ENVIRONMENTAL ASPECTS OF IONIC LIQUIDS IN ENHANCED OIL RECOVERY: AN OVERVIEW

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Abstract: Ionic liquids (IL), are reported to be new environmentally friendly solvents. Due to their unique properties and wide diversity, IL's can be used as surfactants to recover oil from mature fields. However, despite their promising performance, studies have revealed that IL are not environmentally friendly as claimed. In this paper, a brief review of the literature was conducted, including main fundamentals about the properties and application of IL in enhanced oil recovery (EOR); and their potential environmental effect. Finally, it may be concluded the main factor influencing the high toxicity of ILs is the hydrophobicity of the side chain. Therefore, further studies should be developed to design the sustainable LI for use in the EOR process.

Keywords: Ionic liquids; EOR; environmentally friendly; toxicity.

ASPECTOS AMBIENTAIS SOBRE O USO DE LÍQUIDOS IÔNICOS NA RECUPERAÇÃO AVANÇADA DE PETRÓLEO: UMA BREVE REVISÃO

Resumo: Líquidos iônicos (LI) são relatados como novos solventes ambientalmente corretos. Devido a suas propriedades únicas e grande diversidade, os LI podem ser utilizados como surfactantes para recuperar óleo de campos maduros. No entanto, apesar do desempenho promissor, os estudos revelaram que os LI não são ambientalmente corretos, como se afirma. Neste documento, foi realizado uma breve revisão da literatura, incluindo os principais fundamentos sobre as propriedades e a aplicação dos LI na recuperação avançada de petróleo (EOR); e seu potencial efeito ambiental. Concluímos que o principal fator que influencia a elevada toxicidade dos LI é a hidrofobicidade da cadeia lateral. Por conseguinte, mais estudos devem ser desenvolvidos para conceber LI sustentáveis para utilização no processo EOR.

Palavras-chave: líquidos iônicos, EOR, ambientalmente corretos, toxicidade.

1. INTRODUCTION

With the increasing global demand for energy, most oil producing companies are focusing on maximizing the oil recovery factor. In addition, the diminishing reserves are the main challenges faced by companies to produce the remaining oil from the matured oil field. Thus, enhanced oil recovery (EOR) technologies play an important role in increasing the efficiency of oil recovery. [1,2]

Among the various EOR techniques, chemical flooding is one of the most successful techniques, which includes polymer, alkaline and surfactant flooding, and combination of this compounds as alkaline-polymer flooding, and alkaline-polymer-surfactant flooding. Despite of all benefits for oil recovery factor, surfactant flooding has various disadvantages such as high toxicity, high cost and inability to perform in harsh environments.[3] Additionally, insoluble residues left by a surfactant or other chemical formulations can develop environmental impacts to reservoirs.[4] Recently, EOR have been using a new class of surfactant with possible sustainable design: Ionic Liquids (IL).[5]

Ionic liquid has gained attention as a potential alternative to the conventional surfactant as they are considered environmentally friendly, nontoxic, non-corrosive, in addition, they have a negligible vapor pressure, high thermal stability and are considered recyclable.[6,7]

Also, IL are organic salts having a melting point below 100 °C and they are often found as a liquid up to a moderate temperature.[3,6,8] However, many studies have discussed and described limitations of IL, namely the hazardous effects to the environment and biodegradability as well as some cautions on their use in both technological and EOR applications.[9]

From a sustainable perspective, Earle et al., (2006)[10] identified that some IL could be hazardous to the environmental, because their compounds are distillated at low pressure and without proper decomposition. Therefore, they found that the possibility of atmospheric contamination cannot be discarded, at least when IL are used at elevated temperatures.[10]

Despite the various doubts regarding environmental issues, several studies show the effectiveness of the use of IL in EOR process.[11–14] Nadwani *et al.,* (2017)[11] reported that $[C_{16}mim]Br$ IL is more effective in reducing the interfacial tension between the water/oil system than the conventional cationic surfactant cetyltrimethylammonium bromide (CTAB), therefore recovering more oil trapped in the porous media of the reservoir.

In this perspective, the synthesis and investigation of sustainable IL with EOR application have been of great relevancy for the development of research in this field. Therefore, the aim of this work was to analyze the main IL with respect to environmental aspect. Thus, this paper presents a brief review on the use of ionic liquid in EOR chemical flooding method and possible environmental impacts regarding the use of these compounds.

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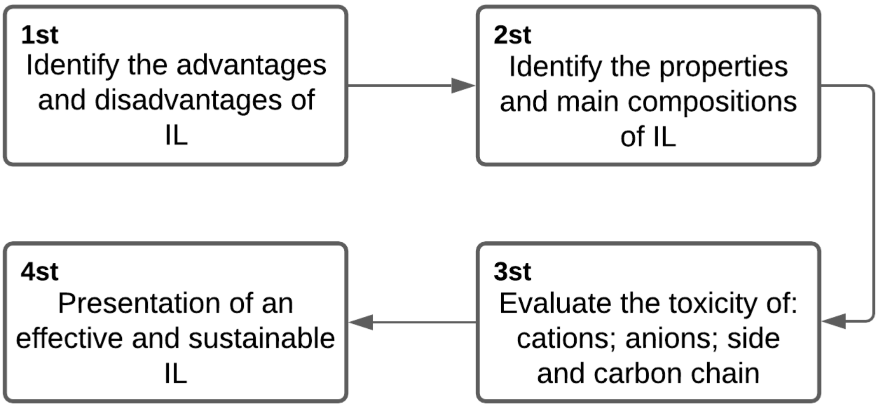
2. METHODOLOGY

First, we identify the main IL used in EOR application, their chemical properties, as well as the main cations and anions, and what advantages these compounds have when compared with commercial surfactants.

Then, we identify which properties can make IL toxic and non-biodegradable, such as cations, anions, and the side chain. Subsequently, we develop a proposed measure scale to make a possible the synthetization of sustainable and effective IL in EOR. Figure 1 shows a block diagram of the main steps of the research methodology.

Figure 1. Detailed description of the methodology adopted.



3. RESULTS AND DISCUSSION

3.1 Analysis of the IL properties

The environmental viability of IL must be made through understanding the principles of green chemistry. The green chemistry principles proposed by Anastas and Warner (1998)[15] presents a guideline of how chemicals interact with each other to build up a larger number of sustainable compounds. The fourth and tenth principles state the following strategies: *(i) chemical products should be designed to preserve efficacy of function while reducing toxicity*, (4th Principle of Green Chemistry[15]); and *(ii) Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products*, (10th Principle of Green Chemistry[15]).

In this perspective, the development of sustainable technology – that are part of green chemistry rules – has grown substantially in the past decade. One out of many chemical compounds that have been studied is a new class of organic solvents called IL. [7,16]

"IL" have the potential to improve both existing processes and those still in development in the most diverse fields of chemistry, as in the oil industry. In that branch, IL can be used to prevent shale inhibition, improve clay stabilization and drilling fluid properties, fracturing fluid composition, control wax and asphaltene deposition,

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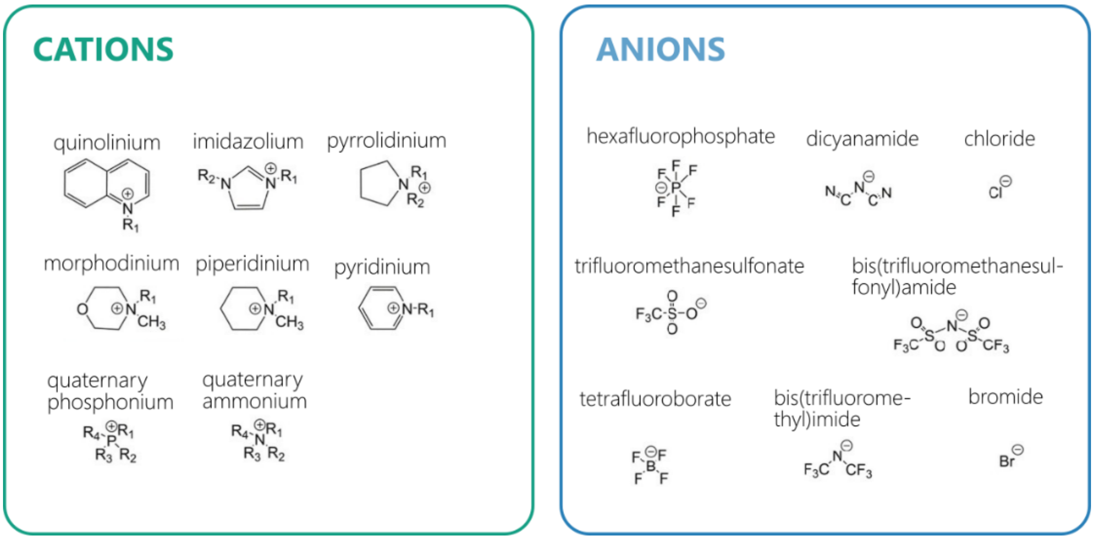
prevent gas hydrates increase additional oil recovery, and improve unconventional oil recovery.[13]

The advantage of IL over volatile organic solvents is negligible vapor pressure. In this way, it is not feasible for these products – as long as they have a high level of purity and stability – to emit volatile organic compounds to nature.[7,17] However, is this characteristic sufficient to consider them "green" or "sustainable" chemicals? Thus, it is necessary, primarily, to discuss and design the potential risks of these compounds when disposed in the environment, aiming to develop sustainable and efficient chemicals for the process to be applied.

IL (also referred to as molten salts) are organic salts formed by ions, in a liquid state at temperatures below 100 °C, a result of their chemical structure, which presents balanced ion-ion and symmetry interactions.[16] The low vapor pressure on these compounds is related to the arrangement of the ions: each ion is surrounded by symmetrical shell of the opposite load, minimizing electrostatic free energy. Furthermore, IL show high thermal stability, with decomposition temperatures around 300-500 °C.[6]

There are two classification categories of these solvents: aprotic ionic liquids (AIL) and protic ionic liquids (PIL). AIL are chemical capable of donating and receiving electrons, following Lewis's acid-base theory. From another aspect, according to Bronsted's acid-base theory, PIL are produced from proton transfer from acid to base.[18] Usually, an IL is composed of an organic cation, which may include one or more substituted alkyl chains [R = $[CH_3(CH_2)]_{nC}$ (nC (carbon number)= 8-20)]; and an organic or inorganic anion. As an illustration, one has alkyl imidazolium $[R^1R^2mim]^+$ or tetraalkylammonium $[NR_4]^+$, associated with tetrafluoroborate $(BF_4)^-$ or chlorine $(Cl)^-$ (Fig.2).

Figure 2. Main chemical structures of representative cations and anions used in ILs synthesis.



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The wide diversity of cation-anion combinations allows the properties of IL to be adjusted to adapt them to a specific application. This uniqueness, combined with the surface activity of these compounds, has presented IL as strong substitutes for surfactants used in the EOR, as current chemicals are less effective under high pressure, high temperature, and high salinity reservoir conditions.[13,19]

Surfactant flooding is one of the main EOR techniques to recover oil from mature fields. The goal of this technique is to minimize the interfacial tension (IFT) between oil and water, since the presence of the surfactant decreases the work required to increase the interfacial area.[19] This process results in reduced capillary forces present in the oil/water interface, increased oil mobility, and increased oil recovery factor.[1,14]

The increased oil recovery factor is due to the amphiphilic structure of the IL influences the adsorption of molecules of these compounds at the oil/water interface. This event enable the formation of a saturated interface and, consequently, reach a minimum IFT. [20,21] For this reason, interest in the application of these compounds in EOR has grown significantly in the last decade, but it should be noted that these compounds have limitations regarding their sustainable designer.

However, the limitations of IL to their toxicity and biodegradability when discarded in the environment are still issues to overcome.[16] Therefore, it is important to analyze how to synthesize more sustainable IL.

3.2 Environmental impact of IL's

As IL present low-pressure organic vapor solvents (negligible volatility) and almost nonflammability, they can be considered environmentally friendly because they do not contribute to air pollution by emission of pollutants. However, it is essential to be aware of the release of IL in the environment, through effluents and wastewater, since this practice can cause pollution of water bodies and soil, in view of the high solubility of these compounds.[16]

The toxicity of IL is a sensitive topic due to dependence on the chemical structure of these compounds. Thus, each component should be analyzed separately from the other components, what makes it difficult to thoroughly analyze the toxicity of IL. The IL toxicity depends on their chemical arrangement: the composition of the cation; the length of alkyl chain; the nature of the anion; and the combined influence of cation and anion.[17]

Imidazolium-based IL are the most widely studied IL structure, followed by pyridinium, phosphonium and ammonium.[22] Imidazolium cation and pyridinium showed strong adsorption in different soils and marine sediments. Furthermore, the addition of hydrophobic chains to these cations increases the geological adsorption in non-interlayer clay systems, resulting in unrestricted transport through soils/sediments and thus, might cause a danger of contamination of surface or ground waters.[23] Looking in an alternative perspective, authors have identified that IL with cholinium-based cation, amino acids and protics are elements that confer less toxicity to the compounds.[9]

In the vast majority of studies, the increase in the alkyl chain confers greater hydrophobicity to the compound, with increases the toxicity of IL in an effect called "side-chain effect". In addition, IL with short polar chain or specially functionalized side-chains (for example, containing ester and ether side-chains - reduced hydrophobicity)

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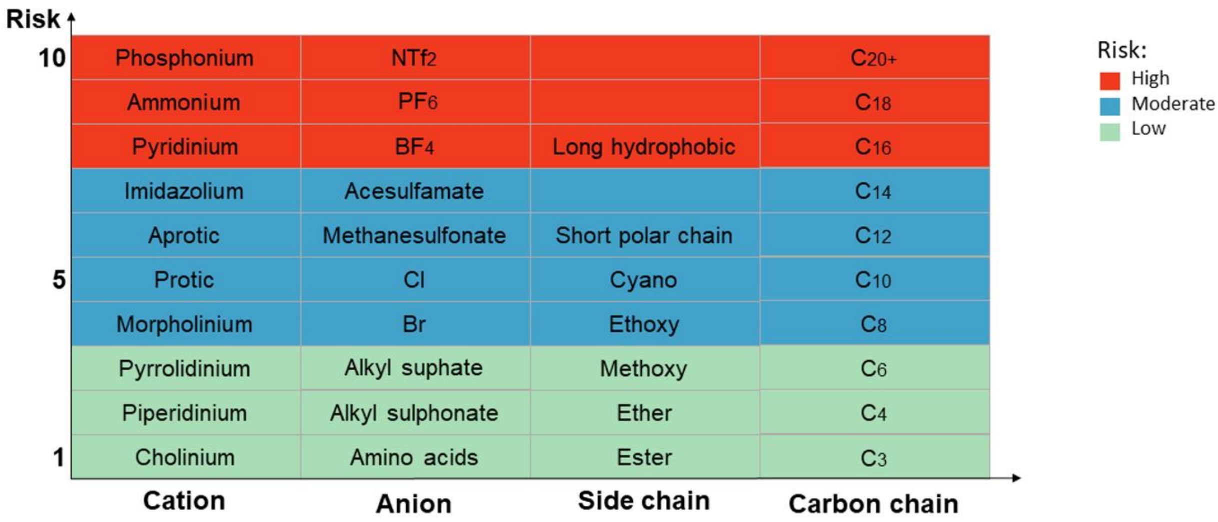
can exhibit low toxicities.[24] Jordan and Gathergood (2015)[25] reviewed approximately 300 IL and concluded that unbranched alkyl chains promote greater biodegradability; with the presence of hydrolysable groups, such as esters and groups that could be easily oxidized, namely alcohols and carboxylic acids.[25]

On the other hand, the effect of anion shows a minor contribution to the toxicity of IL. Kyung-Min et al., (2017)[26] showed that IL with the [NTf_2] anion exhibited significant dermal toxicity and their toxic effects were comparable to those of xylene.[26] It should also be noted that ionic liquids with BF_4 and PF_6 can release HF in the presence of water, and thus contaminate groundwater.[13] Therefore, from an eco-toxicity point of view, the use of fluorine in the IL anion structure should be avoided.

Figure 3 sets out some established guidelines for IL readily sustainable design. According to the current knowledge, it appears that the toxicity of ILs is much more affected by the structure of the cation than the anion whereby the alkyl chain length, which determines IL hydrophobicity, seems to be the main factor influencing its toxicity.[23] Thus, it is possible, that IL with 20-carbon side chain are highly toxic and those with 3- or 4-carbon chain have low toxicity.

Figure 3 Some guidelines on the toxicity and the potential to synthesize environmentally friendly of IL's.



Source: by authors

In view of the difficulty of assessing the toxicity of ILs, Figure 6 details separately the degree of toxicity of cations, anions, side chain and the number of carbon present hydrophobic chain. Therefore, through macro knowledge it is possible to synthesize IL with environmentally friendly character in order to introduce these compounds into EOR on a large scale.

4. CONCLUSION

Based on the understanding of the studies, experiments relate that the main contributors to the toxicity of IL are: the length and composition of the cation side chain

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(functional groups); the core of the cation; and the nature of the anion fraction. The main factor influencing the high toxicity of IL is the hydrophobicity of the side chain, thus the higher the number of carbons in the alkyl chain the more toxic the IL.

Therefore, this paper shows that the topic addressed needs studies that plan the design of sustainable and effective IL for use in EOR. Therefore, this paper suggests ways forward to advance this area of research.

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