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*SURFACTANT ENHANCED
OIL RECOVERY WITH
IONIC LIQUIDS:
LABORATORY TESTS*

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TESE DE DOUTORAMENTO

**SURFACTANT ENHANCED OIL
RECOVERY WITH IONIC
LIQUIDS: LABORATORY TESTS**

Raquel Corchero Morais

ESCOLA DE DOUTORAMENTO INTERNACIONAL

PROGRAMA DE DOUTORAMENTO EN ENXEÑARÍA QUÍMICA E AMBIENTAL

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2020





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LABORATORY TESTS**

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Abstract in English

Approximately two thirds of the crude oil, that ensures our current comfortable lifestyles, still remain inside an already exploited well. This is due to limitations of the current recovery processes. Surfactant enhanced oil recovery methods are promising. The main objective of this thesis is the development of new formulations based on ionic liquids suitable to be used for this application.

Phase diagrams of 1-hexyl-3-methylimidazolium acetate and 1-hexyl-3-methylpyridinium trifluoromethanesulfonate with water and several hydrocarbons (*n*-octane, cyclohexane or toluene) were determined. As the ionic liquids did not show surface active character, the study focused on the possibility of using those salts as co-surfactants in enhanced oil recovery methods. The acetate ionic liquid is miscible with water and shows a low capacity to solubilize oil. It could be used in formulations with lipophilic surfactants. The solid character of the second ionic liquid makes its use in the targeted application problematic. To facilitate the study of any process where these ionic liquids are combined with water and oil, equilibrium data were correlated with the Non-Random Two-Liquid model. Correlations were satisfactory. For the first time, multiple equilibrium regions involving liquid and solid phases of a system with an ionic liquid were simultaneously correlated.

The ionic liquid proline butyl ester dodecyl sulfate showed surfactant and viscoelastic character. The rheological behavior of its mixtures with water and *n*-octane was analyzed. The ionic liquid and its mixtures with water and oil showed shear-thinning and thixotropic behavior. The high values of apparent viscosities obtained suggest the possibility of using the ionic liquid to increase the injection formulation viscosity, thus preventing the formation of digitations when the oil is extracted. As the ionic liquid is a surfactant, a synergic effect is expected.

2-prolinolium dodecylbenzene sulfonate is liquid at room temperature, thermally and hydrolytically stable, acts as a surfactant and is miscible with water. Moreover, its mixtures with water and *n*-octane form a Winsor Type III system leading to ultra-low interfacial tensions. It is an interesting alternative for oil recovery formulations.

Overall, it can be concluded that the use of ionic liquids to design new formulations for enhanced oil recovery is promising.

Keywords: Enhanced Oil Recovery, Phase Behavior, Ionic Liquid.

Resumen (Spanish)

El petróleo es la base de nuestra actual comodidad. Aproximadamente dos tercios del crudo todavía permanecen en un pozo considerado agotado. Los métodos de recuperación mejorada de petróleo con surfactantes son muy prometedores. El objetivo principal de esta tesis es el desarrollo de nuevas formulaciones, basadas en líquidos iónicos, para su uso en esa aplicación.

El estudio se inició determinando los diagramas de fase del acetato de 1-hexil-3-metilimidazolio y el trifluorometanosulfonato de 1-hexil-3-metilpiridinio con agua y varios hidrocarburos (*n*-octano, ciclohexano o tolueno). Se demostró que ambos líquidos iónicos no son surfactantes, por lo que la investigación se enfocó a su uso como co-surfactantes en la recuperación de crudo. El acetato es miscible con agua y muestra una baja capacidad para solubilizar los hidrocarburos, por lo que podría usarse en formulaciones con tensioactivos lipofílicos. El carácter sólido del segundo líquido iónico dificulta su aplicación. Para facilitar el estudio de cualquier proceso con estas mezclas, los datos de equilibrio se correlacionaron con el modelo *Non-Random Two-Liquid*. Los resultados fueron satisfactorios. En este trabajo, por primera vez para un sistema con líquido iónico, se consiguió la correlación simultánea de datos de diferentes regiones de equilibrio que involucran fases líquidas y sólidas.

El líquido iónico dodecilsulfato de prolinio butil éster es surfactante y viscoelástico. Se analizó el comportamiento reológico de sus mezclas con agua y *n*-octano. Tanto el componente puro como las mezclas poseen carácter tixotrópico y pseudoplástico. Los altos valores obtenidos para las viscosidades aparentes, sugieren la posibilidad de utilizar el líquido iónico como agente químico para aumentar la viscosidad de la formulación usada en la extracción de crudo, evitando así la digitación del agua. Este efecto se combinaría con la reducción de la tensión interfacial.

El líquido iónico dodecibencenosulfonato de 2-prolinolio es líquido a temperatura ambiente, térmica e hidrolíticamente estable, tensioactivo y miscible con agua. Además, sus mezclas con agua y *n*-octano forman un sistema Winsor Tipo III que da lugar a tensiones interfaciales ultra-bajas. Es una alternativa interesante para la recuperación de crudo.

En general, se puede concluir que el uso de líquidos iónicos para el desarrollo de nuevas formulaciones en la recuperación mejorada del petróleo es prometedor.

Palabras clave: Recuperación Mejorada del Petróleo, Comportamiento de Fase, Líquido Iónico.

Resumo (Galician)

O petróleo é a base da nosa actual comodidade. Aproximadamente dous terzos do cru aínda permanecen nun pozo considerado esgotado. Os métodos de recuperación mellorada de petróleo con surfactantes son moi prometedores. O obxectivo principal desta tese é o desenvolvemento de novas formulacións, baseadas en líquidos iónicos, para o seu uso nesa aplicación.

O estudo iniciouse determinando os diagramas de fase do acetato de 1-hexil-3-metilimidazolio e o trifluorometanosulfonato de 1-hexil-3-metilpiridinio con auga e varios hidrocarburos (*n*-octano, ciclohexano ou tolueno). Demostrouse que ambos os líquidos iónicos non son surfactantes, polo que a investigación enfocouse ao seu uso como co-surfactantes na recuperación de cru. O acetato é miscible con auga e mostra unha baixa capacidade para solubilizar os hidrocarburos, polo que podería usarse en formulacións con tensioactivos lipofílicos. O carácter sólido do segundo líquido iónico dificulta a súa aplicación. Para facilitar o estudo de calquera proceso con estas mesturas, os datos de equilibrio se correlacionaron co modelo *Non-Random Two-Liquid*. Os resultados foron satisfactorios. Neste traballo, por primeira vez para un sistema con líquido iónico, conseguiuase a correlación simultánea de datos de diferentes rexións de equilibrio que involucran fases líquidas e sólidas.

O líquido iónico dodecilsulfato de prolinio butil éster é surfactante e viscoelástico. Analizouse o comportamento reolóxico das súas mesturas con auga e *n*-octano. Tanto o compoñente puro como as mesturas posúen carácter tixotrópico e pseudoplástico. Os altos valores obtidos para as viscosidades aparentes, suxiren a posibilidade de utilizar o líquido iónico como axente químico para aumentar a viscosidade da formulación usada na extracción de cru, evitando así a digitación da auga. Este efecto combinaríase coa redución da tensión interfacial.

O líquido iónico dodecibencenosulfonato de 2-prolinolio é líquido a temperatura ambiente, térmica e hidroliticamente estable, tensioactivo e miscible con auga. Ademais, as súas mesturas con auga e *n*-octano forman un sistema Winsor Tipo III que dá lugar a tensións interfaciales ultra-baixas. É unha alternativa interesante para a recuperación de cru.

En xeral, pódese concluír que o uso de líquidos iónicos para o desenvolvemento de novas formulacións na recuperación mellorada do petróleo é prometedor.

Palabras chave: Recuperación Mellorada do Petróleo, Comportamento de Fase, Líquido Iónico.



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1. OBJECTIVES





Crude oil is our primary energy source, and the support of the petrochemical industry which produces thousands of products that are the basis of our current comfortable lifestyles. The eventual need to move towards total independence from crude oil is undeniable. However, technological advances in renewable sources of energy take time, and we do not yet have sustainable sources to produce all the materials nowadays obtained from oil. If we want to maintain our present standard of living whilst trying to achieve the required technological development, full exploitation of existing reservoirs is required.

Approximately two thirds of the oil still remain inside an already exploited reservoir. This is due to limitations of the current recovery processes. Surfactant enhanced oil recovery (EOR) methods are promising. A very low concentration of surfactant in brine solution is injected into the reservoir to reduce the water-oil interfacial tension, thus enhancing the mobility of the oil retained in the pores of the rocks. This is a low impact method where, for instance, problems associated with fracking (hydraulic fractures) are avoided. However, the surfactant must meet many requirements: It must be miscible in water, stable in the presence of salts, and show a significant and equilibrated solubilization of oil and water. On many occasions, co-surfactants are required to provide a suitable formulation.

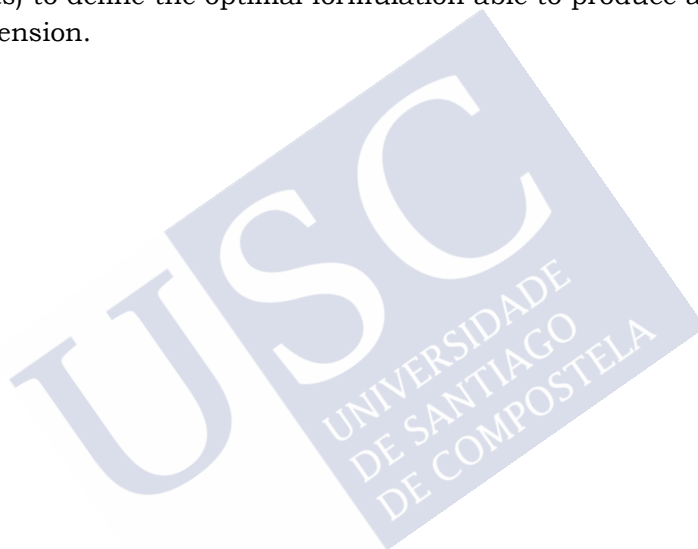
Thanks to the possibility of designing a practically unlimited number of them, ionic liquids (ILs) have become a powerful tool in the improvement of many processes. Thus, **the main objective of this Thesis is the development of new formulations based on these salts, which are suitable to be used in surfactant EOR processes.**

The first study will be focused on ILs with an alkyl chain length of six carbons, namely: 1-hexyl-3-methylimidazolium acetate ($[\text{C}_6\text{mim}][\text{OAc}]$) and 1-hexyl-3-methylpyridinium trifluoromethanesulfonate ($[\text{C}_6\text{C}_1\text{py}][\text{OTf}]$). The objectives are: the analysis of their capacity of aggregation in order to know if they can act as surface active agents, the determination of phase diagrams with water and different kinds of oils, and the treatment of equilibrium data obtained to facilitate their management. According to the results obtained, the role that these compounds could play in formulations for EOR will be analyzed.

A different work will be carried out with the surface active IL (SAIL) proline butyl ester dodecyl sulfate ($[\text{C}_4\text{Pro}][\text{DS}]$). Viscoelastic surfactants show two advantages: they can be used as viscosifiers of water to push out the oil from the reservoir avoiding the formation of fingering, and they are able to effectively sweep oil from blind ends of reservoirs. For that reason,

the rheological behavior of [ⁿC₄Pro][DS] and its mixtures with water and oil (*n*-octane) will be studied. Parameters such as: effects of shear, maintenance of viscosity during flow and injectivity will be analyzed.

The last and overarching objective of this Thesis is the design of a new IL able to accomplish all the requirements needed in EOR applications: a bio-based (no toxic compound) surfactant, that is soluble and stable in water and brine even at high temperature, and with the required solubilization parameters. Several prolinolium SAILs with dodecylsulfate and dodecylbenzenesulfonate anions ([HOPro][DS] and [HOPro][DBS]) will be synthesized, characterized and analyzed for EOR. With the focus on this application, phase behavior with water and oil will be studied qualitatively (pipette tests) to define the optimal formulation able to produce an ultra-low interfacial tension.





2. INTRODUCTION





2.1. ENHANCED OIL RECOVERY (EOR)

2.1.1. Context

The oil industry is a mature sector that encompasses two production lines: energy production, and raw materials for chemical products. Energy demands have been increasing since the Industrial Revolution. According to the U.S. Energy Information Administration [1], global energy consumption will increase even further in the coming years. Renewable sources will rise, but demand for oil will almost remain constant, as can be seen in Figure 2.1. Renewable energy technology develops slowly and not without problems [2]. Thus, while sustainable sources are developing and improving their efficiency, traditional energy sources will still be necessary.

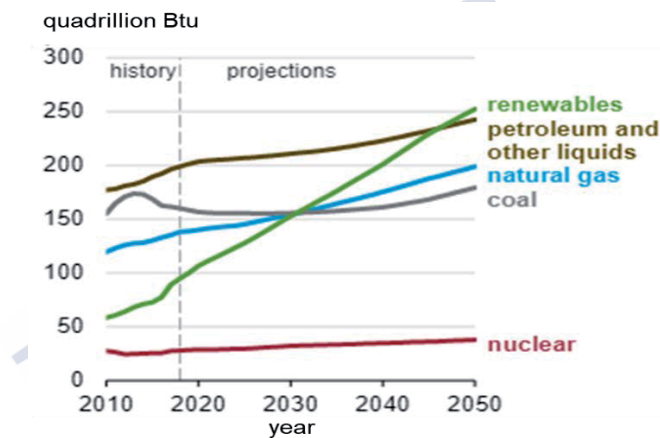


Figure 2.1. Global primary energy consumption by source. U.S. Energy Information Administration [1]

The chemical industry needs oil as feedstock to produce a wide spectrum of synthetic products that are used in everyday life (detergents, adhesives, plastics, dyes, etc). Raw material demand is increasing while reservoirs are depleting. Thus, long-term efforts will be focused on the use of oil as a raw material as long as possible, instead of as an energy source [3].

Three stages can be distinguished in the extraction of the reserves from an oil field [4]. During primary extraction, the oil is either drained naturally, due to the pressure gradient between the bottom and the surface of the well, or by pumping it until the pressure in the well has decreased substantially. The percentage of extraction by means of this method usually corresponds to 10-15% of the crude. The secondary extraction methods consist of injecting a fluid cheaper than oil (e.g. water, natural gas...) into the oil field to maintain a pressure gradient. These fluids are injected

through specific wells (injectors), and they displace or drag a portion of the oil to other wells (producers). By means of these methods, the percentage of crude extraction from a well can reach 40%.

After the primary and secondary extractions, the oil field still contains around 60-80% of the original crude. This is due to two factors limiting the efficiency of the primary and secondary extraction methods:

- At a pore scale, the crude reaches a sufficiently low residual saturation as to be in the form of discontinuous globules trapped by capillary forces.
- At an 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 reservoir is not favorable.

To extract the remaining oil in an already exploited reservoir, tertiary extraction, also called EOR, methods are required. They consist of strategies that increase the mobility of the fluid in the well, applied in combination with secondary extraction methods. The use of EOR technologies allows the extension of the period of use of mature oil reservoirs. The improvement of these methods is necessary in order to maintain living standards until renewable methodologies are mastered.

2.1.2. EOR methods

EOR is oil recovery by injection of gases, chemicals or chemical energy into the reservoir. There have been other attempts based on the use of microorganisms but they are less studied [5].

Thermal methods involve heating the oil field, thus reducing the viscosity of the crude 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 reservoir, e.g. by combustion.

Miscible EOR methods usually involve the injection of a gas - for example natural gas, nitrogen, carbon dioxide or flue gas - into the reservoir at elevated pressures to completely solubilize within the crude, reducing the problems of capillarity and increasing its mobility [6]. Carbon dioxide is the most commonly used gas. Its use in this application also helps to solve an environmental problem. However, the difference of viscosities between gas and oil leads to an inhomogeneous distribution inside the reservoir, with the formation of digitations and preferential paths, thus reducing the effectiveness of the method.

Chemical EOR methods [4] are based on the injection of aqueous solutions of different chemicals such as polymers, surfactants or alkalis.

Polymers are used to increase the displacing polymer solution's viscosity. The mechanism is the reduction of the mobility ratio of displacing fluid to displaced fluid, thus reducing the formation of digitations and improving oil displacement. It has been also shown [7] that viscoelastic polymers pull out the oil from dead ends (inaccessible pore ends), also increasing oil recovery. The key aim in surfactant flooding is to reduce interfacial tension between oil and the displacing fluid. Thus, the capillary number -the ratio of viscous to local capillary forces- is increased, allowing the oil retained in the pores of the rocks to be flushed out. Alkaline flooding involves the use of aqueous solutions of certain chemicals such as sodium hydroxide, sodium silicate or sodium carbonate. These solutions react with substances present in crude oil or at the rock/crude oil interface, producing surfactants in situ.

There are other factors that have to be considered in an oil recovery process. Chemicals can be used to alter wettability in order to improve the extraction. Moreover, preventing these chemicals being adsorbed by the rocks is essential for a successful EOR method. To meet all these requirements, a combination of different methods is not unusual.

It is worth mentioning that there are other methods, such as cement plug treatment or fracking, that are called Improved Oil Recovery (IOR) methods because they are not implemented at the reservoir scale [8].

2.1.3. Surfactant EOR

This method of oil recovery is based on the injection of a diluted surfactant solution into the oil field. This formulation consists of a mixture of brine and surfactant (also frequently containing co-surfactant, alcohol, polymer, etc). This 'slug' moves along the oil field, freeing most of the oil trapped within the rocks.

There are two ways to apply this process [4]. In the first, a relatively low concentration of surfactant (2-4%, or even lower) is injected into large pores to reduce the water-oil interfacial tension, thus increasing extractability. If the formulation is optimal, the interfacial tension with the crude may reach a minimum. In the second option, greater quantities of surfactant (8-12%) are injected into small pores and, in this way, the micelles solubilize the oil and the water in a mobile microemulsion. The displacing fluid can be also a microemulsion formed with these products and the oil (micellar or microemulsion flooding).

In surfactant or microemulsion flooding, when surfactant solution contacts residual oil droplets they are emulsified because of the low interfacial tension. This entrained oil is carried forward and pulled to become long oil threads that deform and pass through pore throats [4]. The

control of mobility is important to ensure effectiveness of the process. To prevent the degradation of the surfactant formulation, an aqueous polymer phase (which will increase the viscosity of water and the efficiency of the sweeping) is usually injected afterwards.

This tertiary extraction method is one of the most efficient, but also one of the most difficult to implement. The main requirements of the method are:

- Minimizing water-oil interfacial tension.
- Minimizing surfactant and co-surfactant adsorption in rocks.
- Improving surfactant resistance to reservoir conditions such as pressure, temperature or salinity.
- Minimizing viscosity difference between oil and aqueous phase.

Besides the reduction of the interfacial tension, the objective is the solubilization of oil and water in the displacing fluid. The bottleneck in the success of the application of these surfactant methods is the need for a surfactant that is miscible in water, stable in the presence of salts, with a significant and equilibrated solubilization of oil and water.

2.1.4. Laboratory tests for surfactant EOR

The capacity of a surfactant to solubilize water and oil is directly related with the reduction of the interfacial tension. Phase diagrams involving these compounds must be studied. The rheological study of microemulsions is also of interest because viscous aqueous formulations are required to ensure mobility control. Therefore, these are the fundamental initial studies required to propose a surfactant for EOR.

2.1.4.1. Phase behavior

The main compounds involved in a surfactant EOR process are water, oil and surfactant. For this reason, triangular diagrams involving those compounds are useful tools that show compositions of the different microemulsions that can be found in these systems. Moreover, when systems are complex, more than one compound is usually combined in a pseudo-component in order to maintain the study of simple ternary systems.

In this context, Winsor defined three types of ternary diagrams at constant temperature and pressure [9] (Figure 2.2).

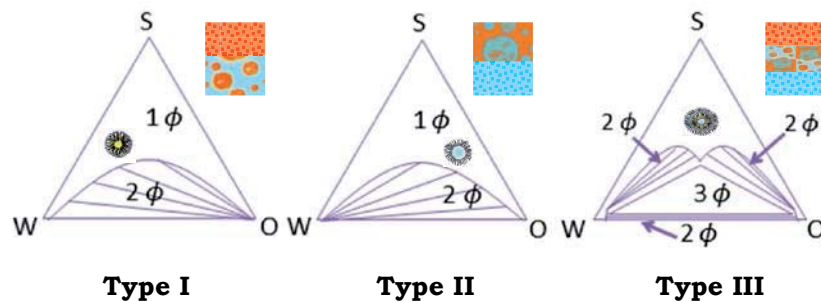


Figure 2.2. Winsor classification for Water + Oil + Surfactant ternary diagrams

Winsor Type I systems are found with hydrophilic surfactants. They show a miscible region (1Φ) at high surfactant concentration and an immiscible area (2Φ) at low concentration of this compound. A mixture of composition inside this biphasic area splits into two equilibrium phases: an aqueous microemulsion and an oily phase. The opposite behavior, Winsor Type II systems, is found with lipophilic surfactants. Mixtures of the immiscible region split into an oily microemulsion and an aqueous phase. In Winsor Type III systems, besides the monophasic region, there is a triphasic region (3Φ) surrounded by three biphasic regions (2Φ). Mixtures in the biphasic regions will split as previously explained. Systems with compositions lying in the triphasic region give rise to three equilibrium phases: water, oil and a middle phase where the surfactant solubilizes water and oil.

The existence of a greater number of compounds (salt, co-surfactant, etc.) makes the rigorous determination of phase equilibria very time-consuming, and sometimes unfeasible. Visual phase behavior studies (usually in pipettes) are preferred. Figure 2.3 shows the behavior of water + oil + surfactant ternary diagrams as a function of salt concentration, and their visualization in pipette tests. As salinity is increased, the negative slope of the tie-lines in Type I systems changes to the positive slope in Type II systems. The transition occurs through Type III systems [8]. When, in these three-phase systems, similar quantities of water and oil are solubilized, a drastic reduction in the interfacial tension associated with high oil recovery occurs. So this is the phase behavior desired in EOR processes.

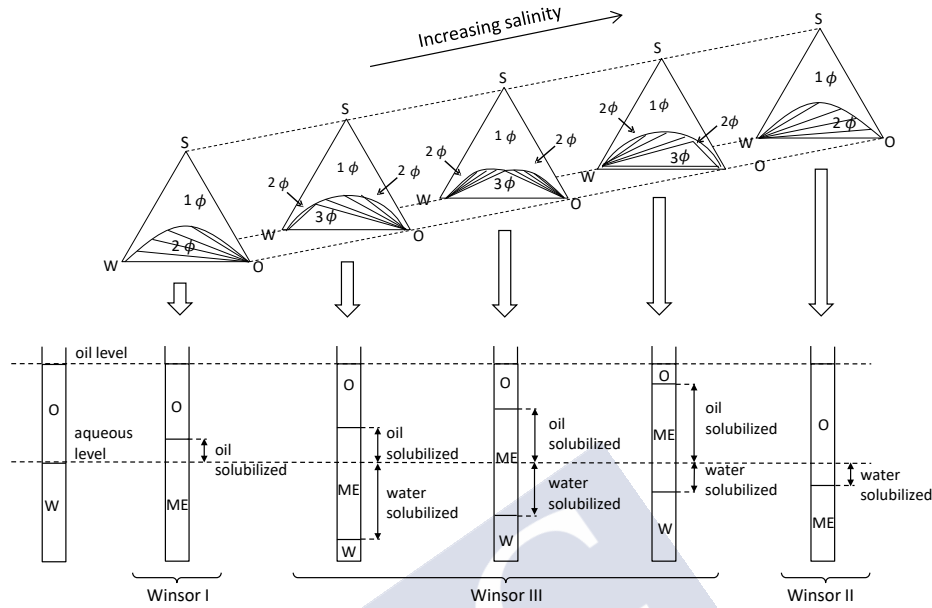


Figure 2.3. Water + Oil + Surfactant ternary diagrams as a function of salt concentration and their visualization in pipette tests.

Pipette tests allow the determination of the volumes of water, oil and middle microemulsion phases in Winsor Type III systems. Thus, the ratio of oil and surfactant volumes (V_o/V_s) and the ratio of water and surfactant volumes (V_w/V_s), the so called solubilization parameters, can be determined. The highest oil recovery (minimum interfacial tension) is usually obtained at the optimal salinity [4], that leading to equal solubilization parameters with values close to or higher than 10. The corresponding interfacial tension can be calculated according to Huh's equation [10],

$$\gamma = C/(\sigma_o)^2 \quad (2.1)$$

being γ the interfacial tension, C a constant ($0.3 \text{ mN}\cdot\text{m}^{-1}$), and σ_o the solubilization parameter.

2.1.4.2. Rheology

Rheology is the science that studies the deformation and flow of matter [11]. It is the study of the manner in which materials respond to applied stress or strain. Thermorheology considers the effect of the temperature on these studies. It is, therefore, a branch of fluid mechanics or thermomechanics.

Most low molecular weight substances are Newtonian. An infinitesimal shear stress initiates flow and the shear stress is directly proportional to the shear rate. The flow curve, at a given temperature and pressure, is therefore linear and passes through the origin (see Figure 2.4). The constant of proportionality is the dynamic viscosity (η).

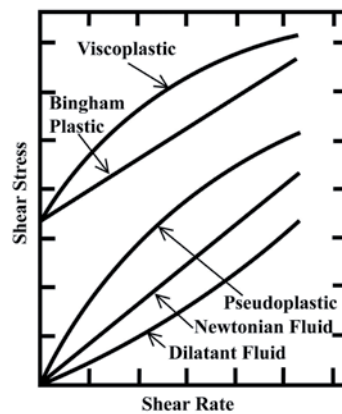


Figure 2.4. Non-Newtonian fluids

However, in many cases, the relation between shear stress and shear rate is not linear, and the fluids are no longer characterized by “a defined viscosity” but an apparent viscosity. These are non-Newtonian fluids and are very numerous. In time-dependent fluids, the apparent viscosities are not only functions of the applied shear stress or the shear rate, but also of the time and their previous kinematic history. Thixotropic fluids are characterized by a decrease of the apparent viscosity under constant shear stress or shear rate, followed by a gradual recovery when the stress or shear rate is removed. Rheopectic fluids exhibit the opposite behavior. Regarding time-independent fluids, their behavior takes as reference Newtonian fluids. Bingham fluids require a non-zero shear stress to flow, and then the shear stress-shear rate dependence is linear (see Figure 2.4). In the case of shear-thinning (pseudoplastic) and shear-thickening (dilatant) fluids, the rate of increase in shear stress with shear rate decreases and increases, respectively, with increasing shear rate (See Figure 2.4). Both follow the well-known power law.

It must be taken into account that the viscous behavior of a fluid can strongly depend on the temperature. There are numerous empirical correlations or physicochemical equations to represent this behavior. An

Arrhenius -exponential- dependence between viscosity and absolute temperature is frequently found.

The most interesting fluids from the point of view of rheology are viscoelastic fluids [12]. These are systems which present both viscous and elastic properties. Fluids with ideal viscous behavior are irreversibly deformed when submitted to a shear stress and they flow, they do not recover the original shape when the force is removed. Conversely, in elastic behavior the original shape is completely recovered when the applied force is removed. The majority of materials exhibit viscoelastic behavior, somewhere between viscous and elastic, and determining the fraction of each effect is the aim of rheology.

A rheometer is an instrument for measuring rheological properties. It can have different configurations (cone and plate, parallel plates, etc.) and can be used for shear tests and torsional tests. Rheometers operate with continuous rotation and rotational oscillation, and allow the determination of the viscoelastic character of a sample through storage and loss moduli. The storage modulus (G') represents the elastic portion of the viscoelastic behavior, in other words, the solid-state behavior of the sample. The loss modulus (G'') corresponds to the viscous portion of the viscoelastic behavior, the liquid-state behavior of the sample. The predominance of one modulus over the other reflects the main character (elastic solid or viscous liquid). It is generally measured with the loss factor or damping factor determined according to equation 2.2.

$$\tan \delta = G''/G' \quad (2.2)$$

Regarding EOR, it has been shown that in the case of heterogeneous reservoirs, a high viscoelasticity of the injection fluid can be even more important to effectively sweeping oil than an ultra-low interfacial tension [13]. High values of G' and G'' obtain greater effectiveness sweeping the residual oil from blind ends.

2.2. IONIC LIQUIDS IN EOR

2.2.1. Context

In the early years of the past decade, ILs started to attract a lot of attention from industry and academia due to their various appealing characteristics. They are salts which are liquid at or near ambient temperature (by definition melting or transition temperature below 100 °C), and so typically combine a negligible vapor pressure in the liquid state with

good thermal and chemical stabilities, among other interesting properties. One intrinsic advantage of ILs is that, by judicious choice and functionalization of the constituent ions, their physical, chemical and biological properties can be tuned to a significant extent in order to fit those required for a specific application [14]. Thus, the core structures of cation and anion, the length and branching of alkyl side chains, and functional groups can be selected in order to obtain a SAIL with a desired set of properties to achieve EOR objectives.

2.2.2. State of art

Since the number of ILs is practically unlimited, a countless number of possible SAILs may be obtained, dramatically increasing the chances of obtaining an optimal surfactant for EOR applications.

The first work proposing SAILs to improve the current methods of EOR [15] was published in 2012 by the research group to whom this author belongs, the Group of Sustainable Separation Processes from the Universidade de Santiago de Compostela. It was demonstrated that the SAIL trihexyl(tetradecyl)phosphonium chloride was able to form a Winsor Type III system with water and oil (*n*-dodecane), producing a significant decrease in the water-oil interfacial tension. However, it was far from the ultra-low value required because the three phase system was formed due to the immiscibility of the pairs, and not to the surfactant solubilization capacity.

Following that pioneering work, the number of publications proposing the use of ILs for EOR has increased exponentially. Some studies can be found in the literature [16-20] that aim to analyze the viability of SAILs for EOR by means of the measurement of dynamic interfacial tensions between the surfactant solution and oil. In these studies, the influence of several variables (type of oil, type and concentration of surfactant and salt, temperature, etc.) is studied. The work carried out by professors Benzagouta [16] and Hezave [17, 18] is particularly notable. They showed that with the use of SAILs, the water-oil interfacial tension can be reduced by up to 90%. Combinations with alkalis further reduce this property [19]. Recently, Zhou *et al.* [20] proposed the use of Gemini SAILs to further reduce the water-oil interfacial tension.

Core flooding experiments, though time-consuming and expensive, are the definitive tests in surfactant EOR. A sample of rock, normally taken from a real reservoir, is inserted in a core-holder. A fluid, or a combination of fluids, are injected to carry out two kinds of studies: interactions between the injecting fluid and the rock, and oil recovery.

In these core-flooding tests, secondary recovery is generally simulated by the injection of water or brine. When no more oil can be extracted, a surfactant solution or microemulsion is injected in an attempt to enhance the recovery. Pereira *et al.* [21] worked with 1-ethyl-3-methylimidazolium tosylate, not a SAIL, but rather an IL that has aromatic rings in the cation and in the anion. After secondary recovery with water, the IL was able to extract more oil from the rock than Petrostep (a traditional surfactant used in EOR). Electrostatic interactions that produce a change in wettability, and π - π interactions with the aromatic hydrocarbons of the crude oil are the reasons for the improved extraction. Sakthivel *et al.* [22, 23] carried out core flooding tests in sand-pack cores with several SAILs. Results clearly surpassed those obtained with sodium dodecyl sulfate. For alkyl-imidazolium chloride ILs, the longer the alkyl chain length the greater extraction. This was also confirmed by Nandwani *et al.* [24] who also showed that chemical flooding with 1-hexadecyl-3-methylimidazolium bromide in brine solution extracted more oil trapped in the core rock when compared to hexadecyltrimethylammonium bromide solution using the same composition. Also Hezave *et al.* [25] and Bin-Dahbag *et al.* [26, 27] were able to enhance oil recovery after secondary extraction using 1-dodecyl-3-methylimidazolium chloride (a SAIL later also proposed by Nabipour *et al.* [28]) and tetraalkyl ammonium sulfate, respectively. I. Rodriguez *et al.* [29] tested a phosphonium IL, namely tributyl(tetradecyl)phosphonium chloride, and results were also encouraging with 8 % additional oil recovery after flooding with brine. In contrast to conventional surfactants, SAILs are normally more effective when salinity is high. Additionally, comparing changes in the wettability to interfacial tension, the most effective mechanism is the latter [30]. In an attempt to improve oil extraction efficiency, the use of mixtures of SAILs and traditional surfactants is also proposed [31]. Core flooding tests showed enhanced recoveries, in some cases, close to 15% of the original oil in place. Another recent proposal to improve the results is the use of poly-ionic liquids, combining thus the effects of polymers and surfactants [32]. All these results are very promising. However, none of these oil recovery studies was carried out with a formulation previously optimized via phase behavior tests. Thus, it should be possible to obtain much better results.

In 2016 Bera and Belhaj published a state-of-the-art review of this topic [33] and indicated that for this application it is crucial to know the phase behavior of the IL microemulsion systems involved in the process. Despite the fact that this is the first required step in evaluating if a SAIL is suitable for EOR applications, rigorous phase behavior studies or, more practical, salinity scans involving water/brine, oil and SAILs are almost non-existent

in the literature. The work published by Nandwani *et al.* [34] presents salinity scans to show that the blend of the SAIL 1-hexadecyl-3-methylimidazolium bromide and the non-ionic surfactant Tergitol is able to produce a Winsor Type III system thus leading to an ultra-low interfacial tension. Oil recovered after water flooding in core-flooding tests was about 10% at an optimal salinity of 30%. These authors have also recently shown that in carbonate reservoirs adsorption of typical ILs is lower than that of the traditional surfactant cetyltrimethylammonium bromide [35].

Deep Eutectic Solvents (DESs) – mixtures of two (or more) compounds with a eutectic point far below the melting points of the individual components, resulting from hydrogen bond complexation between the mixture compounds – have been also proposed for EOR [36]. However, the DESs used up to now are not surfactants, hence the only mechanism of extraction is alteration in wettability, which leads to limited oil recovery.

The literature clearly shows a lack of works on the determination of rigorous liquid-liquid equilibrium (LLE) of ternary systems water + oil + surfactant and visual studies on pipette tests, even though they are essential studies to determine optimal formulations for EOR. Regarding the first kind of studies, only our research group has published some works testing ILs such as: trihexyl(tetradecyl)phosphonium chloride [15,37], trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide [38], 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [39], trihexyl(tetradecyl)phosphonium dicyanamide [40,41], and trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate [42]. Even when all those SAILs led to a Winsor Type III ternary system, none of them led to promising oil and water solubilization. Concerning the second kind of studies, solubilization parameters obtained for tributylmethylphosphonium dodecylsulfate were low [43]. However, a blend of an internal olefin sulfonate with 1-dodecyl-3-methylimidazolium bromide in seawater led to high solubilization parameters and ultra-low interfacial tension [44]. The above mentioned work of Nandwani *et al.* [34] also required a blend to obtain high oil solubilization. These two papers show very good results but a mixture of two surfactants was required.





3. PUBLICATIONS





1.- Phase Equilibria of 1-hexyl-3-methylimidazolium acetate with water and oil.

R. Corchero, I. Rodríguez-Escontrela, O. Rodríguez, A. Soto.

Fluid Phase Equilibria 483 (2019) 144-152.

[DOI: 10.1016/j.fluid.2018.11.010](https://doi.org/10.1016/j.fluid.2018.11.010).

2.- Equilibria and correlation of systems involving 1-hexyl-3-methylpyridinium trifluoromethanesulfonate.

R. Corchero, A. Marcilla, M.M. Olaya, P. Carbonell-Hermida, A. Soto.

RSC Advances 9 (2019) 42524-42532.

[DOI: 10.1039/C9RA09283H](https://doi.org/10.1039/C9RA09283H).

3.- Thermo-rheology of a proline-based surface active ionic liquid and their binary and ternary mixtures with water and *n*-octane

M.D. Torres, R. Corchero, I. Rodríguez-Escontrela, A. Soto, R. Moreira.

Chemical Engineering Technology 42 (2019) 1952-1959

[DOI: 10.1002/ceat.201800269](https://doi.org/10.1002/ceat.201800269).

4.- Ionic Liquids derived from proline: application as surfactants

V. Fernández-Stefanuto, R. Corchero, I. Rodríguez-Escontrela, A. Soto, E. Tojo.

ChemPhysChem 19 (2018) 2885-2893.

[DOI: 10.1002/cphc.201800735](https://doi.org/10.1002/cphc.201800735).





4. GENERAL DISCUSSION





One of the most promising EOR techniques is surfactant flooding. The use of chemical formulations with surfactants to extract oil reduces water-oil interfacial tension and flushes out the oil trapped in the pores of the rocks due to capillary forces. Surface-active chemicals can be injected as an aqueous solution of surfactant, co-surfactant, electrolytes, etc. (surfactant flooding), or the displacing fluid can be a microemulsion formed with these products and the oil (micellar or microemulsion flooding) [8]. Besides the reduction of interfacial tension the objective is the solubilization of oil and water in the displacing fluid. The bottleneck in the success of these surfactant methods is the lack of a suitable surfactant. It must be miscible in water, stable in the presence of salts, and show a significant and equilibrated solubilization of oil and water (corresponding to a Winsor Type III phase diagram). The papers presented in this Thesis aim to make a contribution, based on the use of ILs, to address this key challenge.

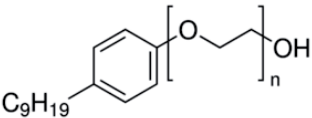
The first difficulty in the use of SAILs for EOR is finding salts with an alkyl chain length long enough to confer a surfactant character to the IL and that are also miscible in water. Smirnova and Safanova [45] reviewed the problem of aggregation of ILs in water and found that $[C_n\text{mim}]X$ ILs ($X = \text{Br}, \text{Cl}, \text{BF}_4, \text{or } \text{PF}_6$) with $n=4$ showed a certain aggregation in water, and a critical micellar concentration could be determined for these salts with $n=8$ to 14. As no information was found in the literature for ILs with $n=6$, the work of this Thesis started with the IL 1-hexyl-3-methylimidazolium acetate ($[C_6\text{mim}][\text{OAc}]$) [46]. The acetate anion was selected to confer hygroscopic character to the salt. Another $n=6$ IL was used in the second paper [47], however, in this case a pyridinium cation was selected due to its greater biodegradability compared with imidazolium [48]. A commercial product was selected: 1-hexyl-3-methylpyridinium trifluoromethanesulfonate ($[C_6C_1\text{py}][\text{OTf}]$).

The surface tension at 298.15 K of aqueous solutions of $[C_6\text{mim}][\text{OAc}]$ continuously decreased with increasing concentration. A plateau in surface tension characteristic of the formation of micelles was not found, thus the IL is not a surface active agent. However, in the first paper of this Thesis [46] the LLE of this IL with water and oil was studied, at 298.15 and 323.15 K, focusing on the possible application of this IL as a co-surfactant. The IL was found to be completely miscible in water and immiscible in oil (only a partial miscibility was found in aromatic oil due to the interactions with the imidazolium ring). Thus, the phase diagrams water + IL + oil were

found to be Treybal Type II (two immiscible pairs). The LLE data obtained were correlated using the NRTL model with a simple objective function that minimizes first activities and then compositions to facilitate convergence. Moreover, topology analysis of the Gibbs energy of mixing curve was used to ensure consistency of the proposed correlation parameters. Thus, these equilibrium data can be easily managed for EOR or any other application involving these components.

Some traditional surfactants suitable for EOR, able to form a Winsor Type III system with equilibrated solubilization of water and oil, are not currently used for this application due to the impossibility of injecting them into the well as aqueous formulations. This is the case of the surfactants: IGEPAL CO-520 (Sigma-Aldrich, ≥ 98 %wt) and Brij L4 (Sigma-Aldrich, ≥ 98 %wt) that are immiscible in water. Table 4.1 shows the structure of these surfactants. A Winsor Type III behavior was found for IGEPAL CO-520 at 298.15 K and a salinity of 2 %wt NaCl, and for Brij L4 at 298.15 K and a salinity of 11 %wt NaCl (See Figures 4.1 and 4.2).

Table 4.1. Structures of traditional surfactants able to form Winsor Type III systems with water and oil

IGEPAL CO-520	
Brij L4	$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2(\text{OCH}_2\text{CH}_2)_n\text{OH}$

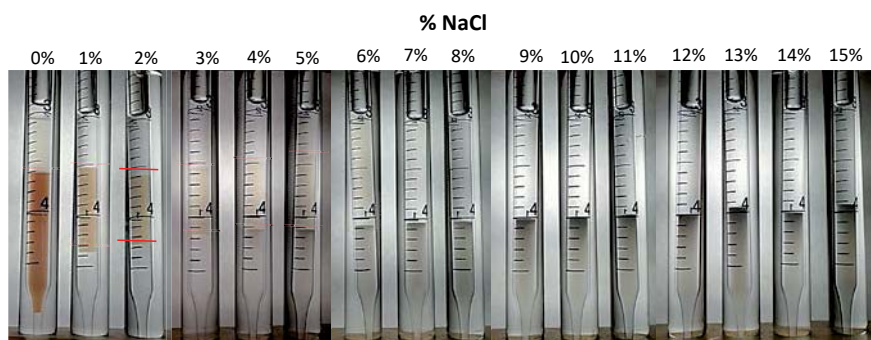


Figure 4.1. Salinity scan for IGEPAL CO-520 at 298.15 K

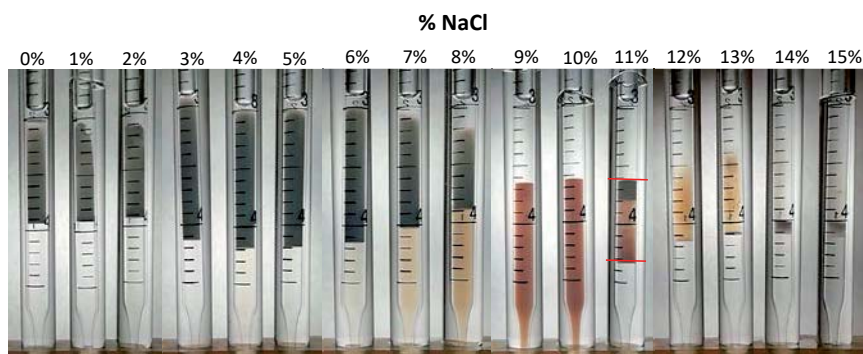


Figure 4.2. Salinity scan for Brij L4 at 298.15 K

Due to the complete miscibility of $[\text{C}_6\text{mim}][\text{OAc}]$ with water, some attempts were carried out (unpublished tests) to use this IL as co-surfactant with those non-injectable traditional surfactants. Blends were carried out ranging from a ratio 9.5/0.5 (Surfactant/ $[\text{C}_6\text{mim}][\text{OAc}]$) to a ratio 5.5/4.5. Vials were prepared with water and *n*-octane at 50 %wt and with a concentration of 2 %wt in surfactant (blend). With both surfactants, IGEPAL CO-520 and Brij L4, the maximum proportion surfactant/IL keeping the Winsor Type III behavior was 8.5/1.5, higher proportion of IL led to Winsor Type I systems. This can be seen, for instance, in Figure 4.3 that shows phase behavior of different IGEPAL CO-520/ $[\text{C}_6\text{mim}][\text{OAc}]$ blends with water and oil.

IGEPAL CO-520/ $[\text{C}_6\text{mim}][\text{OAc}]$
 9.5:0.5 8.5:1.5 7.5:2.5 6.5:3.5 5.5:4.5



Figure 4.3. Blend scan for IGEPAL CO-520/ $[\text{C}_6\text{mim}][\text{OAc}]$ at 298.15 K and 2 %wt salt

The injectability of the blends IGEPAL CO-520/ $[\text{C}_6\text{mim}][\text{OAc}]$ 8.5/1.5 and Brij L4/ $[\text{C}_6\text{mim}][\text{OAc}]$ 8.5/1.5 was tested analyzing their miscibility in brine (salt concentration corresponding to the optimum

of the surfactant) but, unfortunately, they were not miscible enough to reach concentrations of 0.5 %wt, usual in EOR formulations.

Regarding the second paper [47], as with [C₆mim][OAc], [C₆C₁py][OTf] did not show enough aggregation to form micelles in water at 298.15 K. In this case, the chemical being solid, DSC was used to ensure its IL character that was confirmed obtaining a melting temperature of 335.7 K. The binary system water + [C₆C₁py][OTf] showed both a LLE (in a wide range of compositions) and a solid-liquid equilibrium (SLE) region. The application of this IL as co-surfactant in EOR would be problematic. However, the study of the phase diagrams water + IL + oil was carried out, at 298.15 and 323.15 K, for two main reasons. Firstly, those studies are required in a great number of applications where ILs co-exist with oil and water. Secondly, the phase diagrams would have a LLLE in addition to several LLE and SLE regions, and the simultaneous correlation of all these equilibria presented a challenge. A whole data treatment of these kinds of systems was previously absent from the literature.

The solubility of [C₆C₁py][OTf] in *n*-octane and cyclohexane was negligible. Thus, ternary phase diagrams showed a triphasic region limited by three biphasic regions, a SLLE region at low water concentration and a SLE region at high concentration of the IL and null or very low concentration of the hydrocarbon. In the case of the binary system with toluene, pi-stacking interactions with the pyridinium aromatic ring led to the appearance of LLE and SLE regions. The ternary system also showed a triphasic region limited by three biphasic regions, and at high IL concentrations a SLE region with measurable tie-lines appeared. The existence of all these regions involving solid phases greatly complicated the correlation of equilibrium data corresponding to the ternary systems with [C₆C₁py][OTf]. Using the same correlation model as in the case of [C₆mim][OAc], the NRTL model, the procedure required the simultaneous solution of equilibrium conditions, tangent plane equations and mass balances. Several strategies to facilitate the convergence of the optimization procedure were needed. The aim was to obtain a unique set of correlation parameters able to represent all the different equilibrium regions of the system at working pressure and each temperature. Those strategies required the optimization of the correlation parameters step-by-step (firstly binary systems, secondly tie-triangle data and finally SLE and LLE ternary data) and the use of parameters related to mole fractions, rather than the mole

fractions themselves. The correlation was successfully carried out and the obtained deviations were low.

From this point, it was known that the work had to be focused on ILs with alkyl chain lengths longer than $n=6$. Simultaneously a switch to anionic surfactants seemed necessary since these surfactants are the most effective candidates for sandstone reservoirs [49]. At the same time, the tunability of ILs should be exploited to reduce the toxicity of the proposed surfactants. Thus a combination of a dodecylsulfate anion [49], frequently proposed for EOR, and a cation derived from an amino acid, the SAIL proline butyl ester dodecyl sulfate ($[{}^n\text{C}_4\text{Pro}][\text{DS}]$), was selected for the next study [50].

Surprisingly, the mixtures of $[{}^n\text{C}_4\text{Pro}][\text{DS}]$ with water led to a significant increase in viscosity. A similar behavior was found when the SAIL was mixed with oil, thus a mapping of the water + $[{}^n\text{C}_4\text{Pro}][\text{DS}]$ + oil was carried out, and in addition to a biphasic region, a monophasic region with phases of non-Newtonian behavior were found. Recently, viscoelastic surfactants have been suggested as a promising alternative to polymers in EOR [13,51]. These chemicals combine the desirable properties of surfactants and water viscosifiers (used to reduce the fingering generated by the difference of viscosities between water and oil). Furthermore, the use of gels as permeability reducing agents to improve oil recovery has also been proposed [52]. Effects of shear, maintenance of viscosity during flow and injectivity were the studies carried out as the first steps to study the applicability of $[{}^n\text{C}_4\text{Pro}][\text{DS}]$ in EOR.

As a consequence of the formation of aggregates, $[{}^n\text{ProC}_4][\text{DS}]$ exhibited shear-thinning with thixotropic (adequately fitted to the Carreau model) behavior. Its apparent high viscosity decreased with shear rate and temperature. The study at 298.15 K showed that the elastic, G' , and viscous, G'' , moduli increased linearly with increasing angular frequency. A viscoelastic behavior with predominantly viscous behavior ($G'' > G'$), after pre-shear, and the slope of $G' > G''$ for the entire frequency range of study was found. The heating profile exhibited a progressive decrease of G' and G'' moduli with increasing temperature, and a drastic drop at about 311 K (likely associated with the disappearance of aggregates) followed by a plateau above this temperature. Binary mixtures with water or oil led to similar rheological behavior but lower apparent viscosities, decreasing with solvent content.

All ternary mixtures showed a strong shear-thinning character, with a decrease of apparent viscosity with the increase of shear-rate, and thixotropy. However, the viscoelastic behavior of the ternary samples strongly depended on SAIL content. At the lowest [ⁿC₄Pro][DS] concentrations, the mixtures (similarly to binary systems) exhibited a typical liquid-like behavior. Increasing SAIL concentration, G' showed a plateau, with G' > G'' in the lowest frequency range and G'' > G' in the highest range, and both moduli slightly frequency dependent. This indicates weak gel behavior. Lamellar liquid crystals were seen with microscopy. Samples with the highest SAIL content exhibited true gel behavior, with G' > G'' over the tested frequency range and both moduli almost invariant with changing angular frequency. Maltese crosses were seen with microscopy. Flow was favored with the increase of temperature (viscous and elastic moduli decreased). A heating profile with a drastic drop at certain temperature, as in the case of the pure IL, was also observed for ternary mixtures.

During the development of the above mentioned studies, it was noticed that in presence of water, [ⁿC₄Pro][DS] could undergo hydrolysis over time and increasing temperature. So, efforts were carried out to understand this degradation problem and design new biodegradable SAILs stable in water even at high temperatures [53].

To study the decomposition process of prolinium SAILs, water solutions of [ⁿC₄Pro][DS] were heated for some days at different temperatures and it was found that the ester group hydrolyzed, producing prolinium hydroxide, dodecylsulfonic acid and isobutyl alcohol. The solution was the incorporation of an alcohol instead of the ester to the amino acid group. Thus, prolinolium dodecylsulfate [HOPro][DS] was synthesized for the first time. No degradation was observed in water at different temperatures because of the prolinolium cation, however a partial degradation of the dodecylsulfate anion was found after several days at high temperature. This is a well-known problem of the traditional surfactant sodium dodecylsulfate that limits its applications at high temperature. Due to the high stability of the dodecyl benzene sulfonate anion, the synthesis of prolinolium dodecylbenzenesulfonate [HOPro][DBS] SAIL was carried out and its stability demonstrated.

Both [HOPro][DS] and [HOPro][DBS] were found to be miscible with water, which is a good starting point for EOR applications. It was shown that both chemicals were ILs (glass transition or melting point below 100 °C) with a high thermal stability. The capacity to aggregate in water was demonstrated through the determination of the cmc. The

values obtained for this concentration were lower than those corresponding to the parent compounds (sodium dodecylsulfate and sodium dodecylbenzenesulfonate). Moreover, at the same surfactant concentration, they were able to produce a greater reduction of the surface tension of water.

Focusing on EOR, instead of a rigorous determination of the whole phase diagram of these SAILs with water and oil (*n*-octane), salinity scans were carried out, to get an idea of the solubilization capacity of the newly synthesized surfactants. In the case of [HOPro][DS], tests carried out in a wide range of NaCl concentrations and at several temperatures showed a Winsor Type I behavior. In the case of [HOPro][DBS], at 348.15 K and ~8.5 %wt NaCl, a Winsor Type III system with good solubilization parameters was found. Indeed, an estimate of the water-oil interfacial tension that could be obtained in optimal conditions, led to a value of $\sim 3 \cdot 10^{-3}$ mN/m.







5. CONCLUSIONS





In spite of their amphiphilic character, ILs with an alkyl chain length of six carbons, namely: 1-hexyl-3-methylimidazolium acetate ($[\text{C}_6\text{mim}][\text{OAc}]$) and 1-hexyl-3-methylpyridinium trifluoromethanesulfonate ($[\text{C}_6\text{C}_1\text{py}][\text{OTf}]$), do not show the ability to change the surface tension of water to a significant extent, so they cannot be used as surfactants in EOR. The solid character of the trifluoromethanesulfonate makes difficult its application in EOR. The acetate IL is miscible with water and show a low capacity to solubilize oil (*n*-octane, cyclohexane or toluene). It could be of interest for its use as co-surfactant in EOR formulations. Unfortunately, the first attempts carried out in this Thesis in that sense were not promising, but a new research line has been opened and further studies are encouraged.

The water + IL + oil phase diagrams determined for these two ILs are of interest not only for EOR or refinery-related processes, but also for many other applications involving the presence of water and different kinds of oils. NRTL was shown to be useful for the correlation of these systems, thus facilitating their application. In the case of $[\text{C}_6\text{mim}][\text{OAc}]$, a liquid at room conditions, the Treybal Type II systems obtained could be correlated without the requirement of any specific strategy even considering all the studied systems (*n*-octane, cyclohexane or toluene) and temperatures (298.15 and 323.15 K) simultaneously. In the case of $[\text{C}_6\text{C}_1\text{py}][\text{OTf}]$, a solid at room conditions, systems with many different regions (LLE, LLLE, SLE and SLLE) were found, which is why correlation becomes more complicated. Well-defined equilibrium conditions and pivotal strategies were required. As in the case of the acetate IL, NRTL was able to successfully correlate data obtained for all the regions and temperatures. Simultaneous correlation always involved slightly higher deviations. From these two initial works of the Thesis, it can also be concluded that topological analysis based on the Gibbs common tangent criterion is a useful tool to ensure the consistency of the correlation parameters obtained.

The IL proline butyl ester dodecyl sulfate ($[\text{C}_4\text{Pro}][\text{DS}]$) showed surfactant character, however, mixtures with water and oil, far from the Winsor Type III behavior expected for surfactant EOR, showed a palette of systems with a wide range of viscoelastic properties. Both pure IL and its mixtures with water or oil showed shear-thinning, thixotropic and liquid-like behavior. The homogeneous and transparent mixtures obtained with water ensure their injectability for EOR applications. The phase diagram water + SAIL + oil (*n*-octane)

showed a biphasic system at low concentrations of [ⁿC₄Pro][DS] and a region of miscibility where mixtures behave as liquid-like, weak gel with liquid crystals, and true gel behavior with the increase of the SAIL content. The absence of the desired phase behavior and the presence of liquid crystals prohibit the use of this IL as a surfactant in EOR. Nonetheless, the viscoelastic character and the high values of G' and G'' moduli suggest its use as viscosifier and chemical able to sweep the residual oil from blind ends. Further studies at the oil field scale and for specific geometries and conditions are the next logical steps in this research. However, the problem of the hydrolysis of this SAIL over time and increasing temperature is a drawback that has to be considered according to the application.

The problem of hydrolysis of this kind of amino acid derived ILs could be solved avoiding carboxylic acid esterification by its reduction to an alcohol. Exchanging the proline butyl ester cation ([C₄Pro]⁺) mentioned above for the corresponding prolinolium ([OHPro]⁺), has allowed a new family of biodegradable SAILS that are both thermally and hydrolytically stable to be designed. Their stability was further improved by exchanging the dodecylsulfate anion ([DS]⁻) with dodecylbenzenesulfonate ([DBS]⁻). The resulting SAIL, 2-prolinolium dodecylbenzene sulfonate ([HOPro][DBS]), was miscible with water, forming transparent and injectable solutions. A Winsor Type III system with high solubilization parameters, leading to ultra-low interfacial tensions, was found when the phase behavior with brine and oil (*n*-octane) was determined. This SAIL is undoubtedly promising for EOR applications. Core flooding tests are the next steps to ensure EOR without excessive surfactant retention, prior to its application in oil field.

Overall, it can be concluded that ***ILs can be used as chemicals in the development of new formulations suitable for surfactant EOR.*** The improvement of current oil recovery methods requires taking advantage of the capacity of design of these salts and their quasi-infinite possibilities.



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Appendix A: Collaborations



The Globalization that characterizes our century also applies to research. Scientific and technological advances are enhanced due to the combined efforts of different specialists working on the same topic. We would like to acknowledge and recognise in this section several collaborations that have made this work possible.

Publications that constitute the core of this Doctoral Thesis

1.- R. Corchero, I. Rodríguez-Escontrela, O. Rodríguez, A. Soto
Phase Equilibria of 1-hexyl-3-methylimidazolium acetate with water and oil

Fluid Phase Equilibria 483 (2019) 144-152

DOI: 10.1016/j.fluid.2018.11.010

This work was fully developed in the Research Group of Sustainable and Separation Processes of the USC.

2.- R. Corchero, A. Marcilla, M.M. Olaya, P. Carbonell-Hermida, A. Soto

Equilibria and correlation of systems involving 1-hexyl-3-methylpyridinium trifluoromethanesulfonate

RSC Advances 9 (2019) 42524-42532.

DOI: 10.1039/C9RA09283H

The collaboration of the Research Group of Polymers Pyrolysis and Processing of the University of Alicante, allowed the simultaneous correlation of the whole set of equilibrium data obtained. They are internationally recognised experts on this topic. P. Carbonell-Hermida (PhD student) has renounced the presentation of this paper as part of her Doctoral Thesis.

3.- M.D. Torres, R. Corchero, I. Rodríguez-Escontrela, A. Soto, R. Moreira

Thermo-rheology of a proline-based surface active ionic liquid and their binary and ternary mixtures with water and *n*-octane

Chemical Engineering Technology 42 (2019) 1952-1959

DOI: 10.1002/ceat.201800269

This work was developed thanks to the continuous orientation and help of the Research Group of Technologies for Industrial Bioproducts Development of the USC, recognised experts on Rheology. None of the collaborators is a PhD student.

4.- V. Fernández-Stefanuto, R. Corchero, I. Rodríguez-Escontrela, A. Soto, E. Tojo

Ionic Liquids derived from proline: application as surfactants

ChemPhysChem 19 (2018) 2885-2893

DOI: 10.1002/cphc.201800735

The synthesis of the ionic liquids designed in this work was carried out by the Research Group of Biologically Active Organic Compounds and Ionic Liquids of the Organic Chemistry Department of the University of Vigo. Two collaborations were carried out with this Group and V. Fernández-Stefanuto (PhD student) has renounced the presentation of this paper as part of her Doctoral Thesis.

Other publications

5.- B. Rodríguez-Cabo, I. Rodríguez-Palmeiro, R. Corchero, R. Rodil, E. Rodil, A. Arce, A. Soto

Photocatalytic degradation of methyl orange, methylene blue and rhodamine B with AgCl nanocatalyst synthesised from its bulk material in the ionic liquid [P_{6,6,6,14}]Cl

Water Science and Technology 75 (2017) 128-140.

DOI: 10.2166/wst.2016.499

This work was fully developed in the Research Group of Sustainable and Separation Processes of the USC. As first research work of Raquel Corchero, it allowed her to acquire research skills. It is not on the topic of the Doctoral Thesis.

6.- V. Fernández-Stefanuto, A. Somoza, R. Corchero, E. Tojo, A. Soto
Design and Characterization of Naphthalene Ionic Liquids

Frontiers in Chemistry 8 (2020) N: 208

DOI: 10.3389/fchem.2020.00208

The synthesis of the ionic liquids designed in this work was carried out by the Research Group of Biologically Active Organic Compounds and Ionic Liquids of the Organic Chemistry Department of the University of Vigo. Two collaborations were carried out with this Group and R. Corchero has renounced the presentation of this paper as part of her Doctoral Thesis. A. Somoza is a PhD student of the Group of Sustainable and Separation Processes who worked under the supervision of R. Corchero and has also renounced the presentation of this paper as part of her Doctoral Thesis.



**Appendix B: Resumen
(Summary, in Spanish)**



En la actualidad, con la tecnología de la que se dispone, solo se puede extraer en torno a un treinta o cuarenta por ciento del crudo existente en los yacimientos. El petróleo tiene dos usos fundamentales: como fuente de energía y como materia prima en la industria petroquímica. Es evidente que su empleo como fuente de energía está siendo desplazado por otras fuentes renovables menos perjudiciales para el medioambiente. No obstante, las energías alternativas todavía están lejos de ser capaces de desplazar totalmente a los combustibles derivados del petróleo. Por otro lado, su uso en la industria petroquímica es esencial para producir compuestos como detergentes, fertilizantes, plásticos, tintes, adhesivos, etc., siendo difícilmente sustituible por otra materia prima. Por todo ello, la necesidad de seguir extrayendo crudo es innegable. Dado que los yacimientos se están agotando y no se descubren nuevas reservas, se hace necesario llevar a cabo avances tecnológicos que permitan extraer mayor cantidad de crudo de los pozos existentes. En este contexto, las técnicas de recuperación mejorada de petróleo (EOR de sus siglas en inglés) juegan un papel fundamental.

La extracción terciaria, o EOR, consiste en emplear técnicas que facilitan la movilidad del crudo en el yacimiento para conseguir una extracción más eficaz. Entre estas técnicas de recuperación mejorada se encuentran los métodos térmicos, los métodos de desplazamiento por fluido miscible y los métodos químicos. Estos últimos se basan en la inyección en los pozos, de disoluciones acuosas de diferentes productos químicos como polímeros, surfactantes o álcalis. Son considerados los métodos más prometedores, a pesar de su elevado coste, y la alta influencia que variables como: el tipo de crudo, la porosidad y permeabilidad de las rocas de los yacimientos, temperatura, presión, etc., pueden tener en la extracción del crudo. Todo esto, pone de manifiesto la necesidad de estudiar y optimizar estas técnicas para su aplicación de forma eficiente.

La recuperación mejorada empleando surfactantes, consiste en la adición de sustancias tensioactivas al agua. Estos productos químicos reducen la tensión interfacial agua-crudo y por tanto las fuerzas capilares que atrapan el crudo en los poros de las rocas, mejorando así su movilidad y facilitando su extracción. Es el método químico más prometedor, aunque también es uno de los más difíciles de implementar ya que requiere:

- Minimizar la tensión interfacial agua-crudo.
- Minimizar la adsorción de los surfactantes y co-surfactantes en las rocas.

- Mejorar la resistencia del surfactante a las condiciones de la reserva (temperatura, presión, salinidad, etc.)
- Minimizar la diferencia de viscosidad agua-crudo, para conseguir la uniformidad del desplazamiento.

Los líquidos iónicos (LIs) se presentan como una propuesta prometedora para mejorar las técnicas de EOR con surfactantes. Son compuestos que se pueden diseñar de acuerdo con las necesidades específicas de cada tipo de yacimiento, por lo que son especialmente esperanzadores para reservas con condiciones extremas de salinidad o temperatura, donde los surfactantes tradicionales no consiguen los resultados esperados. Dado el elevado número de LIs surfactantes que se pueden diseñar, las posibilidades de este método de recuperación se incrementan enormemente. Por otra parte, estas sales también pueden ser de gran interés para su uso como co-surfactantes, mejorando las propiedades de las formulaciones con surfactantes.

El gran desafío en el éxito de los métodos de EOR con surfactantes, es encontrar el compuesto químico adecuado. Debe ser miscible en agua, estable con la temperatura y en presencia de sales, y mostrar una solubilización significativa y equilibrada de hidrocarburo y agua. ***El principal objetivo de esta tesis doctoral es el desarrollo de nuevas formulaciones, basadas en el uso de LIs, para su uso en EOR con surfactantes.***

Los dos primeros estudios se centraron en LIs con cadenas alquílicas de seis carbonos: acetato de 1-hexil-3-metilimidazolio ($[\text{C}_6\text{mim}][\text{OAc}]$) y trifluorometanosulfonato de 1-hexil-3-metilpiridinio ($[\text{C}_6\text{C}_1\text{py}][\text{OTf}]$). Se pretendía resolver una duda generada del estudio de la bibliografía sobre LIs, determinar si estas sales se comportaban como surfactantes con ese tamaño de cadena. A partir del estudio del comportamiento de fases con agua y diferentes hidrocarburos, se definiría el papel que estas sales podrían jugar en EOR. El tercer estudio se centró en un surfactante viscoelástico, dodecilsulfato de prolinio butil éster ($[\text{C}_4\text{Pro}][\text{DS}]$). Este tipo de compuestos incrementan en gran medida la viscosidad del agua por lo que evitan la formación de digitaciones, y por lo tanto una extracción inefectiva, cuando sus formulaciones acuosas se utilizan en EOR. Debido a su comportamiento reológico, entre líquidos (viscosos) y sólidos (elásticos), se han propuesto además para recuperar crudo de poros de difícil acceso. La investigación se centró en el comportamiento reológico del surfactante con agua y *n*-octano (como crudo modelo). Los esfuerzos del último estudio se enfocaron hacia el diseño de un LI óptimo para EOR, surfactante, miscible en agua, estable térmica e

hidrolíticamente, inyectable y con el comportamiento de fases requerido en EOR (Winsor tipo III). La investigación llevó a diferentes LIs derivados de la prolina. Los objetivos se centraron en su caracterización, y en el estudio de comportamiento de fases con agua y *n*-octano. Estos estudios derivaron en cuatro publicaciones que se resumen a continuación.

Equilibrio de fases del acetato de 1-hexil-3-metilimidazolio con agua e hidrocarburos.

El trabajo se inició comprobando que el LI [C₆mim][OAc] no posee carácter surfactante, en la curva tensión superficial frente a concentración en disolución acuosa no se encontró la línea horizontal propia de la formación de micelas. Como estudio preliminar enfocado al uso de esta sal como co-surfactante en procesos de EOR con surfactantes, se estudió el equilibrio de este LI con agua y diferentes hidrocarburos (*n*-octano, tolueno y ciclohexano) presentes en el petróleo.

Para la determinación de los diagramas de fases se trabajó con células de equilibrio termostatazadas a la temperatura del estudio (298.15 o 323.15 K), y se utilizó cromatografía de gases para el análisis de las composiciones.

Se encontró que el sistema agua + [C₆mim][OAc] es completamente miscible, lo cual es una ventaja importante para la aplicación buscada, ya que la formulación a inyectar en el proceso de recuperación de crudo es acuosa. Su ventaja frente a otros co-surfactantes previamente propuestos, como los alcoholes, es su prácticamente nula volatilidad. Se evitan pérdidas por evaporación y contaminación atmosférica.

El LI [C₆mim][OAc] es capaz de solubilizar una cierta cantidad de tolueno, pero su miscibilidad con *n*-octano y ciclohexano es muy limitada. El estudio de los correspondientes diagramas ternarios (a 298.15 o 323.15 K y presión atmosférica), mostró que prácticamente cualquier mezcla de agua, LI e hidrocarburo, se separa en dos fases: el hidrocarburo, y una disolución acuosa de LI con muy baja proporción del tercer componente. Los resultados sugieren por tanto, que el LI debería combinarse con surfactantes lipofílicos, es decir con una gran capacidad de solubilizar el crudo.

Con el objetivo de hacer los datos de equilibrio más manejables, independientemente de la aplicación considerada, se correlacionaron con la ecuación NRTL (*Non-Random Two-Liquid*). Se usaron dos

funciones objetivo, minimizando primero el desvío en las actividades y después en las fracciones molares, y se obtuvieron desviaciones bajas tanto en la correlación individual de cada sistema a cada temperatura, como en la correlación simultánea de todos los conjuntos de datos, aunque en este último caso los desvíos son ligeramente mayores. El análisis topológico, basado en el criterio de tangente común de Gibbs, demostró la consistencia de los parámetros de correlación obtenidos.

Equilibrio y correlación de sistemas con trifluorometanosulfonato de 1-hexil-3-metilpiridinio.

En este trabajo se seleccionó el LI trifluorometanosulfonato de 1-hexil-3-metilpiridinio ($[C_6C_1py][OTf]$), al igual que en el caso anterior, con una longitud de cadena alquílica que favorece la nano-segregación pero que no le confiere carácter surfactante. El objetivo vuelve a ser el estudio del diagrama de fases del LI con agua y diferentes hidrocarburos. El estudio se justifica no sólo por su interés en EOR, sino porque los LIs se están imponiendo como una opción prometedora para mejorar muchas aplicaciones relacionadas con refinerías, donde el agua y el petróleo coexisten. Sin embargo, la falta en la bibliografía de datos termodinámicos relevantes sobre los procesos de equilibrio involucrados es notoria.

La sal $[C_6C_1py][OTf]$ es sólida a temperatura ambiente, pero se demostró su carácter de LI determinando su punto de fusión que resultó ser 336 K. Debido a este carácter sólido, los diagramas de fases (determinados a 298.15 o 323.15 K y presión atmosférica) con agua e hidrocarburo (*n*-octano, tolueno y ciclohexano) son complejos, incluyendo muchas regiones diferentes (LLE, LLLE, SLE y SLLE). El conocimiento riguroso de estas regiones es necesario para posibles aplicaciones petroquímicas con este LI. Para la determinación de los diagramas de fases, al igual que en el estudio anterior, se trabajó con células de equilibrio y cromatografía de gases.

Todos los sistemas ternarios contienen una región con tres fases líquidas rodeada por tres sistemas bifásicos. La fase enriquecida en LI solubiliza cantidades limitadas de agua e hidrocarburo, muy bajas en el caso de *n*-octano y ciclohexano, y algo mayores en el caso de tolueno debido a las interacciones π - π con el catión piridinio. En todos los sistemas, las regiones cercanas al LI, implican la aparición de fases sólidas. La poca solubilidad en agua y la aparición de fases sólidas descartan, en principio, el uso de este LI como co-surfactante en formulaciones para EOR.

En este trabajo se ha llevado a cabo por primera vez la correlación simultánea de diferentes tipos de datos de equilibrio (LLE, LLE, SLE y SLLE) en un sistema con LI. Para ello se utilizó, al igual que en el trabajo anterior, el modelo NRTL. Sin embargo, en este caso la correlación no fue tan sencilla. Se requirió la definición correcta de las diferentes condiciones de equilibrio y variables a utilizar, y una correlación en diferentes etapas. En todos los casos se obtuvieron resultados satisfactorios, aunque en los sistemas con tolueno las desviaciones fueron algo mayores. Se demostró una vez más la efectividad del análisis topológico para confirmar la consistencia de los parámetros de correlación obtenidos.

Termo-reología de un líquido iónico surfactante basado en prolina: mezclas con agua y *n*-octano.

En este tercer trabajo se estudió el comportamiento termo-reológico de un LI surfactante biodegradable, dodecilsulfato de prolina butil éster ($[{}^n\text{C}_4\text{Pro}][\text{DS}]$), y sus mezclas binarias y ternarias con agua y *n*-octano. Se encontró una gran variedad de comportamientos reológicos que tendrán que ser considerados en cualquier aplicación que implique la mezcla del LI con estos componentes.

El LI $[{}^n\text{C}_4\text{Pro}][\text{DS}]$ es un fluido no Newtoniano cuyo comportamiento depende del tiempo, pertenece al grupo de los fluidos tixotrópicos. La tixotropía se caracteriza por un descenso de la viscosidad aparente del fluido con el tiempo de cizalla, y la recuperación de la misma cuando cesa el flujo o esfuerzo deformador. Para cada instante considerado, las curvas de flujo mostraron un comportamiento pseudoplástico, la viscosidad aparente disminuye con la velocidad de cizalla. Se observó además cierta histéresis (las curvas al aumentar y disminuir la velocidad no coinciden exactamente), propia de fluidos tixotrópicos. Los datos de viscosidad aparente fueron satisfactoriamente correlacionados con el modelo de Carreau.

El estudio reológico sobre el comportamiento viscoelástico del LI mostró que tanto el módulo elástico (G') como el viscoso (G'') aumentaron linealmente con la frecuencia angular, con $G'' > G'$, comportamiento típico de líquidos. Al estudiar el efecto de la temperatura, se encontró que tanto G' como G'' decrecen con esta variable. El LI presenta una transición termorreversible. Al aumentar la temperatura, ambos módulos disminuyen drásticamente su valor a 311 K. Este fenómeno podría deberse a la rotura de los agregados

(*clusters*) que forman los LIs, especialmente los que poseen cadenas hidrocarbonadas largas (como es este caso).

También las mezclas binarias con agua y *n*-octano mostraron un comportamiento tixotrópico y pseudoplástico, con viscosidades aparentes que disminuyen al aumentar la concentración del disolvente (agua o hidrocarburo).

En cuanto al sistema ternario, se encontró una región bifásica para concentraciones bajas de LI. En la región homogénea, todas las mezclas ternarias mostraron un fuerte carácter pseudoplástico, con una disminución de la viscosidad aparente con el aumento de la velocidad de cizalla, y tixotropía. Sin embargo, el comportamiento viscoelástico de las muestras ternarias depende fuertemente del contenido de LI. Cuando el contenido de este compuesto es bajo, las mezclas (de manera similar a la sal pura y los sistemas binarios) mostraron un comportamiento típico de líquidos. Al aumentar la concentración de LI, el comportamiento de las muestras corresponde a un gel débil. Ambos módulos varían muy poco con la frecuencia angular, con $G' > G''$ en el rango de frecuencia más bajo y $G'' > G'$ en el rango más alto. Se utilizó microscopía óptica polarizada para comprobar la existencia de cristales líquidos en forma de lamelas. Las muestras con el mayor contenido de LI mostraron un comportamiento propio de gel, con $G' > G''$ y ambos módulos casi invariables con el cambio de la frecuencia angular. Mediante microscopía se observaron cruces de Malta. El flujo se favorece con el aumento de la temperatura, ambos módulos disminuyen. Y al igual que en el caso del LI puro, para los geles también se observó un perfil de calentamiento con una caída drástica de G' y G'' a una temperatura alrededor de los 321 K, asociada a la ruptura de *clusters*.

La ausencia de cristales líquidos en disoluciones acuosas con baja concentración de LI, y el aumento de viscosidad que este surfactante implica, son puntos de partida interesantes para aplicaciones en EOR. Por otro lado, la formación de geles con este LI puede ser de gran interés para diferentes aplicaciones industriales.

Líquidos iónicos derivados de prolina: aplicación como surfactantes.

Los LIs derivados de aminoácidos presentan las prometedoras cualidades asociadas a estas sales (estabilidad térmica en la mayoría de los casos, presión de vapor despreciable, capacidad de diseño, etc.), pero además al ser derivados de una biomolécula se aproximan al

verdadero concepto de disolvente “verde”, que no siempre se puede asociar al término LI, ya que muchos de ellos son poco biodegradables y altamente tóxicos.

Los LIs obtenidos a partir de aminoácidos por esterificación de ácido carboxílico se presentaron a la comunidad científica como estables y altamente biodegradables, proponiéndose para muchas aplicaciones que implican ambiente acuoso. En este trabajo se hizo un estudio de la estabilidad hidrolítica de estos LIs, en concreto se trabajó con dodecilsulfato de prolinio isobutil éster ($[iC_4Pro][DS]$), dodecilsulfato de prolinio 2-butil-octil éster ($[C_4C_8Pro][DS]$), y dodecilsulfato de prolinio 2-decil-tetradecil éster ($[C_{10}C_{14}Pro][DS]$). También se sintetizaron nuevos LIs surfactantes cambiando el catión dodecilsulfato por dodecilbencenosulfonato. Se demostró que, en todos los casos, el grupo éster incorporado en el catión sufre hidrólisis en presencia de agua, acelerada con la temperatura.

Para solucionar este problema, se propuso y diseñó una nueva familia de LIs derivados de aminoácidos, cambiando la esterificación del ácido carboxílico por su reducción a alcohol. Así, se combinó el catión prolinolilo ($[HOPro]$) con los aniones dodecilsulfato ($[DS]$) y dodecilbencenosulfonato ($[DBS]$). Se comprobó que esta nueva familia de LIs no presentaba problemas asociados a la hidrólisis del catión. Aún así, el primer LI $[HOPro][DS]$ presentó los problemas de los surfactantes clásicos con el anión $[DS]$: hidrólisis del anión con el tiempo y alta temperatura. Sin embargo, el LI $[HOPro][DBS]$ demostró ser completamente estable.

Los nuevos LIs fueron caracterizados térmicamente mediante la determinación de sus eventos térmicos (puntos de fusión y temperaturas de transición vítrea) utilizando calorimetría diferencial de barrido, y sus temperaturas de descomposición mediante análisis termogravimétrico. La capacidad de agregación de estos nuevos surfactantes se estudió mediante la determinación de la concentración micelar crítica (a partir de la medida de la tensión superficial) y diferentes propiedades derivadas de la misma. Se encontró que estos LIs son más efectivos para reducir la tensión superficial del agua que los surfactantes tradicionales correspondientes en forma de sales de sodio, siendo útiles para aplicaciones relacionadas con su buena capacidad de agregación.

Finalmente, y enfocando su aplicación a EOR, se estudió el comportamiento de fases, de manera visual, de los nuevos LIs surfactantes sintetizados ($[HOPro][DS]$ y $[HOPro][DBS]$) con salmuera

y *n*-octano. El primero resultó ser muy hidrofílico, pero el segundo dio lugar a un sistema Winsor III. En este tipo de sistemas, una fase intermedia donde el surfactante solubiliza cantidades proporcionales de agua e hidrocarburo, se encuentra en equilibrio con una fase acuosa y otra de *n*-octano prácticamente puras. Este es el comportamiento deseado en EOR puesto que está asociado a una drástica reducción de la tensión interfacial agua/crudo. En el caso de [HOPro][DBS], este comportamiento se encontró a 348.15 K y una concentración de sal del 8.5 % en peso. Sería por tanto un surfactante de gran utilidad para ser aplicado en las condiciones donde los surfactantes tradicionales fallan, altas temperaturas y salinidades. Se utilizó la correlación de Chung-Huh para estimar la tensión interfacial agua/crudo que se obtendría con esta formulación, y se obtuvo un valor de $\sim 3 \cdot 10^{-3}$ mN/m. Este bajo valor ultra-bajo implica que el surfactante sería capaz de reducir las fuerzas capilares que atrapan el crudo de petróleo en los poros de las rocas y facilitaría su extracción.

Los resultados de estas cuatro publicaciones, que constituyen el cuerpo de la tesis doctoral, se discuten de manera conjunta a continuación, estableciendo las principales conclusiones y trabajo futuro. La primera dificultad en el uso de LIs surfactantes para métodos de recuperación mejorada de petróleo, es encontrar sales con una longitud de cadena alquílica lo suficientemente larga como para conferirles un carácter tensioactivo y que, a su vez, sean miscibles en agua. Atendiendo a esto, se seleccionaron los dos LIs con cadenas alquílicas de 6 carbonos: [C₆mim][OAc] y [C₆C₁py][OTf]. Ninguno de los dos resultó ser surfactante. El segundo al ser un sólido de baja solubilidad en agua no parece adecuado para su aplicación en EOR. El primero, líquido miscible en agua, podría ser utilizado como co-surfactante. Se probó su uso (resultados no publicados) para mejorar la inyectabilidad de surfactantes tradicionales (IGEPAL CO-520 y Brij L4) que son inmiscibles en agua. Sin embargo, no se obtuvieron resultados prometedores. Se espera que estos dos primeros trabajos orienten a los investigadores hacia la consideración de los LIs como co-surfactantes en EOR o cualquier otra aplicación, porque sus posibilidades son tan ilimitadas como sus posibilidades de diseño.

Si el surfactante seleccionado para EOR es viscoelástico, se puede producir un efecto sinérgico puesto que se consigue la reducción de la tensión interfacial y simultáneamente el incremento de viscosidad de la fase acuosa. En esta línea, el LI [n₄C₄Pro][DS] es prometedor porque tiene un fuerte carácter viscoelástico con altos valores de los módulos

G' y G'' . Los siguientes estudios deben centrarse ahora en pozos y condiciones específicas. También podría usarse como gel agente reductor de la permeabilidad, pero en este caso la concentración necesaria de LI es elevada, lo que implica una importante limitación económica. Por otro lado, los problemas de hidrólisis que este LI sufre con el tiempo y la temperatura, tienen que ser considerados antes de su propuesta para cualquier aplicación.

El LI [HOPro][DBS] es líquido a temperatura ambiente y posee carácter “verde”, no sólo por su nula contaminación atmosférica (presión de vapor despreciable) sino por su catión derivado de un aminoácido. Es miscible en agua, estable térmica e hidrolíticamente, y ha permitido definir una formulación óptima, capaz de conseguir una tensión interfacial agua/crudo ultra-baja, a alta temperatura y concentración de sal. Este trabajo es el primero de la bibliografía en el que esto se consigue con un LI puro, sin necesidad de mezclas con otros surfactantes o LIs. Todo ello lo convierte en un surfactante prometedor para EOR. Los pasos inmediatos de la investigación son los ensayos en rocas reales, para analizar tanto su capacidad de extracción como la posible adsorción en la superficie de las rocas.

En general, se puede concluir que **los líquidos iónicos pueden usarse como productos químicos para el desarrollo de nuevas formulaciones útiles en EOR con surfactantes**. La mejora de los métodos actuales de recuperación de petróleo requiere aprovechar la capacidad de diseño de estas sales y sus casi infinitas posibilidades.

