratios, especially when working with heavy crude oils.

c) Chemical flooding. This involves the addition of different chemicals to the injected water in order to recover additional oil. The main chemicals used are: polymers (cause an increase in the viscosity of the displacing fluid and a reduction in permeability), surfactants (reduce the IFT between water and oil and favour emulsification), and alkaline or caustic chemicals (generate a reaction with the organic acids in the crude, producing surfactants in situ). Recently, the use of nanoparticles is also being considered as an EOR method.

It should be mentioned that the use of specific bacteria, which through fermentative activity facilitate oil extraction, is also being considered as a possible EOR method. However, the inconsistency of in situ performance and low ultimate oil recovery factor, among other issues, limit their application [30].

2.3.1 Chemical EOR methods

The chemicals commonly used in EOR are surfactants and polymers. Tests with nanoparticles are extended at laboratory scale, where other techniques such as the combination of ferromagnetic nanomaterials with magnetic fields, or the use of smart water (modification of ionic composition of water) are also being tested. Sometimes the injection of consecutive slugs, each with a different chemical, is proposed. It is also common to inject an aqueous formulation containing several of these products, to take advantage of the synergy of their joint action. The extraction of crude oil from a well is a complex problem with no single solution. Laboratory extraction studies, simulations, field scale tests, and a lot of experience, are necessary for the design of a formulation for each specific case.

2.3.1.1 Surfactants

Two different parts can be distinguished in a surfactant. A polar part that has affinity for polar solvents particularly water, called the hydrophilic part, and a non-polar part with affinity for organic solvents, also called hydrophobic (see Figure 2.3). Conventional surfactants can be classified on the basis of their hydrophilic groups as anionic, cationic, zwitterionic, or non-ionic. To satisfy both affinities, surfactants are frequently found at the frontier of two different phases (liquid-liquid or gas-liquid).

Surfactants show two fundamental properties: adsorption at the surface or interface, and aggregation to form micelles, microemulsions and liquid crystals. Due to their special features, surfactants are used at several stages in the petroleum production and processing industries [23]. In EOR, they are frequently used to reduce the IFT between the oil and the displacement phase [27], and they are also used to form foams in combination with gases as an advanced method of oil recovery [31].

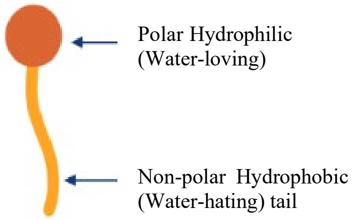

Figure 2.3: Schematic illustration of the surfactant's parts.

Surfactant flooding is an EOR method based on the addition of surface-active chemicals to water at very low concentrations. These chemicals reduce the capillary forces that trap the oil in the pores of the rocks. The surfactant slug displaces the majority of the oil contacted, forming a flowing oil-water bank that is pushed by the displacing fluid. Sometimes instead of surfactant, the displacing fluid is prepared with water, oil, surfactant and co-surfactant (usually an alcohol) along with salts. This method is called microemulsion flooding.

The main displacement mechanism in surfactant flooding is the reduction of the water-oil IFT. Oil droplets must be able to deform to pass through pore throats, and this effect can be achieved at low IFT. Moreover, when the oil is pushed, emulsions are formed and the emulsified and displaced oil coalesces to form an oil bank that exits the reservoir. As the surfactant contacts the rocks, a change in wettability can also be an additional mechanism of oil recovery. However, lowering IFT alone might not result in the optimum oil recovery value. Because of their low viscosity, dilute surfactant solutions occasionally finger into the oil bank and are sensitive to shear stress between rock pores [32]. For this reason, a slug of water containing polymer usually follows the surfactant slug to preserve its integrity.

To avoid high adsorption, anionic surfactants are preferred for sandstone and cationic for carbonate reservoirs. Nonionic surfactants are effective for flooding in formations containing high salinity water or hard water [33], however the cost of these surfactants is rather high. The most used surfactants at the field scale are linear and branched sulphates and sulphonates. The primary problems that companies face when using surfactant flooding are toxicity, high cost, and surfactant deterioration at extreme temperatures and salinities [34].

Surface active ionic liquids

Ionic liquids are salts with melting or glass transition temperatures below 100 °C. Sometimes, these temperatures are low enough that they are liquids at room temperature. Common cations in ionic liquids are rings such as imidazolium, pyridinium, pyrrolidinium, piperidinium or atoms such as ammonium, phosphonium, etc. Common anions are halides, acetate, nitrate, nitrite, etc. The most common constituents of ionic liquids are shown in Figure 2.4. When the hydrophobic chain of these salts (usually attached to the cation) are long enough, they show surface-active character and are named surface active ionic liquids (SAILs).

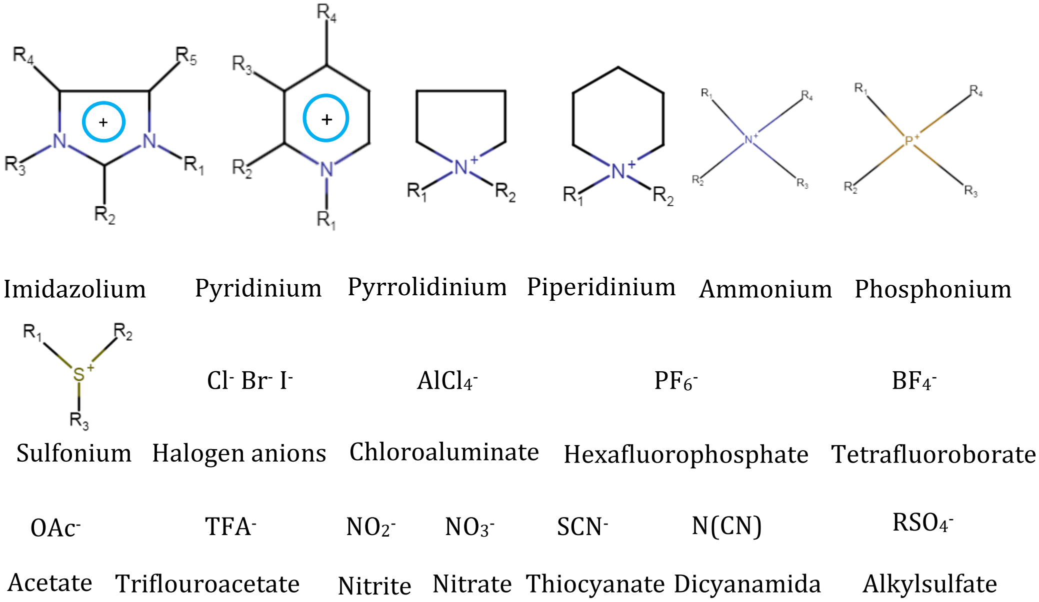

Figure 2.4. Common cations and anions on ionic liquids

It has been demonstrated that SAILs show some advantages in comparison to traditional surfactants when the target application is EOR [35]. Traditional surfactants are usually solids, and working with room temperature SAILs would facilitate their manipulation. Their low vapor pressure, good thermal stability, and solvating capability are additional traits that make them desirable for any application. Focusing on EOR, it has been shown that SAILs are more stable at harsh conditions (high salinity and temperature) than standard surfactants [36]. Their ability to be tuned, though, is their most interesting quality. To create compounds that are tailor-made to a particular purpose, cations and anions can be chosen, allowing for a reservoir-specific design [39,40]. Moreover, several papers have observed a better performance for SAILs in reducing water oil IFT than traditional surfactants, in the specific conditions of high salinity and temperature (where traditional surfactant flooding usually fails) [38].

A recent review [39] has shown the promising possibilities of SAILs for EOR according to results achieved in core-flooding experiments, assays where oil is extracted from real reservoir rocks, the closest laboratory tests to real applications. Encouraging results were shown for these chemicals, with additional recoveries after secondary flooding of up to 32% of the original oil in place. It is surprising that the majority of the tests have been carried out for cationic SAILs (the most common) on sandstone rocks. High adsorption - a parameter rarely studied - is expected with this combination due to the presence of negatively charged components of sand particles. The use of SAILs in carbonate reservoirs is preferable. No works combining SAILs with nanoparticles were found in the literature [39].

2.3.1.2 Polymers

Water-soluble polymers are used as the basis of polymer flooding EOR method [40]. As Sandiford described in a pioneering work [41], the primary role of the polymer is the improvement of the water viscosity used as displacing fluid. As explained in section 2.2.2, reducing the mobility ratio is one technique to increase the macroscopic displacement. The polymer solution affects the relative flow rates of oil and water and sweeps a larger fraction of the reservoir than water alone, thus contacting more of the oil and favouring its extraction [42]. The method is frequently used as a single EOR technique, mainly in heterogeneous reservoirs, but also as a post-slug to increase the efficacy of other methods such as surfactant flooding.

Many factors affect the performance of polymer flooding: temperature, water salinity (including total dissolved solids and the presence of divalent ions), polymer type, content and molecular weight, as well as the reservoir type and structure. The type of polymer is considered a crucial parameter and is currently the subject of many studies [43-45], the advantages of branched over linear polymers recently being highlighted due to their improved viscosifying properties. Hydrolysed polyacrylamides and xanthan gums are the polymers most tested in field applications.

A number of issues are associated to commercial field projects, the stability of the polymer being a particular bottle-neck. These chemicals can be degraded due to mechanical, thermal, chemical or even microbial effects [42]. At high temperature or salinity, the polymers often lose their stability.

2.3.1.3 Nanoparticles

Nanotechnology literally means any technology created on a nanoscale with applications in the real world [46]. This scale is considered to involve matter of sizes from 10 to 100 nm [8]. Many properties are a function of system size. Due to their reduced dimensions, nanoparticles show a great surface area/volume ratio, leading to improved physical, chemical and biological properties compared to the bulk material. Thus, it is not strange that nanotechnology has found many applications in the petroleum industry, with a strong impact in oil recovery. In fact, nano-EOR is being considered as a successful tertiary oil recovery method [47, 48].

Nanofluids, fluids containing nanometre-sized particles, based on water or alcohol have been successfully applied at lab scale for EOR [49]. The main mechanism of oil extraction is the change of wettability to that favourable for oil production. As nanofluids are able to pass through the narrow pores of the rocks, the surface area of reservoir in contact with them is large and the outcome significant. Sometimes the desired effect is very different. The aim can be the blockage of specific pores to improve the sweep efficiency of the displacing fluid. The capacity of nanomaterials to increase water viscosity is limited, and it has been shown that nanoparticles don’t always help to reduce water-oil IFT [48]. For this reason, many formulations proposed for nano-EOR are based on the combination of nanoparticles with surfactants and/or polymers. They may improve nanoparticle performance whilst reducing chemical adsorption on the rocks.

The most challenging task in the preparation of nanofluids is achieving stability. Colloidal particles in a dispersed system show Brownian motion and have a tendency to aggregate and sediment (Figure 2.5). Van der Waals attractive and electrical repulsive forces are the controlling features of the stability of nanoparticles [50]. Besides the combination with other chemicals, such as polymers, the functionalisation of nanoparticles is a powerful tool to increase their stability.

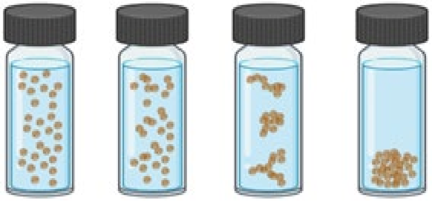

Figure 2.5. Stable and unstable nanofluids

The stability of a nanofluid relies on the functionality (or surface activity) of its nanoparticles. Thus, nanoparticles are usually treated or functionalised by putting shields around them to hinder particle–particle interactions and avoiding aggregation [48]. Usually for EOR applications, this functionalisation is carried out by means of polymers or surfactants, to take advantage of the properties of these chemicals in the application. However, the cost of these designed nanoparticles greatly increases.

What kind of nanoparticles are more promising for EOR applications? Does this depend on the type of reservoir? Is it worth functionalising the nanoparticles to boost stability? Does the combination of chemicals with nanoparticles clearly improve the performance of the EOR method? Have nanoparticles been tested in field applications? Many questions have arisen in studies on the topic, and have led to the first objective of this thesis: to get well acquainted with the possibilities of nano-EOR according to oil extraction tests from reservoir rocks.

2.4 Criteria for chemical EOR processes selection

Chemical EOR processes are considered promising due to their good performance extracting oil. However, their application at field scale is still very limited in comparison to thermal or gas methods. The design of a suitable formulation and the selection of the appropriate chemicals is frequently a difficult task. Many parameters affect the success of these EOR methods. Reservoir type, temperature, oil composition, salinity (with special care to the presence of divalent ions), and formation permeability (specially when using polymers) are critical parameters [17].

Most of the tests at field scale with chemical methods have been carried out in sandstone reservoirs. Despite the existing huge oil reserves in carbonate rocks, they are challenging due to their natural fractures characterised by a high heterogeneity and frequent low permeability. Anionic surfactants are commonly used in EOR but they show a high adsorption in carbonate reservoirs [28]. Clay minerals, in sandstone or carbonate reservoirs, can also be problematic due to their high tendency to absorb surfactants and polymers [17].

Oil composition drastically affects its viscosity. This is not a key factor in polymer flooding but the effect is significant in surfactant flooding [51,52]. For this reason, and due to the cost of the surfactants, a polymer is usually injected after or with the surfactant flooding to improve the displacement efficiency. For both surfactants and polymers, temperature, formation water salinity and divalent ions, are critical parameters in their performance. High temperatures of reservoirs can lead to the thermal degradation of the chemicals. Few polymers show tolerance to high salinity, and ionic surfactants frequently show precipitation problems in the presence of divalent ions. Sometimes the use of fresh water instead formation water is proposed for the injection of the chemicals, this is also common with nanoparticle formulations, but poor distribution and precipitation problems inside the reservoir remain. Low permeability drastically reduces the effect of displacement fluids and generates excess retention problems, this problem being more significant in the case of polymers [17].

Nanoparticles can help to limit the issues of these methods. Moreover, chemical products and materials are being improved, thus increasing the possibilities of their successful application in EOR. Neoteric products, such as SAILs, increase the possibilities of surfactant flooding.

3. PUBLICATIONS

Nanoparticles in Chemical EOR: a Review on Flooding Tests

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Nanofluid based on 1-dodecylpyridinium chloride for enhanced oil recovery

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Enhanced oil recovery with nanofluids based on aluminum oxide and 1-dodecyl-3-methylimidazolium chloride ionic liquid

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4.GENERAL DISCUSSION

Although first discovered at least one hundred years ago, it was not until the 21st century that the international scientific community began to become aware of the huge possibilities of ionic liquids. Their promising environmentally friendly character, thanks to the lack of atmospheric contamination (due to their negligible volatility), soon took second place to a likely more interesting property: their tunability. At present, a great number of possible applications for these salts are being studied: electrochemistry, analysis, catalysis, separations, materials, etc. [53]. Some of them are currently an industrial reality [54]. Within this family, SAILs show appealing characteristics as surface-active agents [55]. In combination with water, they expand the possibilities of traditional surfactants in operations that require aggregation and micellization. They show promising features as antifoaming agents, for water in oil or oil in water emulsification, or as wetting or solubilising agents. Thus, they have been successfully tested in separations (mainly extraction processes), for biomolecule stabilisation, drug delivery, organic synthesis and catalysis, synthesis of nanoparticles, liquid crystal applications, etc. [55].

With a consolidated trajectory in the study of phase equilibria, the group of Sustainable Separation Processes from the University of Santiago de Compostela (the research group where this thesis was developed), has been pioneering in the application of SAILs to EOR. Since a first publication in 2012, where rigorous equilibria of systems containing the SAIL trihexyl(tetradecyl)phosphonium chloride with water and oil were studied [56], to the ongoing research in collaboration with the Spanish petrochemical company CEPSA [57,58] aiming to test several formulations based on SAILs for extracting oil from carbonate reservoirs, the possibilities of SAILs in the application have been widely explored. The capacity of SAILs to reduce IFT, and their ability to form many kinds of microemulsions (water in oil, oil in water, or bicontinuous), have to be highlighted as promising features of these salts for EOR. However, the most promising formulations, those achieving competitive laboratory performance, require the combination of SAILs with traditional surfactants.

Nanotechnology has also emerged in recent decades as a method to create materials with new properties and functions, due to their increased surface area to volume. One widely studied application is EOR. Several reviews on the topic [47, 48, 59-69] show the mechanisms by which nanoparticles can greatly improve crude oil extraction. Regarding microscopic displacement, the main mechanism seems to be wettability alteration. Low concentrations of nanomaterials can change rock wettability, thus helping remove oil from the rock surfaces and increasing well productivity. The effect on oil-water IFT is not clear, with some nanoparticles helping to reduce its value and others having no or negative effects. Concerning macroscopic displacement, nanoparticles can improve the sweep efficiency by increasing the viscosity of the displacing fluid. Pore plugging, causing the pressure to increase in the adjacent pores thus forcing oil displacement, can be another significant EOR mechanism. However, the increase of viscosity that can be achieved is moderate and excessive blocking limits oil extraction instead of improving it. The combination of nanoparticles with other chemicals also appears beneficial in the literature [47, 48, 59-69]. Nanomaterials can help to reduce the adsorption of surfactants and polymers when used in the injecting fluids, and also to increase suspension stability.

As the methods are promising individually, a logical step in the improvement of EOR techniques was the combination of SAILs with nanoparticles, a pairing surprisingly not tested at the beginning of this thesis. However, some doubts have emerged about the method. One of the immediate questions was whether it would be worthwhile to combine the two types of chemicals. If the use of nanoparticles was as promising as it seemed, perhaps adding SAILs would not be advantageous. In fact, the literature was inconclusive as to whether the addition of traditional surfactants to nano-fluids clearly improved oil recovery.

At the conception of this work, it was also unclear which nanoparticles were the most promising to be used individually or in combination with surfactants, according to the type of reservoir (sandstone or carbonate). So the first objective in this thesis was to carry out a state-of-the-art study regarding the use of nanoparticles as a method of EOR.

About one hundred studies were reviewed in the first paper of this thesis. As the focus was the analysis of the performance of nanoparticles in oil recovery, only works including core-flooding tests were considered. In these tests, a rock usually taken from a real reservoir is first flooded with oil and then submitted to secondary oil recovery with water or brine. When this method does not allow more oil to be extracted, the nano-fluid to be tested is injected. Thus, the additional oil recovery can be easily determined through mass balance. Sometimes, nano-fluid injection is directly tested as a secondary EOR method. This is the closest laboratory test to real applications, and only formulations found promising at this stage should be considered for simulation and field applications.

Most of the reviewed papers start with a stability study, as this is a critical issue in nano-EOR. Then, mechanism studies such as wettability change, viscosity measurements, and IFT alteration are carried out. Finally, core-flooding studies are performed, and results analysed according to the mechanisms studied. It is worth mentioning some weaknesses found in the papers reviewed, which greatly hindered the overall conclusions that were intended to be drawn from this study. Some of them were related to reporting practice and some others associated to experimental issues.

Inadequate reporting was found rather frequently. The stability of many nanoparticles in the presence of different salts using varied compositions of both compounds is often tested initially. Mechanism tests are also carried out at different conditions. Finally, the formulation tested in core-flooding studies is not well defined. Questions arise as to whether the formulation was prepared in water or brine, what kind of brine, what concentrations were used, etc. This problem multiplies when the nano-fluid contains not only nanoparticles but also other chemicals such as surfactants and/or polymers. Another issue commonly found is the presentation of oil recovery results just as plots, lacking numerical values. Also, it is sometimes unclear whether oil recovery percentages are defined with respect to the original oil in place, or if they are defined as a function of oil remaining after secondary flooding. This greatly hinders obtaining comparative values.

Concerning experimental issues, two main problems were found that suggest some results of the publications reviewed should be treated with considerable scepticism. Sometimes the equipment used for core-flooding tests is inadequate. Manual columns are prepared, and the rock is not adequately pressurised. Therefore, preferential paths are likely formed next to the holder and fast transport of the oil can take place. Another problem detected is the use of unconsolidated sand packs. Oil displacement is clearly easier in this material than in real reservoir rocks, so extraction numbers quoted are not especially realistic.

These kinds of experimental problems explain why some papers report additional oil recoveries (after water flooding) clearly higher than average. Moreover, even considering only the work carried out under strict experimental conditions, the range of oil recovery values when only nanoparticles are used is very wide. The reason is that the experimental conditions are rather diverse. The porosity and permeability of the rocks used, in addition to their nature (sandstone or carbonate), can be very different and this drastically affects the extraction. Other factors such as temperature or salinity, and obviously the type of oil, are variables that significantly influence oil recoveries. However, one clear finding from this study is that the type of nanoparticle, among the standard ones, is not a key factor in EOR. Functionalised nanoparticles usually involve expensive and difficult syntheses.

SiO_2 is the most commonly used nanoparticle, but when the goal is use in reservoirs at high temperature, Al_2O_3 nanoparticles are recommended due to their resistance. The same applies to the size. In the nano-range, the particles pass through most of the reservoir rock pores which are generally of larger dimensions. However, the nano-fluid concentration must be considered carefully, especially in low permeability reservoirs. High nanoparticle concentrations elevate costs, cause stability problems, and increase the possibility of generating aggregation and blocking issues. It was also clear from the literature revision that nanoparticle stability would become a research bottleneck. In fact, many studies prepare the displacing fluid in water instead of brine. This avoids the problem of the stability of the injecting fluid, but instability issues and precipitation are expected to take place inside the reservoir. Some studies work with suspensions prepared in NaCl aqueous solutions, and very few include divalent cations, which is the real challenge.

The combination of alcohols with nanoparticles has also been proposed in the literature. However, the cost of the method is prohibitive. In contrast, the use of aqueous slugs with very low surfactant concentration seems promising. In fact, as far as we know, the only nano-EOR application at field scale involved the use of surfactants and nanoparticles [70]. The question of the type of nanoparticle to be used depending on the surfactant, or vice versa, could not be answered despite the literature review. It is well known that cationic surfactants are greatly adsorbed in sandstone rocks because they have negatively charged surfaces, whilst the positively charged surfaces of carbonate rocks result in high adsorption of anionic surfactants [71]. For this reason, most papers propose the combination of anionic surfactants, such as sodium dodecyl sulphate or sodium dodecyl benzene sulphonate, with nanoparticles for sandstone reservoirs. Nonetheless, combinations with cationic and non-ionic surfactants are also being proposed. Due to the challenges of carbonate reservoirs (low permeability, heterogeneity, unfavourable wettability conditions, etc.) [72], the number of tests in carbonate rocks is very limited and expensive surfactants were tested in most cases. Regarding the question of the value of combining nanoparticles with surfactants to improve extraction, most studies perform comparative tests and higher recoveries are always achieved with the mixture. Unfortunately, no economic studies have been found that allow a definitive comparison of the two methods, a study of huge interest. As in the case of nanoparticles, and despite the fact that some surfactants have been shown to improve the stability of the nanomaterial, this is still a problem that often leads to the preparation of the displacing fluid in pure rather than formation water.

Even adding nanoparticles to water, the difference of viscosities between the aqueous formulation and the crude oil is significant, generating poor volumetric sweep efficiency and adversely impacting recovery. So, the addition of polymers to nanofluids (with or without surfactants) is very common. Polyacrylamide or hydrolysed polyacrylamide are those most often proposed for practical applications. Nonetheless, polyvinylpyrrolidone (PVP) shows better heat resistance, so when designing formulations for reservoirs at high temperatures this polymer would be preferred. The addition of polymers is also considered as a technique to improve the stability of displacing fluids that are frequently multicomponent mixtures (salts, surfactants, co-surfactants, etc.).

A significant proportion of the world's oil reserves are found in carbonate reservoirs. Recovering this oil using the existing infrastructure would be of high interest. Cationic surfactants are preferred to anionic in this kind of rock, and the majority of SAILs correspond to the first category. For these reasons, the experimental work of this thesis focused on the design of formulations containing SAILs and nanoparticles for carbonate reservoirs.

The main challenge of this work was obtaining stable formulations. Three components were involved: nanoparticles, salt, and SAIL. The term “nanoparticle stability” is widely used to describe the preservation of a particular nanostructure property ranging from aggregation, composition, crystallinity, shape, size, and surface chemistry [73]. The inherent great surface area/volume of individual nanoparticles confers them high surface energy, so as a consequence they are in a non-thermodynamically favoured state thus tend to adopt bulk configurations, in other words, to aggregate. Electrolytes reduce the electrostatic repulsion among nanoparticles by offsetting the surface charges [74]. The presence of NaCl can dramatically accelerate aggregation, a phenomenon seen to a greater extent with divalent salts due to their stronger shielding effect. The influence of other chemicals usually found in displacing fluids for EOR, such as surfactants, on the dispersion and stability of nanoparticles is not well understood. Repulsive interactions (electric double layer forces, steric hindrances, and hydration forces) must be larger than attractive interactions (van der Vaals, cation bridging and hydrophobic forces) in order to overcome the inherent instability of nanoparticles [75]. Surfactants are sometimes introduced to coat nanoparticles for stabilisation purposes, but since SAILs are ionic surfactants, electrostatic interactions with salts and in some cases ion exchange can also give rise to precipitates.

Suspensions of cationic SAILs such as benzydimethyldodecylammonia chloride, dodecyltrimethylammonium bromide, 1-dodecylpyridinium chloride ([C_{12}py]Cl), and 1-dodecyl-3-methylimidazolium chloride ([C_{12}mim]Cl) in the presence of NaCl (5 wt% as representative of sea water salt content) were prepared at 1 wt% of SAIL (a concentration commonly used in surfactant flooding). Nano-fluids with concentrations ranging from 0.01 to 0.20 wt.% of different nanoparticles such as ZnO, TiO_2, Fe_2O_3, Fe_3O_4, Al_2O_3, etc. were formulated and found unstable. Precipitation appeared instantaneously or over time (with stability decreasing as nanoparticle concentration increased), and stable formulations lasting at least one week were not achieved. It is known that the stability of nano-fluids depends heavily on the preparation method [76,77]. So, many strategies were employed attempting to improve stability. Stock solutions in water of NaCl, SAIL and nanoparticles were prepared and mixed, with mechanical stirring, in every possible way. It was clear that the order of mixing affected stability, but none of the sequences led to satisfactory results. Previous studies [78] showed that sonication can help to reduce the aggregated size of nanoparticles leading to an increase in stability. Thus, mixing with different sonication periods and methods (ultrasonication bath and probe) were also tested with unsatisfactory results. Easily observed aggregation and precipitation problems always appeared. As alternatives, amphoteric (1-octyl-3-methylimidazolium dodecylbenzene sulphonate and 1-dodecyl-3-methylimidazolium dodecylbenzene sulphonate) and even anionic (poly(ethylene glycol)-4- nonylphenyl 3-sulfopropyl ether potassium salt), though not of interest for carbonate rocks, were tested with similar results. In all these tests, no appreciable variations were found according to the nanoparticle type. After all this unsuccessful work, the decision to use a stabilizing agent was made.

The SAILs to be used in the formulations were selected according to their ability to reduce water-oil IFT. Preliminary work carried out in the research group led to the selection of $[C_{12}py]Cl$ and $[C_{12}mim]Cl$, among many others tested. This was in agreement with previous studies in the literature [79-84] also proposing these ionic liquids for EOR. The novelty of our proposal would lie in their combination with nanoparticles. As this thesis is focused on the design of formulations useful where traditional ones fail (mainly in harsh conditions of salinity and temperature), Al_2O_3 nanoparticles were selected due to their resistance to high temperature. PVP was selected as the stabilizing agent. Besides its high thermal resistance and capacity to increase the stability of nano-fluids [76,77], the use of a polymer in the formulation would increase its viscosity, thus favouring sweep efficiency.

The same methodology was used in the two papers that constitute the experimental part of this thesis. The optimised method to prepare stable nanofluids required the preparation of stock solutions of PVP, SAIL and NaCl in water. The formulations in water were prepared by dispersing Al_2O_3

nanoparticles, then the required amount of SAIL solution was added to this suspension. The combination was vortex mixed to obtain a stable and homogeneous dispersion. For formulations prepared in brine, two further steps were required: the addition of the PVP solution followed by brine, always with the masses required to achieve the desired compositions. Formulations were then mechanically stirred and ultrasonicated during a short period of time to achieve homogeneity.

The stability of the nano-fluids was confirmed after one week visually and by means of a Zetasizer Nano ZS (Malvern). This equipment performs size measurements using dynamic light scattering, illuminating the particles with a laser and analysing intensity fluctuations in the scattered light. Brownian motion is measured and related to the particle size. The instrument also measures the zeta potential of the suspension via electrophoretic mobility. Generally, the frontier between stable and unstable suspensions is taken at 30mV (either positive or negative value). However, as this method only accounts for electrostatic repulsive interactions [85], the polymer invalidated the use of the technique for stability analysis when present in the formulations.

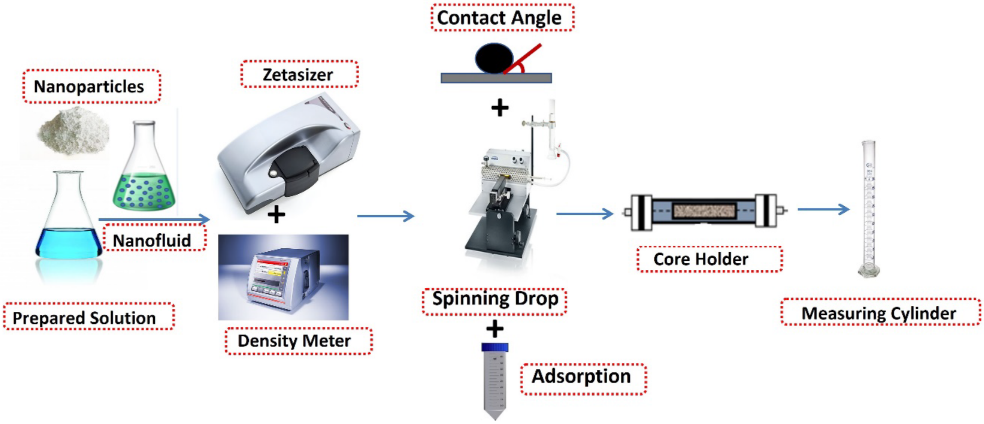

Figure 4.1. Experimental protocol used in the experimental papers of the thesis.

As shown in Figure 4.1, the steps required in the experimental studies were as follows: physical characterisation of the nanofluids, measuring density and viscosity, IFT measurements, adsorption studies, contact angle measurements and core-flooding tests.

Viscosity and density measurements were carried out with an Anton Paar LOVIS 2000 ME micro-viscometer module attached to an Anton Paar DMA 5000 M oscillating U-tube density-meter, both values being determined simultaneously. Density is always a property of interest because the energy required in the pumping process is directly related to this parameter. In addition, as explained in section 2.2 (oil recovery mechanisms), viscosity affects the microscopic displacement through the capillary number (ratio of the viscous-to-capillary forces). The increase of the viscosity raises this value and favours oil recovery. More significantly, this variable also affects macroscopic displacement because it allows for a mobility ratio suited to homogeneous transport without undesirable fingering. As suspensions containing nanoparticles can readily behave as non-Newtonian fluids, a rheological study was initially carried out with the most concentrated nano-fluids. As expected, due to the low concentration of nanoparticles used, all the formulations proposed followed Newton’s Laws, so the selected viscometer was suitable to carry out the measurements.

Directly related the mobility ratio, the other variable of high interest in this kind of work is the IFT between oil and the displacing fluid. This was measured using a spinning drop tensiometer (Krüss SITE100). According to the Vonnegut equation, the shape of a fluid drop (in this case oil) in a horizontal rotating tube filled with a liquid of higher density (in this case the aqueous formulation) can be used to calculate the IFT among phases when the diameter of the drop along the axis of rotation, the speed of rotation, and the difference of densities between the two phases are known [86]. In surfactant flooding, ultra-low IFT is preferred. To achieve these values a specific phase behaviour, where the surfactant solubilises high and equilibrated contents of water and oil, is needed. This is difficult to achieve and usually requires the combinations of surfactants and co-surfactants, besides specific conditions of salinity and temperature. So, these ultra-low values were not expected with the simple use of [C_{12}py]Cl or [C_{12}mim]Cl alone, but the synergy of their combination with nanoparticles was expected to give competitive results as an EOR method.

Adsorption of the chemicals is one of the main factors making chemical EOR unprofitable. When using nanoparticles, a certain retention of this material is also expected. This could be a handicap, both for environmental and economic reasons. This topic requires further studies from the scientific community, since very few papers collected in the review conducted look at nanoparticle adsorption. The experimental retention of nanoparticles is difficult to ascertain. Nonetheless, it has been shown that the use of nanoparticles can drastically reduce the adsorption of surfactants and/or polymers. Thus, static adsorption tests of the chemicals in the proposed formulations were carried out in carbonate rocks (Figure 4.2). Crushed carbonate rocks were put in contact with the nano-fluid in several vials and, at different periods of time, samples were withdrawn and centrifuged for analysis. To that aim, an Agilent UV-Vis 8453 spectrophotometer was used. A calibration was performed previously. Unfortunately, due to overlapping peaks, independent adsorption for each

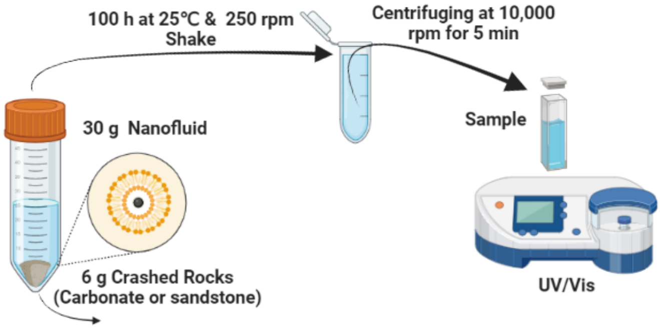

Figure 4.2. Experimental protocol for static adsorption measurements.

chemical could not be determined, so the adsorption of the surfactant-polymer mixture was considered jointly. Crushed rocks have a larger surface area than those found in reservoirs, so adsorption values thus calculated are much higher than those expected in real applications. The interest of these tests lay in the comparison of adsorption with and without nanoparticles.

The contact angle, the angle of intersection of the interface between two fluids at a solid surface, is measured to determine the wetting characteristics of a surface. Small and large angles indicate water-wet or oil-wet surfaces, respectively. Angles near ninety degrees are intermediate-wetting. In this thesis, a home-made glass cell with a holder to fix a polished (surface roughness affecting the equilibrium contact angle) rock sample was used for contact angle measurements (Figure 4.3). An oil droplet was injected below the carbonate disc submerged in brine. The rocks were previously submerged in crude oil for a long period of time (at room conditions or high temperature for ageing) and then in the surfactant, surfactant-PVP, or nanofluid formulations. Measurements were carried out at different periods of time to monitor wettability change. Rocks are frequently water-wet, however, the ageing process mainly at high temperature can change their state. This study aimed to discover the capability of nanoparticles to move that state towards water-wet (water-wet rocks exhibit higher permeability thus facilitate oil recovery) in comparison to the use of the formulation without nanomaterials.

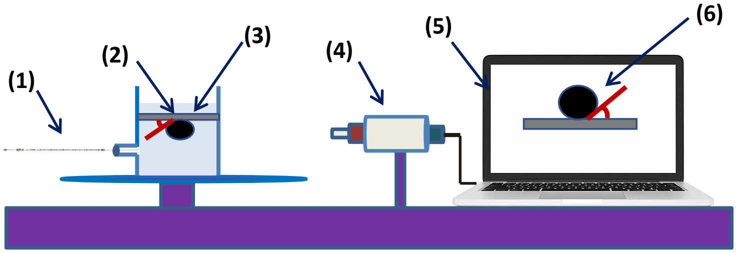

Figure 4.3. Equipment for contact angle measurements: 1- Syringe, 2- rock disc, 3- brine solution, 4- camera, 5- computer with ImageJ software, 6- drop image.

The closest study to the extraction of crude oil in an oil field is the core-flooding test. A rock, taken from a real reservoir, was inserted in a holder and several fluids were injected. Different tests were carried out to determine the rock permeability using Darcy's law, and its porosity by means of the dry versus wet rock weights. Recovery studies were also carried out. Equipment used in the thesis consisted of a Hassler Core Holder H00-021-0, an Enerpac P142 manual hydraulic pump to apply a confining pressure and avoid preferential paths, and two floXlab BTSP 500-5 piston pumps equipped with pressure sensors, for crude oil and aqueous formulation injection (see Figure 4.4).

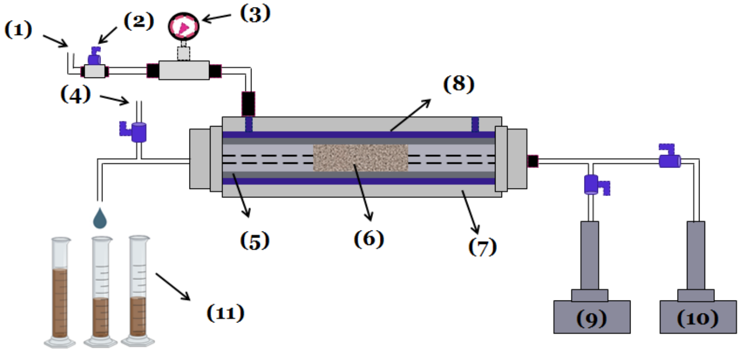

Figure 4.4. Core-flooding equipment: 1- From manual hydraulic pump, 2- non-return valve, 3- confining pressure, 4- to vacuum pump, 5- rubber sleeve, 6- core sample, 7- core holder, 8- hydraulic oil, 9- crude oil piston pump, 10- brine/formulation piston pump, 11- collected samples.

In flooding experiments, the rock was first saturated with brine and then crude oil, to calculate the original oil in place. A first extraction was carried out with brine to simulate secondary recovery, then another with the displacing fluid to determine additional oil recovery. Due to limitations of the equipment, all the tests were carried out at room conditions. The comparison of EOR achieved with surfactant, surfactant-PVP, and nanofluid formulations allow an easy visualisation of the best method from a performance point of view.

Results achieved with both SAILs, [C_{12}py]Cl or [C_{12}mim]Cl, were very similar. In the absence of an inorganic salt, the stability of Al_2O_3 was relatively high (up to 3 wt%) at very low concentration of SAIL, and increasing the concentration of the surfactant, the stability drastically decreased (0.01 wt% at 1 wt% SAIL concentration). This may be due to electrostatic repulsion between the cationic surfactants and the positively charged alumina surface generating aggregation of the nanoparticles and precipitation. Zeta potential measurements showed the stability of the selected solutions. As expected, problems arose in presence of NaCl. The addition of 1.0 wt% of PVP was required to achieve stable formulations. Again, without significant differences between the SAILs, the higher the NaCl concentration, the lower the nanoparticle stability. In this case, the stability values being practically independent of SAIL concentration. Only a slight increase of nanoparticle concentration could be achieved at the higher surfactant and lower salt concentrations. Thus, the maximum concentration of nanoparticles in brine solutions (0.13 and 0.15 wt% for [C_{12}py]Cl and [C_{12}mim]Cl, respectively) was achieved at 1.0 wt% SAIL and 0.5 wt% NaCl. The SAIL's cation type (pyridinium or imidazolium) hardly affected stability results. Unfortunately, stable solutions could not be achieved when divalent cations were added to the brine with either of the surfactants.

The increase of surfactant content, in the range of concentrations tested and at a given salt concentration, hardly affected the density of the formulation and slightly increased the viscosity. More significant was the increase of viscosity when increasing nanoparticle concentration, increments of this property being very favourable for EOR operations. Obviously, the higher increment of viscosity in the prepared formulations was due to the addition of PVP, favouring nanofluid stability and improving macroscopic fluid displacement.

A significant difference was found in the behaviour of [C_{12}py]Cl and [C_{12}mim]Cl regarding IFT. In the case of the pyridinium SAIL, the curve of the IFT between a light crude oil (kindly provided by Repsol) and brine solutions showed a minimum at 0.5 wt% NaCl, so that concentration was fixed for the formulation. The addition of [C_{12}py]Cl decreased IFT, but SAIL concentrations higher than 0.5 wt% hardly produced any variation. So this was selected as the optimal surfactant concentration in the displacing fluid. The addition of nanoparticles also helped to slightly reduce IFT, but the increase of nanoparticle concentration from 0.05 to 0.1 wt% hardly had any effect. Based on these results, a formulation consisting of 0.05 wt% Al_2O_3, 0.5 wt% $[C_{12}py]Cl$, 1.0 wt% PVP and 0.5 wt% NaCl was considered optimal. This discounts their use in high salinity reservoirs. In the case of the imidazolium SAIL, previous studies showed that an increase in salt concentration led to a continuous reduction of the IFT [79-84], thus a salt concentration of 5 wt% NaCl (seawater salinity) was selected for the formulation design. It is difficult to account for the different behaviour in the presence of salt depending on the ring of the SAIL, both being aromatics. Further studies with molecular simulations, out of the scope of this thesis, are encouraged to understand this phenomenon. The greatest reduction of the IFT was found increasing SAIL concentration to 0.05 wt%, while further increases led to less significant reductions. In this case, the addition of nanoparticles hardly affected the IFT, nonetheless, the maximum value according to stability studies was selected to favour wettability alteration. The final optimised formulation contained 0.05 wt% Al_2O_3, 0.05 wt% $[C_{12}mim]Cl$, 1.0 wt% PVP and 5.0 wt% NaCl.

Adsorption studies were carried out at room conditions with the $[C_{12}py]Cl$-formulation, with and without nanoparticles in both sandstone and carbonate rocks. As expected, both the surfactant formulation and nanofluid were highly adsorbed by the silicate rocks. Moderate adsorption (2.56 mg/g) was found in carbonate rocks that was further reduced due to the presence of nanoparticles (2.23 mg/g). Adsorption of the $[C_{12}mim]Cl$-formulation, only tested in carbonate rocks, was higher, with values of 2.74 and 2.51 mg/g without and with nanoparticles, respectively. Nonetheless, values with the different SAILs are not directly comparable due to the higher NaCl content in the second formulation. It is known that salinity increases surfactant adsorption due to a reduction of repulsion forces of their charged heads [87]. The highest adsorption corresponded to the polymer, which was present in a significantly higher proportion than the other chemicals.

Contact angles were also measured in carbonate rocks to analyse the capacity of nanoparticles to alter wettability. When the disc was aged at room conditions, the rocks were found to be water-wet, and no treatment with the formulations was able to change this state. When the ageing process was carried out at high temperature, the rock was oil-wet and treatment with the surfactant formulations and nanofluids changed the wettability towards less oil-wet and intermediate-wet. None of the nanofluids was able to produce the optimum water-wet state in a relatively short period of time. The improvement in wettability in the presence of Al_2O_3 nanoparticles is due to the formation of nanostructures on the rock surface [88], generating a disjoining pressure able to increase the contact angle and facilitate the detachment of the oil from the rock.

To test the efficacy of the proposed formulations for EOR, core-flooding experiments were carried out. Different pieces of the same rock were used to favour the comparison between different SAILs, and formulations without or with nanoparticles. Nonetheless, certain differences in porosities and permeabilities are unavoidable. Even so, the values are considered sufficiently close to make the relevant comparisons. In the case of the pyridinium SAIL, three tests were carried out following secondary flooding: surfactant, polymer-surfactant, and nanofluid flooding. Additional oil recoveries were, respectively, 3.39 % OOIP (2.7 pore volumes added), 7.39 % of OOIP (3.9 pore volumes added) and 11.96 %OOIP (3.7 pore volumes added). The quantity of fluid injected was that required until no more oil was extracted. The presence of nanoparticles clearly improved oil recovery. In the case of the imidazolium SAIL, as previous work showed best performance of the surfactant-polymer method in comparison to the surface-active agent alone, only two tests were carried out. Additional oil recoveries achieved were 10.4 %OOIP (4.1 pore volumes added) and 14.8 % of OOIP (3.4 pore volumes added) for the surfactant-polymer and nanofluid flooding, respectively. Again, the use of nanoparticles improving the results. The results achieved with the imidazolium SAIL led to the highest recoveries. This was expected because the literature shows that oil recovery increases as the injected water salinity increases [89]. In fact, each formulation was designed for a specific salinity and should be applied in those conditions. As indicated when discussing the review, few papers testing formulations containing surfactants and nanoparticles for EOR present the whole picture including adsorption studies. Nonetheless, the results presented here can clearly be considered competitive.

Core flooding tests were carried out in an approach closer to laboratory than field scale studies. Injection velocities (2 mL/min) are much higher than those used in real applications (~0.05 mL/min) to facilitate experimentation. Moreover, due to the core-flooding equipment used, the rocks could not be aged at high temperature, and extraction tests were carried out with water-wet rocks, so the effect of the nanoparticles was not as significant as it could potentially be. The optimisation of the method could also be done by using a limited quantity of formulation, due to its cost, followed by chase water. In any case, the tests carried out showed the suitability of these formulations for EOR, which is the main purpose of this thesis.

5. CONCLUSIONS

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In this thesis, a literature review of nanoparticle-based EOR methods was carried out. With a clear applied approach, the scope of the work was limited to studies in which experimental oil recovery tests were performed with the proposed formulations. From this review, a number of conclusions were drawn that were useful for defining the experimental work of the thesis.

The use of nanoparticles to extract oil from, in principle, exhausted reservoirs is promising. The efficiency of nanofluids to extract more oil when secondary methods fail has been demonstrated. However, the formulation stability is always a challenge and a concern. The type of nanoparticle seems not to be a critical factor, regardless of the type of reservoir, Al_2O_3 being preferred in applications at high temperatures. Working at nano-dimensions, the size of the particles should not be a problem, but aggregation must be avoided. Concentrations lower than 0.2 wt% are preferred. The combination of nanoparticles with surfactants and/or polymers leads to higher oil recovery because the mechanisms of extraction are multiplied, but those chemicals can have positive or negative influences on the stability of the nanofluids. It is expected that nanoparticles will reduce adsorption of other chemicals and help to increase the viscosity of the injecting fluid, however the effect on IFT in particular must be analysed. Special care is required in the preparation method of nanofluids containing different chemicals and salts. From an economic standpoint, the nanofluid must be applied as a tertiary instead of secondary EOR method. Due to the promising features of SAILs to increase the possibilities of traditional surfactants in any kind of application, their use in nano-EOR must be encouraged.

According to these conclusions, formulations based on the SAILs [C_{12}py]Cl or [C_{12}mim]Cl and Al_2O_3 nanoparticles were designed and tested for EOR. Several conclusions must be highlighted from the experimental work carried out. Getting stable mixtures with nanoparticles, SAILs, and salts is a very difficult task. PVP is a good stabilising agent, but even with its inclusion in the mixture the maximum achievable nanoparticle concentration is low, and depends heavily on SAIL and salt concentration. Stability in the presence of divalent ions is a big problem, since it has as yet proved unattainable.

Working with SAILs, IFT reduction must be the target property to define SAIL and NaCl concentration in the displacing fluid, being the concentration of the nanoparticles the maximum possible according to stability. Following this rule, the proposed optimal formulation with the pyridinium SAIL contains 0.05 wt% Al_2O_3, 0.5 wt% $[C_{12}py]Cl$, 1.0 wt% PVP and 0.5 wt% NaCl, and with the imidazolium SAIL contains 0.05 wt% Al_2O_3, 0.05 wt% $[C_{12}mim]Cl$, 1.0 wt% PVP and 5.0 wt% NaCl. The imidazolium ring favours the work at higher salinity. Formulations containing cationic SAILs must be used for carbonate reservoirs, adsorption discourages their use in sandstone rocks. The presence of nanoparticles reduces the adsorption of the other chemicals (surfactant and polymer) on the rock surface. Both formulations achieved interesting EOR values, clearly improving the surfactant or surfactant-polymer traditional methods. The mechanisms involved in oil extraction are IFT reduction, and improvement of the sweep efficiency through the increase of the viscosity of the displacing fluid by means of the polymer. In the case of oil-wet rocks, the wettability change is an additional mechanism to improve the performance of the extraction.

The main conclusion of this thesis is that the combination of SAILs and nanoparticles is a promising new cutting-edge EOR method that must be further explored. The immediate challenges are: the stability in presence of divalent ions, the analysis of the nanoparticles adsorption and their environmental consequences, and the study of the economy of the process.

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Appendix A:

Journal articles in which this thesis is based

Nanoparticles in Chemical EOR: a Review on Flooding Tests

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Journal: Nanomaterials (2022), MDPI. (ISSN: 2079-4991), 12(23), 4142.

DOI: https://doi.org/10.3390/nano12234142

Impact factor = 5.719 (2021), ranking it 44/178 in Applied Physics (Q1).

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Author contribution (CRediT taxonomy): Methodology, Formal analysis, Investigation, Writing – Original draft, Visualisation.

Chapters reproducing the article content: Chapter 3.

Nanofluid based on 1-dodecylpyridinium chloride for enhanced oil recovery

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Journal: Petroleum Science (2023), ed. Elsevier B.V. on behalf of KeAi (ISSN: 1995-8226), 20, 600-610.

DOI: https://doi.org/10.1016/j.petsci.2022.08.018

Impact factor = 4.757(2021), ranking it 3/19 in Petroleum Engineering (Q1).

Author contribution (CRediT taxonomy): Formal analysis, Investigation, Writing – original draft, Conceptualization.

Chapters reproducing the article content: Chapter 3

Enhanced oil recovery with nanofluids based on aluminum oxide and 1-dodecyl-3-methylimidazolium chloride ionic liquid

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Journal: Journal of Molecular Liquids (2022), ed. Elsevier. (ISSN:1873-3166), 363, 119798.

DOI: https://doi.org/10.1016/j.molliq.2022.119798.

Impact factor = 6.633 (2021), ranking it 6/36 in physics, atomic, molecular & chemicaL (Q1).

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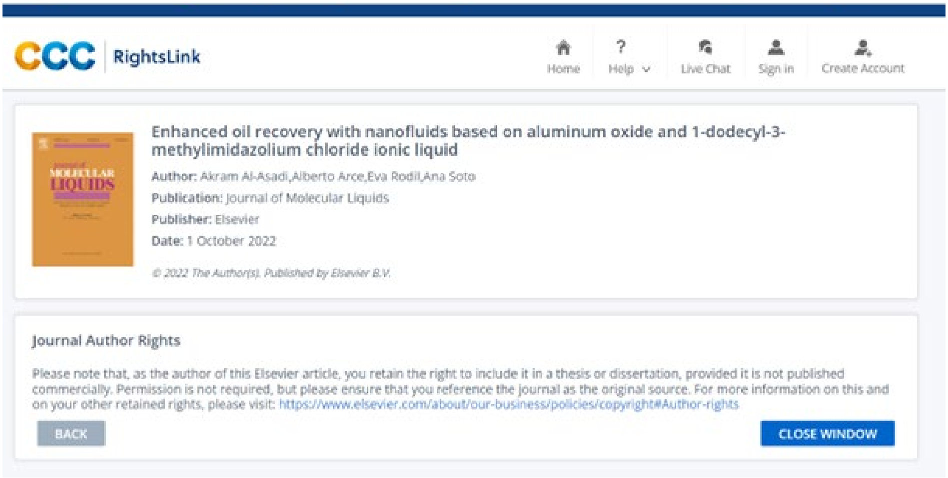

Enhanced oil recovery with nanofluids based on aluminum oxide and 1-dodecyl-3-methylimidazolium chloride ionic liquid

Author: Akram Al-Asadi,Alberto Arce,Eva Rodil,Ana Soto

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Author contribution (CRediT taxonomy): experimental, original draft preparation.

Chapters reproducing the article content: Chapter 3


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Appendix B:

“Resumo” (Summary, in Galician)

Introdución

O petróleo, e os seus produtos derivados, seguen a desempeñar un papel fundamental nas nosas vidas, de eles depende o noso actual confort. Debido ao seu carácter non renovable e ao seu impacto ambiental, sen dúbida estamos obrigados a atopar substitutos. De feito, a transición dos combustibles fósiles ás fontes de enerxía renovables está a converterse nunha realidade. Sen embargo, a disposición de bio-materiais para cubrir todas as nosas necesidades está lonxe de ser posible. A completa explotación de xacementos de petróleo en principio esgotados, aproveitando as infraestruturas xa existentes e sen novos investimentos industriais, é unha necesidade para conseguir a transición ecolóxica se comprometer o noso actual estilo de vida durante o proceso.

Tras a recuperación primaria (saída natural) e secundaria (principalmente bombeo con auga), aproximadamente o 60-80% do petróleo permanece aínda nun xacemento. Os métodos de recuperación mellorada de petróleo (EOR, das siglas en inglés) pretenden mellorar a produción coa súa extracción. Entre estes métodos, dous destácanse actualmente como prometedores: o emprego de nanopartículas e de líquidos iónicos surfactantes (SAILs). No caso das nanopartículas, a mellora na extracción do petróleo asociase fundamentalmente a unha alteración na mollabilidade da roca que produce o desprendemento do cru. Os SAILs son capaces de reducir significativamente a tensión interfacial auga-cru (IFT), mellorando a mobilidade do petróleo que sae dos poros das rocas, e poden deseñarse para calquera xacemento. A pesar de que a combinación de métodos para a recuperación de petróleo produce un efecto sinérxico que multiplica as posibilidades dos métodos individuais, a combinación destas técnicas non tíñase probado no momento de iniciar este traballo.

Obxectivos

O obxectivo principal desta tese foi o deseño de formulacións que contivesen SAILs e nanopartículas como base dun novo método de EOR. Para lograr este obxectivo, definíronse varios obxectivos específicos: realizar un estudo do estado da arte en relación ao uso de nanopartículas en EOR, deseñar unha formulación óptima baseada no SAIL cloruro de 1-dodecilpiridinio e Al_2O_3 como nanopartículas, e por último estudar o efecto do catión do SAIL na eficacia da formulación, para o que se traballou co SAIL cloruro de 1-dodecil-3-metilimidazolium. Os tres obxectivos cumpríronse coa publicación dos seguintes traballos:

> Nanoparticles in Chemical EOR: A Review on Flooding Tests. *Nanomaterials* 12, 2022, 4142.
>
> Nanofluid based on 1-dodecylpyridinium chloride for enhanced oil recovery. *Petroleum Science* 20, 2023, 600.
>
> Enhanced oil recovery with nanofluids based on aluminum oxide and 1-dodecyl-3-methylimidazolium chloride ionic liquid. *Journal of Molecular Liquids*, 363, 2022, 119798.

Discusión

Traballo de revisión

No primeiro artigo desta tese revisáronse arredor de cen estudos. Como a interese centrábase na mellora da recuperación de petróleo mediante o uso de nanopartículas, só se tiveron en conta os traballos que incluían ensaios de extracción de cru. Nestas probas, unha roca tomada normalmente dun xacemento real inúndase primeiro con petróleo e despois sométese a recuperación secundaria con auga ou salmoira. Cando este método non permite extraer máis petróleo, inxéctase o nanofluído que se vai probar. Así, a recuperación adicional de petróleo pode determinarse facilmente mediante o balance de masa. Ás veces, a inxección de nanofluídos próbase directamente como método de extracción secundario. Trátase da proba de laboratorio máis próxima á aplicación real, e só as formulacións que se consideren prometedoras nesta fase deben terse en conta para a simulación do pozo e as aplicacións de campo.

A maioría dos artigos comezan cun estudo de estabilidade, xa que se trata dunha cuestión crítica en nano-EOR. A continuación, levan a cabo estudos de mecanismos, como cambios na mollabilidade, medicións da viscosidade e alteracións da IFT. Por último, realízanse estudos de extracción e analízanse os resultados en función dos mecanismos estudados. Cabe mencionar algúns puntos débiles atopados nos traballos revisados, que dificultaron en gran medida as conclusións xerais que se pretendían extraer deste estudo. Algúns deles estaban relacionados coa presentación de resultados e outros con cuestións experimentais.

A inadecuada presentación dos resultados do traballo foi atopada con bastante frecuencia. En moitas publicacións próbase inicialmente a estabilidade de diversas nanopartículas en presenza de diferentes sales e utilizando composicións variadas de ambos compostos. Tamén lévanse a cabo probas de mecanismos en diferentes condicións. Por todo iso, cando se presentan os ensaios correspondentes á extracción de cru, a composición da formulación finalmente probada non está clara. Aparecen dúbidas sobre se a preparación foi en auga ou en salmoira, que tipo de salmoira, que concentracións utilizáronse, etc. Este problema multiplícase cando o nanofluído contén, ademais de nanopartículas, outras substancias químicas como surfactantes e/ou polímeros. Outro problema habitual é a presentación dos resultados de extracción de cru unicamente como gráficos, sen valores numéricos. Isto dificulta a obtención de valores comparativos. Ademais, ás veces non queda claro se as porcentaxes de recuperación de petróleo defínense con respecto ao petróleo orixinal ou en función do petróleo restante tras a extracción secundaria.

En canto a dificultades experimentais, atopáronse dous problemas principais que suxiren que algúns resultados das publicacións revisadas deben tratarse con bastante escepticismo. Ás veces, o equipo utilizado para as probas de extracción é inadecuado. As columnas prepáranse manualmente e a roca non se presuriza adecuadamente. Por tanto, é probable que se formen camiños preferentes no exterior da roca, e que se produza un transporte rápido do petróleo. Outro problema detectado é o uso de rocas non consolidadas (preparadas mediante areniscas). O desprazamento do petróleo é claramente máis fácil neste material que nas rocas reais do xacemento, polo que as cifras de extracción non son especialmente realistas.

Este tipo de problemas experimentais xustifican que algúns traballos informen de recuperacións adicionais de petróleo (tras a inundación con auga) claramente superiores á media. Ademais, incluso considerando só os traballos realizados en condicións experimentais estritas, a gama de valores de recuperación de petróleo cando só se utilizan nanopartículas é moi elevada. A razón é que a casuística experimental é bastante diversa. A porosidade e permeabilidade das rocas utilizadas, ademais da súa natureza (silíceas ou carbonatadas), poden ser moi diferentes e isto afecta drasticamente á extracción. Outros factores como a temperatura ou a salinidade, e obviamente o tipo de cru, son variables que inflúen significativamente nas recuperacións de petróleo. En calquera caso, o estudo reflexou que o tipo de nanopartícula, entre as estándar, non parece ser un factor crave na recuperación. As nanopartículas funcionalizadas implican sínteses custosas e difíciles. As nanopartículas de SiO_2 son as máis utilizadas, pero se o obxectivo é o traballo en xacementos a elevadas temperaturas, recoméndanse as nanopartículas de Al_2O_3 pola súa resistencia. Tampouco parece ser un factor clave o tamaño. No rango nanométrico, as partículas atravesan a maioría dos poros das rocas do xacemento que, polo xeral, son de maiores dimensións. Sen embargo, compre ter moi en conta a concentración do nanofluído, sobre todo en xacementos de baixa permeabilidade. Unha concentración elevada de nanopartículas implica un custo elevado, problemas de estabilidade, e a posibilidade de xerar problemas de agregación e bloqueo. Da revisión bibliográfica tamén se desprendía claramente que acadar a estabilidade das nanopartículas sería un dos puntos críticos da investigación. De feito, en moitos dos estudos revisados, o fluído de desprazamento preparábase en auga en lugar de salmoira. Isto evita o problema da estabilidade do fluído de desplazamento, pero espérase que os problemas de inestabilidade e precipitación prodúzanse dentro do xacemento. Algúns estudos traballan con suspensións preparadas en disolucións acuosas de NaCl, e moi poucos inclúen catións divalentes, o verdadeiro reto.

Tamén proponse na literatura a combinación de alcois con nanopartículas, o que implicaría un alto coste de operación. Pola contra, o uso de formulacións acuosas que conteñan unha concentración moi pequena de surfactante parece prometedor. De feito, na bibliografía soamente atópase información dunha única aplicación de nano-EOR a escala de campo, e ademais de nanopartículas contiña surfactantes. A cuestión do tipo de nanopartícula que debe utilizarse en función do surfactante, ou viceversa, non puido responderse a pesar da revisión bibliográfica. É ben sabido que os surfactantes catiónicos se adsorben en gran medida nas rocas silíceas porque son superficies cargadas negativamente, e as superficies cargadas positivamente das rocas carbonatadas provocan unha gran adsorción dos surfactantes aniónicos. Por este motivo, a maioría dos traballos propoñen a combinación de surfactantes aniónicos, como o dodecilsulfato sódico ou o dodecilbenceno sulfonato sódico, con nanopartículas para os xacementos silíceos. Sen embargo, algúns traballos propoñen o uso de surfactantes non iónicos (normalmente de alto coste) e, sorprendentemente, tamén se están a propoñer combinacións con surfactantes catiónicos para este tipo de roca. Debido ás dificultades dos xacementos carbonatados (baixa permeabilidade, heteroxeneidade, condicións de mollabilidade desfavorables, etc.), o número de ensaios en rocas carbonatadas é moi limitado e na maioría dos casos probáronse surfactantes de síntese complexa que encarecen a economía do proceso. Nos traballos nos que se propón a combinación de nanopartículas con surfactantes para mellorar a extracción, a maioría dos estudos realizan probas comparativas e sempre se conseguen recuperacións máis altas coa mestura. Desgraciadamente, non se atoparon estudos económicos que permitan unha comparación definitiva dos dous métodos, un estudo que sería de enorme interese. Como no caso das nanopartículas, e a pesar de que se demostrou que algúns surfactantes melloran a estabilidade do nanomaterial, este segue sendo un problema que a miúdo leva a preparar o fluído de desprazamento en auga pura en lugar de en auga de formación.

Incluso engadindo nanopartículas á auga, a diferenza de viscosidades entre a formulación acuosa e o cru é significativa, e isto conduce á formación de dixitacións e un mal desprazamento do cru. Por iso, a adición de polímeros aos nanofluídos (con ou sen surfactantes) é moi habitual. A poliacrilamida ou a poliacrilamida hidrolizada son os polímeros máis propostos para a aplicación. Con todo, a polivinilpirrolidona (PVP) mostra unha maior resistencia ao calor, polo que se recomenda para xacementos a altas temperaturas. A adición de polímeros tamén se considera unha ferramenta útil para mellorar a estabilidade das formulacións para a extracción de cru, mesturas multicompoñentes (sales, surfactantes, co-surfactantes, etc.) e complexas.

Traballos de experimentais

De acordo co atopado na revisión bibliográfica que supón o primeiro traballo da tese, e dadas as prometedoras posibilidades dos SAILs na recuperación de cru, decidiuse combinar nanopartículas e SAILs para a extracción de cru de rocas carbonatadas. O principal reto deste traballo foi conseguir a estabilidade das formulacións. Tres compoñentes son a causa deste problema: as nanopartículas, o sal, e o surfactante. A gran superficie/volume inherente ás nanopartículas fai que presenten unha elevada enerxía superficial, polo que se atopan nun estado non favorecido termodinámicamente e tenden a agregarse. Os electrólitos reducen a repulsión electrostática entre as nanopartículas compensando as cargas superficiais polo que a presenza de NaCl, e en maior medida de sales divalentes porque teñen un efecto de apantallamento máis forte, pode acelerar drasticamente a agregación. A influencia dos surfactantes na dispersión e estabilidade das nanopartículas non está clara. As interaccións repulsivas (forzas de dobre capa eléctrica, impedimentos estéricos e forzas de hidratación) deben ser maiores que as interaccións atractivas (van der Vaals, ponte catiónico e forzas hidrofóbicas) para superar a inestabilidade inherente das nanopartículas. Ás veces introdúcense surfactantes para recubrir as nanopartículas e conseguir a súa estabilización, pero os SAILs son surfactantes iónicos, as interaccións electrostáticas co sal, e nalgúns casos o intercambio iónico, tamén poden dar lugar a precipitados.

Inicialmente prepáronse suspensións de SAILs catiónicos como cloruro de dodecil dimetil bencil amonio, bromuro de dodecil trimetil amonio, cloruro de 1-dodecilpiridinio ([C_{12}py]Cl), e cloruro de 1-dodecil-3-metilimidazolio ([C_{12}mim]Cl), en presenza de NaCl (5 % en peso como representativo do contido de sal da auga de mar). A concentración seleccionada de SAIL foi 1% en peso, posto que é unha concentración utilizada habitualmente en EOR con surfactantes. Posteriormente, formuláronse nanofluídos con concentracións comprendidas entre o 0,01 e o 0,20% en peso de diferentes nanopartículas como: ZnO, TiO_2, Fe_2O_3, Fe_3O_4, Al_2O_3, etc., que resultaron inestables. A precipitación apareceu instantaneamente ou co tempo (diminuíndo o tempo de estabilidade co aumento da concentración de nanopartículas), pero non se conseguiron formulacións estables durante polo menos unha semana que era o que se pretendía. Sábese que a estabilidade dos nanofluídos depende drasticamente do método de preparación. Por iso, leváronse a cabo numerosos intentos para alcanzar a estabilidade. Prepáronse disolucións en auga de NaCl, SAIL, e nanopartículas, e mesturáronse con axitación mecánica de todas as formas posibles. Atopouse que a orde de mestura afecta á estabilidade, pero ningunha das secuencias conduciu a resultados satisfactorios. Dado que a sonicación axuda a reducir o tamaño dos agregados de nanopartículas e mellora a estabilidade, tamén probouse a mestura con diferentes períodos e métodos de sonicación (baño de ultrasóns e sonda), de novo con resultados insatisfactorios. Sempre apareceron problemas de agregación e precipitación visualmente observables. Como alternativa, ensaiáronse surfactantes anfóteros (dodecilbencenosulfonato de 1-octil-3-metilimidazolio e dodecilbencenosulfonato de 1-dodecil-3-metilimidazolio), e mesmo aniónicos (sal potásica de poli(etilenglicol)-4-nonilfenil 3-sulfopropil éter), aínda non sendo de interese para as rocas carbonatadas, con resultados similares. En todos estes ensaios non se atoparon variacións apreciables en función do tipo de nanopartícula. Despois de todos estes traballos infrutuosos, tomouse a decisión de utilizar un axente estabilizador.

Os SAILs que se utilizaron nas formulacións seleccionáronse en función da súa capacidade para reducir o IFT auga-cru. As probas preliminares realizadas no grupo de investigación conduciron á selección de [C_{12}py]Cl e [C_{12}mim]Cl, entre outros moitos probados, en concordancia co que tamén reflectía a literatura. Como a idea da tese centrábase no deseño de formulacións capaces de traballar onde as formulacións tradicionais fallan (principalmente condicións drásticas de salinidade e temperatura), seleccionouse Al_2O_3 como nanopartícula debido á súa resistencia á temperatura. Como axente estabilizador seleccionouse PVP. Ademais da súa alta resistencia térmica e a súa capacidade para aumentar a estabilidade dos nanofluídos, o uso dun polímero na formulación aumentaría a súa viscosidade, favorecendo así a o "varrido" homoxéneo do cru no momento da extracción.

Nos dous traballos que constitúen a parte experimental desta tese utilizouse a mesma metodoloxía. O método optimizado para preparar nanofluídos estables requiriu a preparación de disolucións de PVP, SAIL e NaCl en auga. As formulacións en auga prepSaráronse disolvendo as nanopartículas de Al_2O_3 no disolvente, e a esta suspensión engadiuse a cantidade necesaria de disolución de SAIL. A disolución resultante mesturouse en vórtex ata formar unha dispersión estable e homoxénea. No caso das formulacións preparadas en salmoira, foron necesarios dous pasos máis: adición da disolución de PVP e, por último, a de salmoira. Obviamente, sempre coas masas necesarias para lograr as composicións desexadas. A continuación, as formulacións axitáronse mecanicamente e sometéronse a ultrasóns durante un breve período de tempo para lograr a homoxeneidade.

A estabilidade dos nanofluídos confirmouse ao cabo dunha semana visualmente e mediante un Zetasizer Nano ZS (Malvern). O instrumento mide o potencial zeta da suspensión a través da mobilidade electroforética. Polo xeral, a fronteira entre as suspensións estables e inestables sitúase en 30 mV (valor positivo ou negativo). Con todo, como o método só ten en conta as interaccións electrostáticas repulsivas, a presenza do polímero invalidou o uso da técnica para a análise de estabilidade de formulacións que contiñan dito compoñente.

Unha vez demostrada a estabilidade do nanofluído, procedeuse á súa caracterización física mediante a medición da densidade e a viscosidade, determinouse a IFT agua-cru, e realizáronse estudos de adsorción, medicións de ángulo de contacto, e ensaios de extracción de cru. A medición da viscosidade levouse a cabo cun microviscosímetro LOVIS 2000 ME de Anton Paar incorporado a un densímetro de tubo en U oscilante DMA 5000 M tamén de Anton Paar, polo que ambas medicións realizáronse simultaneamente. A densidade é sempre unha propiedade de interese porque a enerxía requirida no proceso de bombeo está directamente relacionada con este parámetro. A viscosidade afecta o desprazamento microscópico a través do número capilar (relación entre as forzas viscosas e capilares), o aumento da viscosidade eleva este valor e favorece a recuperación do cru. Esta variable tamén afecta, e máis significativamente, ao desprazamento macroscópico porque permite ter unha relación de mobilidade adecuada para conseguir un transporte homoxéneo sen dixitacións indesexables. Dado que as suspensións que conteñen nanopartículas poden comportarse facilmente como fluídos non newtonianos, inicialmente realizouse un estudo reolóxico cos nanofluídos máis concentrados. Como era de esperar, e debido á baixa concentración de nanopartículas utilizada, todas as formulacións propostas seguiron a lei de Newton, polo que o viscosímetro seleccionado era adecuado para realizar as medicións.

Directamente relacionada coa relación de mobilidade, a outra variable de gran interese neste tipo de traballos é o IFT entre o fluído desprazante e o cru. Mediuse utilizando un tensiómetro de pinga xiratoria (Krüss SITE100). Nos métodos de EOR con surfactantes, búscase un IFT ultra-baixo. Para alcanzar estes valores necesítase un comportamento de fase específico, no que o surfactante solubilice contidos elevados e equilibrados de auga e cru. Isto é difícil de conseguir e adoita requirir combinacións de surfactantes e co-surfactantes, ademais de condicións específicas de salinidade e temperatura. O obxectivo coas formulacións aquí deseñadas non era acadar eses valores tan baixos de IFT, senón que o sinerxismo da combinación de [C_{12}py]Cl ou [C_{12}mim]Cl (con boa capacidade surfactante) coas nanopartículas, dese resultados competitivos como método de EOR.

A adsorción das substancias é un dos principais factores que fan que os métodos de EOR químicos non sexan rendibles. Ao utilizar nanopartículas, espérase unha certa retención deste material. Isto podería supoñer unha desvantaxe por motivos ambientais e económicos. Este tema require máis estudos por parte da comunidade científica. De feito, moi poucos traballos recolleitos na revisión realizada estudan a adsorción de nanopartículas, experimentalmente é moi complexo. Sen embargo, unha das maiores vantaxes do uso de nanopartículas e que poden reducir drásticamente a adsorción de surfactantes e/o polímeros. Por iso, leváronse a cabo estudos de adsorción estática dos produtos químicos das formulacións propostas en rocas carbonatadas. As rocas carbonatadas trituradas puxéronse en contacto co nanofluído en varios viais e, en diferentes períodos de tempo, retiráronse mostras e centrifugaronse para a súa análise. Para iso utilizouse un espectrofotómetro Agilent UV-Vis 8453, preparando primeiro curvas de calibración. Debido ao solapamento dos picos, lamentablemente non se puido estudar a adsorción independente para cada substancia química, polo que se considerou conxuntamente a adsorción da mestura de surfactante e polímero. Compre aclarar que as rocas trituradas teñen unha superficie moito maior que as que se atopan nos xacementos, polo que os valores de adsorción así calculados son moi superiores aos esperados na aplicación real. O interese destas probas reside na comparación da adsorción con e sen nanopartículas.

O ángulo de intersección da interfase entre dous fluídos nunha superficie sólida, ou ángulo de contacto, mídese para determinar as características de mollabilidade dunha superficie. Os ángulos pequenos e grandes indican superficies molladas por auga e cru, respectivamente. Os ángulos próximos a noventa graos indican unha mollabilidade intermedia. Para medir o ángulo de contacto nesta tese utilizouse unha celda de vidro, de fabricación caseira, cun soporte para fixar a mostra de roca pulida (a rugosidade da superficie afecta ao ángulo de contacto de equilibrio). Para a medida, inxectouse unha pinga de cru debaixo do disco de carbonato mergullado en salmoira. Previamente, as rocas mantivéronse en cru durante un longo período de tempo (en condicións ambientais ou a alta temperatura para o seu envellecemento), e despois nas formulacións de surfactante, surfactante-PVP ou nanofluído. Realizáronse medicións durante distintos períodos de tempo para controlar o cambio na mollabilidade. Con frecuencia as rocas son molladas preferentemente pola auga, sen embargo o proceso de envellecemento, principalmente a altas temperaturas, pode cambiar o seu estado. Este estudo realizouse para coñecer a capacidade das nanopartículas para trocar o estado das rocas preferentemente molladas por cru a preferentemente molladas por auga (o que favorece o paso da formulación e facilita a recuperación de cru), en comparación co uso da formulación sen nanomaterial.

Finalmente, as rocas caracterizáronse (permeabilidade e porosidade), e facéronse ensaios de extracción de cru. A tal efecto, usouse un equipo consistente nun Hassler Core Holder H00-021-0, unha bomba hidráulica manual Enerpac P142 para aplicar unha presión de confinamento e evitar traxectorias laterais preferentes, e dúas bombas de pistón floXlab BTSP 500-5 equipadas con sensores de presión, para a inxección de cru e formulación acuosa. Nos experimentos de extracción, a roca saturouse primeiro con salmoira e despois con cru, para calcular o petróleo orixinal *in situ*. Realizouse unha primeira extracción con salmoira para simular a recuperación secundaria e, a continuación, co fluído desprazante para determinar a recuperación adicional de petróleo. Debido ás limitacións do equipo, todas as probas realizáronse en condicións ambientais. A comparación da EOR conseguida coas formulacións de surfactante, surfactante-PVP e nanofluído permitiu visualizar facilmente o mellor método dende o punto de vista do rendemento.

Os resultados obtidos con ambos SAILs, [C_{12}py]Cl ou [C_{12}mim]Cl, foron moi similares. En ausencia de sal inorgánico, a estabilidade do Al_2O_3 era relativamente alta (ata un 3 % en peso) cunha concentración moi baixa de SAIL, e ao aumentar a concentración do surfactante, a estabilidade diminuía drasticamente (0,01 % en peso cunha concentración de SAIL do 1 % en peso). Isto pode deberse á repulsión electrostática entre os surfactantes catiónicos e a superficie de alúmina cargada positivamente, que xera agregación das nanopartículas e precipitación. As medicións do potencial zeta mostraron a estabilidade das solucións saturadas. Como era de esperar, xurdiron problemas en presenza de NaCl. Foi necesario engadir 1,0 % en peso de PVP para conseguir formulacións estables. De novo, sen diferenzas significativas entre ambos SAILs, canto maior era a concentración de NaCl, menor era a estabilidade das nanopartículas. Neste caso, os valores das solubilidades sendo practicamente independentes da concentración de SAIL. Só se puido conseguir un lixeiro aumento da concentración de nanopartículas coas concentracións máis altas de surfactante e máis baixas de sal. Así, a concentración máxima de nanopartículas en disolucións de salmoira (0,13 e 0,15 % en peso para [C_{12}py]Cl e [C_{12}mim]Cl, respectivamente) alcanzouse con 1,0 % en peso de SAIL e 0,5 % en peso de NaCl. O tipo de catión do SAIL (piridinio ou imidazolio) practicamente non afectou os resultados de estabilidade. Lamentablemente, non puideron conseguirse solucións estables cando se engadiron cationes divalentes á salmoira con calquera dos dous surfactantes.

O aumento do contido de surfactante, no rango de concentracións ensaiado e a unha concentración de sal dado, practicamente non afectou á densidade da formulación e aumentou lixeiramente a viscosidade. Máis significativo é o aumento da viscosidade ao aumentar a concentración de nanopartículas, sendo o incremento desta propiedade moi favorable para as operacións de EOR. Obviamente, o maior incremento de viscosidade nas formulacións preparadas debeuse á adición de PVP, que favorece a estabilidade dos nanofluídos e mellora o desprazamento macroscópico do cru.

Atopouse unha diferenza significativa no comportamento de [C_{12}py]Cl e [C_{12}mim]Cl con respecto ao IFT. No caso do SAIL de piridinio, a curva do IFT entre un cru lixeiro (proporcionado por Repsol) e as disolucións de salmoira mostrou un mínimo ao 0,5% en peso de NaCl, polo que se fixou esa concentración para a formulación. A adición de [C_{12}py]Cl diminuíu o IFT, pero as concentracións de SAIL superiores ao 0,5 % en peso apenas produciron variación. Así pois, seleccionouse esta como a concentración óptima de surfactante na formulación. A adición das nanopartículas tamén axudou a reducir lixeiramente a propiedade, pero o aumento da concentración de nanopartículas de 0,05 a 0,1% apenas modificou o IFT. A partir destes resultados, considerouse como óptima a formulación composta por 0,05% de Al_2O_3, 0,5% de [C_{12}py]Cl, 1,0% de PVP e 0,5% de NaCl (todos os porcentaxes en masa). Isto descarta o seu uso en xacementos de alta salinidade. No caso do SAIL de imidazolio, a bibliografía demostraba que o aumento da concentración de sal conducía a unha redución continua do IFT, polo que se seleccionou unha concentración de NaCl do 5% en masa (salinidade da auga de mar) para deseñar a formulación. É difícil entender o diferente comportamento en presenza de sal dependendo do anel do SAIL, sendo ambos aromáticos. Compre realizar máis estudos con simulacións moleculares, fóra do alcance desta Tese, para comprender este fenómeno. A maior redución do IFT atopouse incrementando a concentración de SAIL ata 0,05%, incrementos posteriores conduciron a reducións menos significativas. Neste caso, a adición de nanopartículas practicamente non afectou ao IFT, con todo, seleccionouse o valor máximo segundo os estudos de estabilidade para favorecer a alteración da mollabilidade. A formulación final optimizada contiña 0,05% Al_2O_3, 0,05% [C_{12}mim]Cl, 1,0% PVP e 5,0% NaCl (porcentaxes en masa).

Realizáronse estudos de adsorción en condicións ambientais coa formulación [C_{12}py]Cl, con e sen nanopartículas, en rocas silíceas e carbonatadas. Como era de esperar, tanto a formulación con surfactante como o nanofluído foron excesivamente adsorbidos polas rocas de silicato. Nas rocas carbonatadas atopouse unha adsorción moderada (2,56 mg/g) que se reduciu aínda máis debido á presenza das nanopartículas (2,23 mg/g). A adsorción da formulación [C_{12}mim]Cl, só ensaiada en rocas carbonatadas, foi superior, con valores de 2,74 e 2,51 mg/g sen e con nanopartículas, respectivamente. Con todo, os valores cos distintos SAILs non son directamente comparables debido ao maior contido de NaCl da segunda formulación. Sábese que a salinidade aumenta a adsorción dos surfactantes debido á redución das forzas de repulsión das súas cabezas cargadas. A maior adsorción asóciase ao polímero, que se atopa nunha proporción significativamente maior que os demais produtos químicos.

En relación á medición dos ángulos de contacto en rocas carbonatadas, cando o disco envelleceuse en condicións ambientais, comprobouse que as rocas estaban molladas pola auga e que o tratamento con calquera das formulacións non cambiaba este estado. Cando o proceso de envellecemento levouse a cabo a alta temperatura, a roca estaba mollada por cru e o tratamento coas formulacións con surfactantes e os nanofluídos modificou a mollabilidade. No caso das formulacións cos SAILs, a roca non estaba tan preferentemente mollada polo cru, e no caso dos nanofluídos a mollabilidade pasou a ser intermedia. Ningún dos nanofluídos foi capaz de alcanzar o estado óptimo de mollabilidade por auga nun período de tempo relativamente curto. A mellora da mollabilidade en presenza de nanopartículas de Al_2O_3 débese á formación de nanoestructuras na superficie da roca, xerando unha presión disxuntiva capaz de aumentar o ángulo de contacto e facilitar o desprendemento do cru.

Para comprobar a eficacia das formulacións propostas para EOR, levaronse a cabo experimentos de extracción. Utilizáronse diferentes anacos da mesma roca para favorecer a comparación entre diferentes SAILs, e entre as formulacións sen ou con nanopartículas. Con todo, son inevitables certas diferenzas nas porosidades e permeabilidades. Aínda así, os valores considéranse suficientemente aproximados para realizar as comparacións pertinentes. No caso do SAIL de piridinio, realizáronse tres probas tras a extracción secundaria: inundación con surfactante, polímero-surfactante e nanofluído. As recuperacións adicionais de petróleo foron, respectivamente, 3,39% do OOIP (2,7 volumes de poros engadidos), 7,39 % do OOIP (3,9 volumes de poros engadidos), e 11,96% do OOIP (3,7 volumes de poros engadidos). A cantidade de fluído inxectado foi a necesaria ata que non se extraeu máis petróleo. A presenza de nanopartículas mellorou claramente a recuperación de cru. No caso do SAIL de imidazolio, e dado que o traballo anterior mostraba o mellor rendemento do método surfactante-polímero en comparación co uso exclusivo do axente surfactante, só se realizaron dous ensaios. As recuperacións adicionais de cru alcanzadas foron 10,4% do OOIP (4,1 volumes de poros engadidos) e 14,8% do OOIP (3,4 volumes de poros engadidos) para a extracción con surfactante-polímero e nanofluído, respectivamente. Unha vez máis, o uso de nanopartículas mellora os resultados. Os resultados obtidos co SAIL de imidazolio deron lugar ás recuperacións máis altas. Isto era de esperar porque a bibliografía amosa que a recuperación de cru aumenta a medida que aumenta a salinidade da auga inxectada. De feito, cada formulación deseñouse para unha salinidade específica e debe aplicarse nestas condicións. Como se indicou ao analizar a revisión, poucos traballos nos que se ensaien formulacións que conteñan surfactantes e nanopartículas para EOR presentan o panorama completo, incluídos os estudos de adsorción. Con todo, os resultados aquí presentados poden considerarse claramente competitivos.

As probas de extracción leváronse a cabo cun enfoque máis próximo aos estudos a escala de laboratorio que a escala de campo. As velocidades de inxección (2 mL/min) son claramente superiores ás utilizadas na aplicación real (~0,05 mL/min) para facilitar a experimentación. Ademais, debido ao equipo utilizado, as rocas non puideron envellecerse a alta temperatura e as probas de extracción realizáronse con rocas preferentemente molladas por auga, polo que o efecto das nanopartículas non foi todo o significativo que podería ser. A optimización do método tamén pode facerse utilizando unha cantidade limitada de formulación, debido ao seu custo, seguida da auga usada na recuperación secundaria. En calquera caso, as probas realizadas demostraron a idoneidade das formulacións como método de EOR, obxectivo principal da Tese.

Conclusións

Do traballo de revisión feito nesta tese establecéronse unhas conclusións que xa foron comentadas posto que se usaron para definir o traballo a realizar experimentalmente. Destacaremos simplemente que o uso de nanofluídos é un método prometedor de EOR e que a combinación das nanopartículas con surfactantes e/o polímeros conduce a unha maior recuperación de cru porque se multiplican os mecanismos de extracción, non obstante eses produtos químicos poden mostrar efectos positivos ou negativos dende o punto de vista da estabilidade do nanofluído.

Do traballo experimental realizado cabe destacar varias conclusións. Conseguir estabilidade ao mesturar nanopartículas, SAIL e sales é unha tarefa moi difícil. O PVP é un bo axente estabilizador, pero mesmo coa súa inclusión na mestura, a concentración máxima de nanopartículas é baixa e depende drasticamente da concentración de SAIL e sales. A estabilidade en presenza de ións divalentes é un problema que ten que solventarse en futuras investigacións.

Traballando con SAILs, a redución do IFT debe ser a propiedade obxectivo para definir a concentración de SAIL e NaCl no fluído desplazante, sendo a concentración das nanopartículas a máxima posible en función da estabilidade. O anel imidazolio favorece a redución da IFT a maior salinidade. As formulacións que conteñen SAIL catiónicos deben utilizarse para xacementos carbonatados, a adsorción desaconsella o seu uso en rocas silíceas. A presenza de nanopartículas reduce a adsorción dos demais produtos químicos (surfactante e polímero) na superficie da roca. As formulacións estables de SAILs ([C_{12}mim]Cl ou [C_{12}py]Cl) e PVP son prometedoras para EOR, sen embargo, a extracción mellora significativamente se a formulación contén nanopartículas de Al_2O_3. Os mecanismos implicados na extracción de petróleo con este tipo de formulacións son: a redución da IFT, e a mellora da eficacia de varrido mediante o aumento da viscosidade do fluído desprazante debido ao polímero. No caso de rocas molladas por cru, o cambio da mollabilidade é un mecanismo adicional na mellora do rendemento da extracción.

A principal conclusión desta tese é que a combinación de SAILs e nanopartículas é un novo e prometedor método de EOR que debe seguir explorándose. Os retos inmediatos son: a estabilidade en presenza de ións divalentes, a análise da adsorción de nanopartículas e as súas consecuencias ambientais, e o estudo da economía do proceso.

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During the ecological transition the full exploitation of, in principle, exhausted oil reservoirs is required to maintain current standards of living. The main objective of this thesis was the design of formulations containing surface-active ionic liquids and nanoparticles as the basis of an improved enhanced oil recovery (EOR) method. A state-of-the-art study regarding the use of nanoparticles as a method of EOR was carried out. This review provided the basis of the experimental work conducted. Two formulations were designed containing aluminum oxide nanoparticles and 1-dodecylpyridinium chloride or 1-dodecyl-3-methylimidazolium chloride, for carbonate reservoirs containing low and high salt concentration, respectively. Low chemicals adsorption and good oil recovery performance were achieved. The main conclusion of this thesis is that the cutting-edge EOR method proposed here must be further explored.