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Perspectives of Ionic Liquids Applications for Clean Oilfield Technologies

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1. Introduction

Ionic liquids (ILs) are gaining wide recognition as potential environmental solvents due to their unique properties (Wasserscheid & Keim, 2004, Martínez-Palou, 2007, Martínez-Palou, 2010) and their applications in Organic Synthesis (Wasserscheid & Welton, 2008, Martínez-Palou, 2006), catalysis (Gu et al., 2009, Toma et al., 2009, Olivier-Bourbigou, 2010), biocatalysis (Muginova et al., 2010, Moniruzzaman et al., 2010), in separation (Han & Row 2010), extraction (Poole & Poole, 2010) and dissolution processes (Torimoto et al., 2010, Zakrzewska et al., 2010), nanomaterials synthesis (Li et al., 2008), polymerization reactions (Srivastava, et al., 2009, Lu et al., 2009) and electrochemistry (McFarlane et al. 2010, Ohno & Fukumoto, 2008). ILs are an excellent alternative to substitute volatile organic solvents in more environmental friendly technologies, also known as "green technologies" (Rogers & Seddon, 2002) since their very low vapor pressures, their thermal and chemical stability, their ability to act as catalysts, and their non-flammability and non-corrosive properties which decreases the risk of worker exposure and the loss of solvent to the atmosphere.

Petroleum industry is one of the most important industry in the world and in the last decades it has enter in a continuous process of modernization and transition for becoming to a more clean and "green industry" around the world. This industry present typical operational and old technological problems, like corrosion, emulsions formation (oil/water and water/oil), asphaltenes flocculation during oil production and processing, contamination of hydrocarbons feeds and other which need new and more efficient solutions (Speight, 2009).

For their versatility and properties, ILs have a wide range of potential applications for chemical industry and especially for petroleum industry, as have been demonstrate with the increased number of papers about the evaluation of ILs for applications in areas as improvement of petroleum properties for their exploration, exploitation and transportation, elimination of toxic substances from fuels (sulfurated, nitrogenated and aromatics compounds), develop of new "green" additives with application as corrosion inhibitors, demulsifier and desalting agents, and several applications of the ILs as catalysts and solvents for petrochemical processes. ILs have also been explored in membranes technologies for selective separation of gases, liquids fuels and contaminants, and in another alternative fuels technologies like biofuels and fuel cells.

In this chapter, some of the most important advances about the study of ILs for potential oilfield applications are reviewed.

2. Ionic Liquids. Generalities

2.1 Definition

An ionic liquid (IL) is a salt in the liquid state. In our contexts, the term has been restricted to salts whose melting point is below of 100 °C. To a difference of a molten salt characterized by high-melting, highly viscous and very corrosive medium, ILs are already liquid at low temperatures (< 100 °C) and have relatively low viscosity, with exceptional properties for application as solvents to substitute high toxic and volatile organic solvents (Wasserscheid & Keim, 2004).

ILs are formed with a large organic cations, that can be symmetric or assymetric one. The asymmetry lowers the lattice energy, and hence the melting point, of the resulting ionic medium. Invariably the cation is organic (heterocyclic or acyclic) and the anion can be a halogen ("first generation ILs"), inorganic (i.e. $[BF_4]^-$, $[PF_6]^-$, $[SbF_6]^-$, $[AlCl_4]^-$, $[FeCl_4]^-$, $[AuCl_4]^-$, $[InCl_4]^-$. $[NO_3]^-$, $[NO_2]^-$, $[SO_4]^-$, $[SCN]^-$) or organic (i.e. $[AcO]^-$, $[N(OTf)_2]$, $[CF_3CO_2]^-$, $[CF_3SO_3]^-$, $[PhCOO]^-$, $[C(CN)_2]^-$, $[RSO_4]^-$ $[OTs]^-$) . In some cases, even the anions are relatively large and play a role in lowering the melting point. The composition and properties of the ILs depend on the cation and anion combinations. Some typical structures for the cation (i.e. 1, imidazolium, 2, pyridinium, 3, isoquinolonium, 4, ammonium, 5, phosphonium, 6, sulfonium)-type for ILs are showed in Figure 1. Where, R, R', R''and R'' are essentially alkyl and sometime aryl, and alkyl chains.
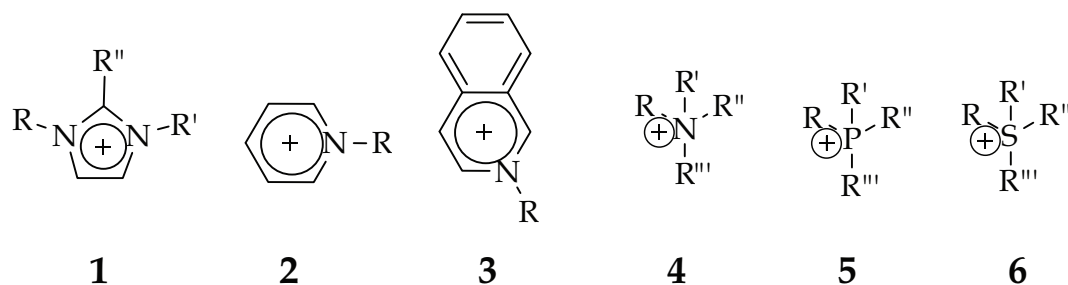

Fig. 1. Typical structures for ILs cations

2.2 Ionic Liquids synthesis

The first step in the synthesis of ILs is the quaternization of a nitrogenated heterocycle, like imidazole, pyridine, isoquinoline or tertiary amine or phosphane for example, to form the cation. Generally, the quaternization is carried out by alkylation reaction using an alkyl halide. The IL obtained after this step is known as "first generation ILs".

In the second step, the desire the anion could be introduced by anionic exchange or metathesis reaction using the corresponding acid (HY) or metallic salt (MeY).

The reaction time in each step depend on the reactivity of the involved reagents, but in general the first step is carried out in several hours by conventional heating (Δ), but the reaction time can be reduced considerably using non-conventional energy sources as ultrasound ( )))) or microwave irradiation (MW) (Martínez-Palou, 2010).

A general scheme for the synthesis of imidazolium type ILs from imidazole is presented in Figure 2.
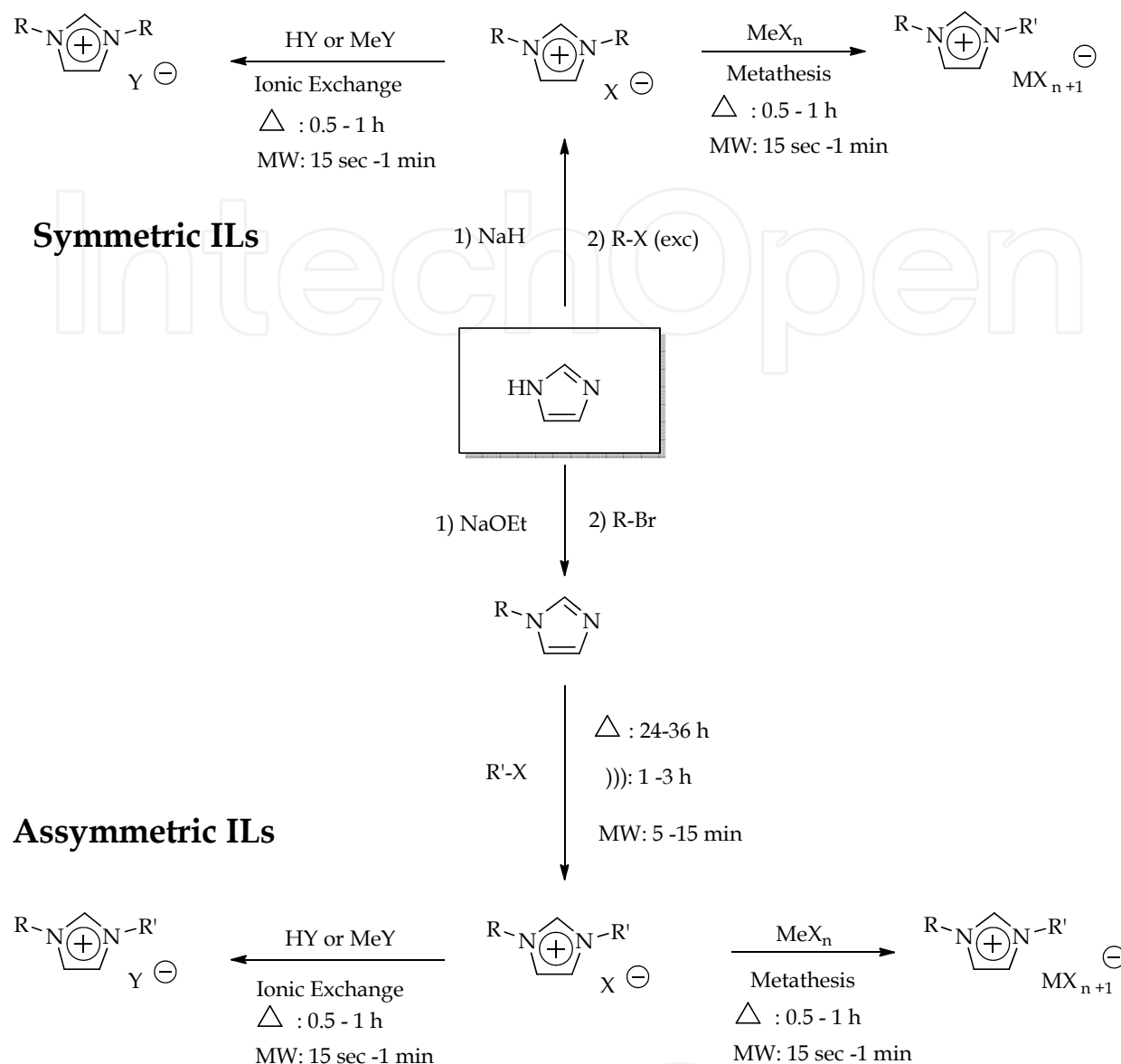
Fig. 2. General scheme of synthesis of imidazolium type ILs

2.3 Physicochemical properties

The physical and chemical properties of ILs can be fine-tuned by changing the structure of the cations and anions. The most important properties of ILs that are converted them in very attractive compounds are the following:

- **Extremely low vapor pressure.** To a difference of the classical organic solvents, ILs are known to have a negligible vapor pressure below their decomposition temperature. This is the main reason because ILs are considered environmental friendly solvents.
- **Thermal Stability:** The thermal stability of ILs is limited by the strength of their heteroatom-carbon and their heteroatom-hydrogen bonds, respectively. The nature of the ILs, containing organic cations, restricts upper stability temperatures, pyrolysis generally occurs between 350-450 °C. In most cases, decomposition occurs with complete mass loss and volatilization of the component fragments. The onset of thermal

decomposition calculated from fast thermogravimetric analysis (TGA) indicates high thermal stability for many ILs, generally higher than 350 °C.

- **Solubility:** ILs can be tailored to be immiscible with water or with certain organic solvents. Many ILs possess the ability to dissolve a wide range of inorganic and organic compounds. This is important for dissolving combinations of reagents into the same phase. Hydrophilicity/hydrophobicity properties depend significantly to the structure of the cations and anions.
- **Electrochemical Stability**. ILs often have wide electrochemical potential windows, they have reasonably good electrical conductivity. The electrochemical window of an IL is influenced by the stability of the cation against electrochemical reduction-processes and the stability of the anion against oxidation-processes. ILs exhibit broad range of conductivities from 0.1 to 20 mS cm^{-1}. In general the higher conductivities are found for imidazolium-based ILs.
- **Non-flammability**. ILs are safe for hanging, because ILs are non-volatile and consequently non-flammable at ambient and higher temperatures, however ILs can be combustibles.
- **Catalytic properties**. The catalytic properties in organic and inorganic synthesis have been widely described (Olivier-Bourbigou et al., 2010) and many efforts have been carried out toward understanding the origin of effects of ILs on catalysis (Lee et al., 2010). In this chapter, some examples with potential application to oilfield will be discussed. In addition, biocatalytic transformations in ILs have been performed using a range of different enzymes and some whole cell preparations, mainly in biphasic aqueous systems using hydrophobic dialkylimidazolium ILs.

3. Ionic liquids as extractants

Clean fuels processing and production has become an important subject of environmental research area worldwide. Dramatic changes occurred in many countries concerning the regulations for fuel qualities in the past decade and the US Environmental Protection Agency (EPA) has applied new regulations, and government regulations in many countries call for the production and use of more environmentally friendly transportation fuels (Rogers & Seddon, 2002).

Compared to conventional volatile organic solvents, the use of ILs for extraction has a number of advantages determined by their properties. ILs are miscible with substances having very wide range of polarities and can simultaneously dissolve organic and inorganic substances (Huddleston et al., 1998, Zhao et al., 2005).

These features of ILs offer numerous opportunities for modification of existing and for the development of new extraction processes. In some cases, such processes would be impossible with conventional solvents because of their limited liquid range or miscibility and low boiling point and toxicities.

3.1 Desulfurization of light oil using ionic liquids

Recently, a high emphasis has been placed on the deep desulphurization of oil products because hydrocarbon combustion releases SOx; which are responsible of acid rain, air contamination and ozone consumption. Environmental regulations have been modified to allow that lower levels of sulfured compounds to be ejected to the atmosphere. Industrially,

the removal of organosulfur and organonitrogen compounds in fuel oils is being carried out by means of a simultaneous hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) process at around 350 °C using catalysts based on CoMo or NiMo, which involves the C-S and C-N bond cleavage to produce H_2S and NH_3, respectively (Zaczepinski, 1996, Kabe et al., 1999; Ferrari et al., 2001; Caeiro, et al., 2007).

Deep desulfurization of diesel fuels is particularly challenging due to the difficulty of reduce aromatic sulfur compounds, particularly 4,6-dialkyldibenzothiophenes, using conventional hydrodesulfurization processes (HDS). The HDS process is normally only effective for removing organosulfur compounds of aliphatic and alicyclic types. The aromatic sulfur molecules including thiophenes, dibenzothiophenes (DBT), and their alkylated derivatives are very difficult to convert to H_2S through HDS.

New processes and nonhydrodesulfurization technologies for production ultra-low sulfur clean oils have been studied to remove sulfur from the different cuts in the refinery industry (Babich, & Moulijin, 2003, Song, 2003, Brunet et al., 2005, Ito & Veen, 2006, Ann et al., 2007, Stanislaus et al., 2010).

One alternative called extractive desulfurization (EDS) seems very attractive for this purpose because of its low energy cost, the elimination of hydrogen usage, the retaining of the chemical structures of fuels and no requirements of special equipment.

In this sense, the first published paper described the extractive properties of sulfur-containing compounds (SCs) by liquid-liquid extraction employing ILs was described by Bosmann and coworkers (Bosmann et al., 2001). In this work, a serie of ILs with properties for removing SCs from a model solution (500 ppm of dibenzothiophene in *n*-dodecane) were described, however, deep desulfurization (higher than 90% of sulfur removed) were obtained only when Lewis acid ILs containing tetracloroaluminates, particularly [BMIM]Cl/AlCl$_3$. (0.35/0.65).

Anion effect was also evaluated employing the same cation ([BMIM]) working at the same experimental conditions. The alkylsulfate anions shows the best extractive properties between the neutral ILs. On the other hand, the effect of the *N*-alkyl chain also play an important role in the performance of these compounds, increasing the extractive properties from *n*-C2 to *n*-C8.

Finally the authors tested the efficiency of the best three ILs prototypes in a multistage desulfurization experiment using a real predesulfurized diesel oil sample (without additives, sulfur content: 375 ppm) at 60 °C with mass ratio oil/IL = 5/1 and 15 minutes of reaction time. Lewis acid ILs showed the best performance after four extraction steps (Table 1).

Extraction stage	[BMIM]Cl/AlCl$_3$	[HN(C_6H_{11})Et$_2$]MeSO$_3$/ [HNBu$_3$] MeSO$_3$ (1/1)	[BMIM]Octylsulfate
1	41.3	12.0	14.7
2	57.3	20.0	25.3
3	65.3	28.0	30.6
4	80.0	36.0	37.3

Table 1. Percentage of total sulfur remotion in multistage desulfurization of predesulfurized diesel sample with ILs.

The same authors studied newly the desulfurization by extraction with similar Lewis acids and halogen-free ILs. In this paper, the influence of *S*-especies and *S*-concentration on extraction with halogen-free ILs, cross solubility of oil in the IL and vice versa, extraction of *N*-compounds, continuous extraction in a mixer-settler system, possibilities of regeneration of S-loaded ILs and the possible scenarios for the integration of this technology in the existing refinery network were studied. The results show the selective extraction properties of ILs, especially with regard to those *S*-compounds, which are hard to remove by HDS, e. g. dibenzothiophene derivatives present in middle distillates like diesel oil. The application of mild process conditions (ambient pressure and temperature) and the fact that no hydrogen is needed are additional advantages compared to HDS. Very promising ILs are [BMIM][OcSO$_4$] and [EMIM][EtSO$_4$], as they are halogen-free and available from relatively cheap starting materials (Eβer et al., 2004).

In 2004, Bowing and Jess studied the kinetic and continuous reactor design aspects for scaled synthesis of [EMIM]EtSO$_4$, one of the most promising halogen-free ILs for sulfur extraction. Compared to batch reactors, the hold-up is by a factor of 1000 lower, which is particularly advantageous for toxic reactants (here diethyl sulfate). The results are beyond synthesis of [EMIM][EtSO$_4$] instructive for other ILs, and probably also for other exothermic reactions with a temperature limit (Bowing and Jess, 2007).

Many other papers have been published about the desulfurization of oils by liquid-liquid extraction using ILs that is presented in the Table 2.

Reference	ILs evaluated	Conditions of desulfurization	Observations
(Zhang & Zhang, 2002)	[EMIM]BF$_4$, [BMIM]BF$_4$, [EMIM]PF$_6$	Ratio IL/gasoline, 1/2, 15 minutes, rt	[EMIM]BF$_4$: 17% of sulfur removal for low sulfur gasoline (240 ppm) and 11% for high sulfur gasoline (820 ppm). Using [BMIM]PF$_6$: 29% and 13% of sulfur removal were obtained for the same samples.
(Zhang et al., 2004)	[EMIM]BF$_4$, [BMIM]PF$_6$, [BMIM]BF$_4$ Me$_3$NHCl/AlCl$_3$	Ratio IL/gasoline, 1/5, 30 minutes, rt	Sulfur removal of 11-14% for [BMIM]BF$_4$, 15% for Me$_3$NHCl /AlCl$_3$ (2/1) and 20% for Me$_3$NHCl/AlCl$_3$ (1.5/1)
(Huang et al., 2004)	[BMIM]CuCl (1:2)	Ratio IL/gasoline, 1/5, 30 minutes, rt	23% of sulfur removal for model oil and 16-37% for gasolines with different sulfur contents (196-950 ppm). The extraction increase when sulfur content decrease.
(Nie et al., 2006)	[MMIM][DMP] [EMIM][DEP] [BMIM][DBP] DMP: dimethyl phosphate; DEP: dimethylphosph ate and DBP: dibutyl phosphate	K$_N$ was determined by 1) A known weight IL and gasoline were mixed. 2) A known amount of S-concentrated IL was added and stirred for 15 min at rt. 3) 10 min for phase splitting and settling.	K$_N$ for each phosphoric IL and S-component (namely, 3-MT, BT, and DBT) is virtually a constant irrespective of the S-content in gasoline. K$_N$ was between 0.94-1.81.

Reference	ILs evaluated	Conditions of desulfurization	Observations
(Alonso et al., 2007)	[C$_8$MIM][BF$_4$]	Mass ratio IL:model gasoline (MD) (1:1). MD: 28 wt% of n-hexane, 28 wt cyclohexane, 28 wt% i-octane, 10 wt% toluene, 3 wt% thiophene and 3 wt% DBT, stirring 2 h at 298 K, 4 h settle down and analyzed by GC.	Thiophene distribution ratio (β), and solvent selectivity (S) were determined to calculated solvent extraction capacity for ternary systems involved in desulfurization.
(Nie et al., 2007)	[MMIM][DMP] [EMIM][DEP] [BMIM][DBP]	1) 5996 ppm S content by dissolving DBT in MIM was prepared. 2) A known weight of S-free solvent and fuel oil is mixed under vigorous stirring. 3) A known amount of S-concentrated solvent was added to the above biphasic mixture, magnetically stirred for 15 min at rt.	K_N values was measured between straight-run fuel oil and *N*-ethylimidazole, *N*-methylimidazole and its mixture with a dialkylphosphate IL, viz. [EMIM][DEP] or [BMIM][DBP]. The results indicate that both EIM and MIM have excellent EDS performance with K_N above 3.1 for dibenzothiophene.
(Mochizuki et al., 2008)	[MMIM]MeSO$_4$ [EMIM]EtSO$_4$ [EMM]MeSO$_4$ [EEIM]EtSO$_4$ [BMIM]MeSO$_4$ [BEIM]EtSO$_4$	The model fuel was prepared from DBT and *n*-dodecane. The ILs were mixed with the model fuel in a certain ratio and stirred for a certain time interval at rt. A GC-MS was used to determine S-content.	When the mass ratio of the IL/model fuel was 1/1, DBT was successfully extracted using [EMIM] MeSO$_4$ and [MMIM]MeSO$_4$ with yields of 40 and 70%, respectively, after one round of extraction.
(Schmidt, 2008)	[BMIM]AlCl$_4$	The fuels were dried prior to use with activated 13X molecular sieve. Each fuel was then added to freshly prepared IL in an initial volume ratio of 1/6 (10 mL of IL/60 mL of fuel). The two-phase mixture was stirred for 5 min at rt.	High level of S and N remotion (90-95%) were obtained after dried the fuel with molecular sieves. In spite of water was first removed, in all cases, the dark green IL turned black immediately when it contacted the fuels, indicating IL decomposition of the Lewis acid ILs.
(Gao, et al., 2008)	[BPy][BF$_4$] [HPy][BF$_4$] [OPy][BF$_4$]	The mass ratios of ILs to model diesel or diesel fuel were 1:1 or 1:3. The ILs were added to the model	The extractive performance using pyridinium-based ILs followed the order [BPy][BF$_4$] < [HPy][BF$_4$] < [OPy][BF$_4$], and selectivity of

Reference	ILs evaluated	Conditions of desulfurization	Observations
	B: Butyl, H: hexyl and O: octyl.	diesel or diesel fuel, magnetically stirred for 15 min at rt to reach thermodynamic equilibrium, and then allowed to settle for 5 min to obtain phase splitting and settling.	SCs followed the order thiophene < benzothiophene < dibenzothiophene. Sulfur extraction was only 46.7% and 36.7% after three time extractions with [OPy][BF$_4$] and [HPy][BF$_4$], respectively.
(Ko et al., 2008)	[BDMIm]Cl/FeCl$_3$ [HDMIm]Cl/FeCl$_3$ [HMIm]Cl/FeCl$_3$ [HHIm]Cl/FeCl$_3$	The extraction was conducted at rt with the model oil containing 5000 ppm of DBT and 20000 ppm of *n*-octane as an internal standard in *n*-heptane. Weight ratio of model oil/IL 1/5 with molar ratio of FeCl$_3$/[BMIm]Cl of 1, 2 and 5. Diesel oil with 1180 ppm of S was also used.	[BMIm]Cl/FeCl$_3$ and[BDMIm]Cl/FeCl$_3$ in ratio higher than 2 (Lewis acidic ILs) shows quantitative extraction of SCs in model and real oil.
(Jiang et al., 2008)	[EMIM][DMP] [EEIM][DEP] [BEIM][DBP]	A straight-run gasoline was used. Before experiment, a concentrated IL solution with known S-content in mg(S) kg(IL) was prepared using gravimetric method by dissolving a definite amount of 3-MT, BT or DBT in a known quantities of IL, which was used as S-source in the following extraction experiments. K$_N$ was calculated.	For each S-component studied, the K$_N$ between IL and gasoline followed the order of [BEIM][DBP] > [EEIM][DEP] > [EMIM][DMP], and for a specified IL, the sulfur partition coefficient always followed the order of DBT > BT > 3-MT. The K$_N$ was significantly lower that that obtained with Lewis acidic IL containing AlCl$_3$. A study for recovering of used ILs was made.
(Liu et al., 2008)	[BMIM][BF$_4$ [BMIM][PF$_6$ [BSAMIM]HSO$_4$ [BSAPy]HSO$_4$ [BSAEt$_3$N]HSO$_4$ [BSAMIM]PTSA [BSAMIM]PTS PTSA: *p*-toluene sulfonic acid; PTS: *p*-toluene-sulfonate; BSA:	Extraction experiments were carried out at 60°C , mass ratio model oil/IL 4/1; extraction time 15 min; initial sulfur content, 500 ppmw. Effect of the extraction time, ratio gasoline/IL and regeneration of Sulfur-Loaded ILs was also studied.	1-(4-sulfonic acid) butyl-3-methyl-imidazolium hydrogen sulphate (52%) and 1-(4-sulfonic acid) butyl-3-methyl-imidazolium *p*-toluene-sulfonate (50%) were the best extractants.

Reference	ILs evaluated	Conditions of desulfurization	Observations
	4-butilsulfonic acid		
(Gao, et al., 2009)	3-MePy-based ILs	Experiments were conducted in a 50 mL flask. The mass ratios of ILs to model diesel or diesel fuel were 1:1 or 1:3. The ILs were added to the model diesel or diesel fuel, magnetically stirred for 15 min at room temperature to reach thermodynamic equilibrium, and then allowed to settle for 5 min to obtain phase splitting and settling.	The extractive performance followed the order of [C8MPy][BF$_4$] > [C6MPy][BF$_4$] > [C4MPy][BF$_4$]). For real diesel (97 ppm), 60 % of sulfur removed was obtained after 3 steps of extraction at ratio 1:1 with [C8MPy][BF$_4$].
(Gao, et al., 2009)	[BMIM]FeCl$_4$	The mass ratios of ILs to model diesel or diesel fuel were 1:3. The ILs were added into model diesel or diesel fuel, magnetically stirred for 15 min at room temperature to reach thermodynamic equilibrium, and then laid aside for 5 min for phase splitting and settling.	40% of sulfur was removed after three extraction at 1:1 ratio at rt.

Table 2. Papers describing desulfurization of oils by liquid-liquid extraction using ILs.

Theoretical studies of desulfurization by ILs have also been carried out. Zhou, Mao and Zhang employing ab initio calculations using thiophene as model sulfur-containing compound and two ILs, [BMIM][PF$_6$] and [BMIM][BF$_4$], according with the experimental results obtained by the same research group (Zhang and Zhang, 2002, Zhang et al., 2004, Su, et al., 2004).

The results showed that the interactions of thiophene with the anion and cation of the ILs mainly depends on electrostatic attractions. The absorption capacity of thiophene in the ILs is strongly dependent on the structure and property of the anion and the compactness between the cation and the anion of the ILs. For [BMIM][PF$_6$], due to the strong electron donation of phosphor atom to fluorine atoms, the fluorine atoms in PF$_6^-$ possess a relatively high negative charge and PF$_6^-$ can also provide more native charged fluorine atoms to thiophene molecules compared with the BF$_4^-$. Moreover, the compactness degree of [BMIM]PF$_6$ is lower than that of [BMIM]BF$_4$, which allows a facile restructuring of the IL in the process of thiophene dissolution (Zhou, et al., 2008).

Holbrey et al. studied the influence of structural aspects of the ILs in their performance as extractant of SCs. With varying classes (imidazolium, pyridinium, and pyrrolidinium) and a

range of anion types using liquid-liquid partition studies and QSAR (quantitative structure-activity relationship) analysis. The partition ratio of dibenzothiophene to the ILs showed a clear variation with cation class (dimethylpyridinium > methylpyridinium > pyridinium approximate to imidazolium approximate to pyrrolidinium), with much less significant variation with anion type. Polyaromatic quinolinium-based ILs showed even greater extraction potential, but were compromised by higher melting points (Holbrey et al., 2008).

Very recently, a screening of ILs for the extraction of SCs with ILs employing for the first time a real sample of natural gasoline (highly volatile liquid recovered from natural gas and whose vapor pressure is between those of condensates and liquefied natural gas) was published. Desulfurizations with ILs have been focused on gasoline and diesel coming from FCC units.

In this study, the effect of the molecular structure of 75 ILs on the desulfurization efficiency of natural gasoline with high sulfur content was evaluated. Analysis indicated that anion played a more important role than cation on the desulphurization process. ILs based on halogen-ferrates and halogen-aluminates displayed the highest efficiency in sulfur removal, this becomes highly improved when there is an excess of metallic salt (Lewis acid ILs). Additionally, a method to recovery, regeneration and reuse of the water sensitive tetraclhoroferrate ILs simple method to recover of the precursor halogenated IL was developed. A theory for predicting the ability of metallic ILs to remove SCs from NG, based on the ratio of the ionic charge to the atomic radius, is proposed.

In contrast to the results obtained by Holbrey et al., this study showed that under most drastic experimental conditions of evaluation (real system containing many hydrocarbons and more that 15 SCs. The extracting properties of an IL containing a NTf_2^- anion was very poor, yet any ILs containing an organic anion displayed good performance as sulfur removal. Only for Lewis acid ILs containing an anion with Fe, Al or Mo, extractions higher than 90% of SC were obtained. In these cases, the anion played the most important role on the IL efficiency (Likhanova et al., 2010). For this work, a Density Functional Theory study of the interaction between the most abundant SC in the studied sample of NG (ethanothiol) and Fe-containing ILs was studied.

The excellent performance of $[BMIM][FeCl_4]$ to remove sulfur compounds from natural gasoline when exists an excess of $FeCl_3$ was explain because the mixture contains $Fe_2Cl_7^-$ anions, whose Fe-Cl-Fe bonds are larger and less strength than those in Fe-Cl of $FeCl_4^-$ anions, being the former bonds actives for ethanethiol chemisorption. Molecular orbitals and atomic charges revealed the high desulfurization performance could be due to a donation-backdonation Dewar-Chatt-Duncanson-like model mechanism among sulfur of ethanethiol molecules and the metallic centers of $Fe_2Cl_7^-$ anions, and this mechanism is promoted because of the symmetry relationship among molecular orbital of ethanethiol HOMO and the atomic d_{xy}-type orbital on Fe sites in $Fe_2Cl_7^-$ LUMO (Martínez-Magadán et al., 2010).

3.2 Oxidative desulfurization of fuels using ionic liquids

The oxidative desulfurization (ODS) is another alternative of fuel desulfurization by liquid-liquid extraction, widely studied in the last years. This procedure consist in the oxidation of SCs to sulfoxides and sulfones or SCs are extracted from fuels and then oxidized in the extractant with the object of increasing their polarity and to make the liquid-liquid

extraction more efficient to remove SCs. Due to the short reaction time at ambient conditions, high efficiency, and selectivity, ODS combined with extraction, process known as is considered to be one of the most promising alternative processes to HDS for desulfurization of fuel. The oxidation process can be carried out without or with catalyst. In some case the ILs act as solvent for extraction but also as catalyst. One of its catalytic roles is to decompose hydrogen peroxide to form hydroxyl radicals.

The ODS system is more complicated process that the extraction of SCs in one step without oxidation, however with the former the efficiency of extraction generally increase considerably with the same IL at the same ratio, especially for water stable ILs.

Different ODS processes have used different oxidants such as molecular oxygen (Lu et al., 2007), H_2O_2 in combination with polyoxometalate (Gao et al., 2006, Huang et al., 2007, Al-Shahrani et al. 2007), and acetic acid (Liu et al., 2009), ozone (Zaykina et al., 2004) and *tert*-butylhydroperoxide (Ishihara et al., 2005).

The extraction of oxidized SCs can be carried out using conventional volatile and toxic organic solvents, or using a combination of catalytic oxidation and extraction with ILs is regarded to the "green desulfurization system".

Lo, Yang & Wei (Lo et al., 2003) reported in 2003 the first procedure of ODS using ILs as extractant. In this paper tetradecane doped with DBT was used as model light oil for the investigation of sulfur removal. The ILs [BMIM]PF$_6$ and [BMIM]BF$_4$, which are immiscible with light oils, were selected as solvents for the liquid-liquid extraction systems. DBT was extracted from the model light oils and oxidized in the ionic-liquid phase. The desulfurization system (H_2O_2-acetic acid/[BMIM]PF$_6$). The oxidation of dibenzothiophene in [BMIM]PF$_6$ resulted in a high oxidation rate and the desulfuration process was more efficient than those using the same ILs as sulfur extractant without previous oxidation (Figure 3).

In a one-pot operation, the SCs in the light oils were extracted into ILs and then S-oxidized (H_2O_2–AcOH) to form the corresponding sulfones at 70 °C. The sulfur content of unoxidized light oil was 7370 and 7480 ppm in the presence of [BMIM]PF$_6$ and [BMIM]BF$_4$, respectively; after 10 h of oxidation and extraction and ratio IL:hydrocarbon of 1:1. The sulfur content was reduced to 1300 and 3640 ppm, respectively. Thus, for a combination of oxidation and extraction with ILs, the use of [BMIM]BF$_4$ and [BMIM]PF$_6$ increased the desulfurization yields from 7 to 55% and 8 to 84%, respectively.
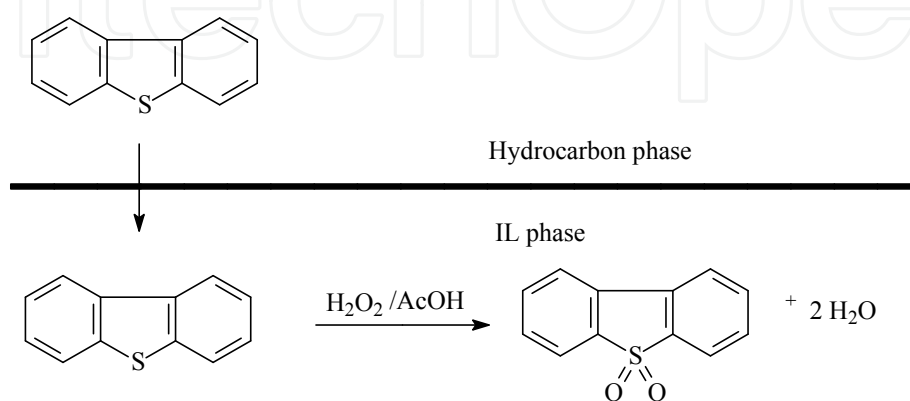

Fig. 3. ODS process using ILs as extractants.

When Brønsted acidic ILs 1-hexyl-3-methylimidazolium tetrafluoroborate [HMIM]BF$_4$ (Lu et al., 2007) and *N*-methyl-pyrrolidonium tetrafluoroborate [HNMP]BF$_4$ (Zhao et al., 2007) were used for desulfurization in the presence of H$_2$O$_2$, sulfur compounds can be deeply removed due to formation of hydroxyl radicals. For [HMIM]BF$_4$ the DBT remotion was 93% when a mixture of 3.2 mL of model oil and 5.0 mL of the IL were stirring at 90 °C during 6 h. In the case of [HNMP]BF$_4$ the efficiency of sulfur extraction was 99.4% for fuel diesel (total sulfur: 3240 ppm) at ratio of 1:1 and 2 h of reaction time at 60 °C. The IL was recycled 7 times without a significant decrease in desulfurization.

Some other published papers describing ODS procedures employing ILs are summarized in Table 3.

Reference	IL/catalyst/oxidizing agent	Conditions of desulfurization	Observations
(Huang et al., 2007)	Octadecyl-(STAB), cetyl-(CTAB), and tetradecyl-(TTAB), and dodecyl-(DTAB)/Phospho-tungstic acid (TPA)/ 30% H$_2$O$_2$.	DBT (500 ppm) in alkane. A certain amount of STAB and 0.06 g of TPA were added under vigorous stirring. 1 mL of 30% H$_2$O$_2$ was dropped in and the oxidation reaction was started. Concentrations of the model sulfur compound in alkane were analyzed by HP-GC.	A conceptual model was established in the DBT oxidation process based on the interaction between TPA and STAB. It is suggested that the mass transfer of DBT from the organic media toward the interface, rather than the oxidized TPA phase transfer step, may be rate limiting.
(Zhu et al., 2007)	[BMIM]BF$_4$ or [OMIM]BF$_4$ or [BMIM]PF$_6$ or [OMIM]PF$_6$/ H$_2$O$_2$/ WO(O$_2$)$_2$.Phen.H$_2$O	Model oil was prepared by dissolving DBT in *n*-octane to give solutions with a sulfur content 1000 ppm, (complex I) [WO(O$_2$)$_2$.Phen.H$_2$O], (complex II) [MoO(O$_2$)$_2$.Phen]. The reaction conditions were as follows: T = 70 °C, t = 3 h, model oil = 5 mL, IL = 2 mL, [n(DBT)/n(catalyst) = 25], [n(H$_2$O$_2$)/n(DBT) = 10].	The ODS with 30 wt % H$_2$O$_2$ in IL, model oil was 30.0-63.0%. While H$_2$O$_2$ and catalyst were introduced together, the removal of sulfur increased sharply. In the case of the system containing H$_2$O$_2$, WO(O$_2$)$_2$. Phen.H$_2$O and [BMIM]BF$_4$, extraction and catalytic oxidation increased the sulfur removal to 98.6%. However, the ODS for WO(O$_2$)$_2$.Phen.H$_2$O/H$_2$O$_2$ was only 50.3% of sulfur removal in the absence of IL.
(Chan et al, 2008)	[BMIM]PF$_6$/K$_2$O-AcOH or [BMIM]PF$_6$/H$_2$O$_2$-AcOH. K$_2$O is a superoxide.	Experiments were carried out using, model gasoline, Diesel and fuel oil. IL was employed as PTC in ratio hydrocarbon/IL (2:1) solutions, once prepared, was continuously stirred with a	Using potassium superoxide as oxidant very similar desulfurization efficiencies in both model compounds and real diesel samples was achieved, with a significantly lower sulfur/oxidant ratio. In

Reference	IL/catalyst/oxidizing agent	Conditions of desulfurization	Observations
		magnetic stirrer in a 70 °C water bath and the oil and acid/IL phases were separated by a centrifuge. The oil phase was mixed with alumina powder for sulfone adsorption, and the sulfur content in the oil phase was measured.	comparison with H_2O_2 potassium superoxide is safe and stable even in high purity. Less mass and less volume is required when using potassium superoxide as an oxidant, thus shipping, storage requirement, and volume of the reactor can be reduced significantly.
Cheng & Yen, 2008)	[BMIM]$MeSO_4$/H_2O_2-trifluoroacetic acid	5 g of 500 ppm of model compounds of sulfides in mineral oil or n-dodecane is mixed with 5 g of 30% H_2O_2 and 1.5 g of 20% trifluoroacetic acid and 0.3 g of tetraoctylammonium fluoride is introduced. The total ILs, [BMIM]$MeSO_4$, are 5 g hydrocarbon/IL (1:1) The mixture was heated to 50 °C and under ultrasound for 10 min with subsequent stirring for 170 min.	In this work ultrasound-assisted oxidative desulfurization (UAOD) was employed to accelerate the oxidation process. The newly UAOD process was also used for desulfurization of Navy diesel (F-76) with a sulfur concentration of 4220 ppm. The overall sulfur renoval was 100%.
(He et al., 2008)	[BMIM]BF_4/ Three peroxophosphomolybdates $Q_3\{PO_4[MoO(O_2)_2]\}$/H_2O_2 where Q: $[(C_4H_9)_4N]^+$, $[C_{14}H_{29}N(CH_3)_3]^+$ and $[C_{16}H_{33}NC_5H_5]^+$)	The ODS experiments of the model oil (1000 of sulfur ppm as DBT in n-octane) were carried out with 0.00156 mmol of catalyst [n(DBT)/n(catalyst) 100], 0.032 mL of 30 wt % H_2O_2 [$n(H_2O_2)/n$(DBT) = 2] and the extracting solvent with IL (1 mL) was dissolved in the flask and then 5 mL of model oil (S = 1000 ppm) was added. The resulting mixture was stirred vigorously and heated to 70 °C in oil bath.	The S content in the model oil decreased from 1000 to 8 ppm, which was superior to the solvent extraction with ILs. The reactivity of sulfur compounds in the ECODS system decreased in the order of DBT > 4,6-DMDBT > BT. The catalyst with the short alkyl chain exhibited higher catalytic activity than that with the long alkyl chain. The deep desulfurization system containing $[(C_4H_9)_4N]_3\{PO_4[MoO(O_2)_2]_4\}$, H_2O_2, and [BMIM]BF_4 can be recycled four times without significant loss of activity.

Reference	IL/catalyst/oxidizing agent	Conditions of desulfurization	Observations
Zhu et al., 2008)	[BMIM]BF$_4$, [OMIM]BF$_4$, [BMIM]PF$_6$, [OMIM]PF$_6$, [BMIM]TA and [OMIM]TA doped with the catalyst (such as Na$_2$MoO$_4$·2H$_2$O, H$_2$MoO$_4$, (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O, H$_3$PMo$_{12}$O$_{40}$·13H$_2$O, (NH$_4$)$_3$PMo$_{12}$O$_{40}$·7H$_2$O and Na$_3$PMo$_{12}$O$_{40}$·7H$_2$O/H$_2$O$_2$	Model oil was prepared by dissolving DBT, BT and 4,6-DMDBT in *n*-octane to give a corresponding sulfur content of 1000, 1000 and 500 ppm. The mixture, containing 5 mL of model oil, 0.064 mL of 30 wt% H$_2$O$_2$ [n(H$_2$O$_2$)/n(DBT) = 4], 1 mL of IL and catalyst [n(S)/n(Mo) = 20], was stirred vigorously at 70 ºC for 3 h. The upper phase (model oil) was withdrawn and analyzed by GC-FID.	The S-removal of DBT containing model oil in [bmim]BF$_4$ could reach 99.0% at 70 °C for 3 h, which was the remarkable advantage of this process over the desulfurization by mere solvent extraction with IL or catalytic oxidation without IL. Moreover, the catalysts hardly dissolved in oil. The catalytic oxidation system containing Na$_2$MoO$_4$·2H$_2$O, H$_2$O$_2$ and [bmim]BF$_4$ could be recycled five times without a significant decrease in activity and oxidized sulfur could be reclaimed by centrifugation.
(Xu et al., 2009)	[BMIM]BF$_4$/V$_2$O$_5$, 30wt% H$_2$O$_2$	Experimental conditions: model oil = 5 mL, IL = 1 mL, [n(DBT)/n(V$_2$O$_5$) = 20], [n(H$_2$O$_2$)/n(DBT) = 6], T = 30 °C, t = 4 h	In the described experimental conditions, 98.7 % of sufur remotion was obtained for model gasoline.[BMIM]BF$_4$ can be recycled seven times without a significant decrease in activity.
(Li et al., 2009)	[BMIM]BF$_4$, [BMIM]PF$_6$, [OMIM]BF$_4$, and [OMIM]PF$_6$/ H$_3$PW$_{12}$O$_{40}$·14H$_2$O/ H$_2$O$_2$	The extraction and catalytic ODS was carried out with 5 mL of model oil, 0.048 mL of 30 wt % H$_2$O$_2$ [n(H$_2$O$_2$)/n(DBT) = 3], 1 mL of IL, and catalyst [n(DBT)/n(HPW) = 100], 30°C for 1 h .	At room temperature and short reaction time a commercially available H$_3$PW$_{12}$O$_{40}$·14H$_2$O combined with H$_2$O$_2$ and ILs [BMIM]BF$_4$, [BMIM]PF$_6$, [OMIM]BF$_4$, and [OMIM]PF$_6$ is effective for removing DBT, 4,6-DMDBT, and BT.
(Kuhlmann et al., 2009)	Several imidazolium phosphate IL were tested. Supported ILs phases (SILP) materials were also evaluated.	Dibenzothiophene/dodecane and butylmercaptan/ decane mixtures were used as model systems. Single-stage extractions reduced the sulfur content from 500 ppm to 200 ppm. In multistage extractions the sulfur content could be lowered to less than 10 ppm within seven stages.	SILP materials, obtained by dispersing the IL as a thin film on highly porous silica, reducing the sulfur content to less than 100 ppm in one stage. Multistage extraction with these SILP materials reduced the sulfur level to 50 ppm in the second stage. The SILP technology offers very

Reference	IL/catalyst/oxidizing agent	Conditions of desulfurization	Observations
		Regeneration of the IL was achieved by distillation or re-extraction procedures.	efficient utilization of ILs and allows application of the simple packed-bed column extraction technique.
(Seeberger & Jess, 2010)	[EMIM]DEP/*n*-dodecane containing dibenzothiophenone sulfone and real predesulfurized and completly oxidized Diesel	The efficiency of the extraction of S-compounds increases if the S-species are previously oxidized to the corresponding sulfoxides and sulfones. IL regeneration was also studied.Model oils containing single sulfones as well as real pre-oxidized diesel oils were investigated.	The evaporation of water from the IL is the crucial step with regards to the energy consumption of the process. The energy demand is comparable to classical HDS, if a multi-stage evaporation is used.

Table 3. Papers describing oxidative desulfurization of oils using ionic liquids.

Additional to the cited works, several other papers have been recently published about ODS using ILs as solvents (Lissner et al, 2009 Zhang et al., 2009), as catalysts (Li et al., 2009, Zhao et al., 2009, Gao et al., 2010) and in processes involving catalytic (b Li et al., 2009, Conte et al., 2009, Chao et al., 2010) and photochemical oxidation (Zhao et al., 2008).

Deep desulfurization processes using ILs without (Bosmann et al., 2003, Likhanova et al., 2009, Martínez-Palou et al., 2010, Guzmán et al., 2010) and with oxidating agent (Schoonover & Roger, 2006, Cheng, 2009) have also been patented, as such as, a method for the recovery of Lewis acid ILs after sulfur extraction (Guzmán et al., 2010).

In our considerations, in spite of the advances in the researches about the liquid-liquid extractions of SCs employing ILs, since the practical point of view, the industrial implementation of these technologies presents the following limitations:

- Many ILs show extractive properties of hydrocarbon contaminants (sulfurated and nitrogenated compounds), however much of these compounds required several extraction cycles for "quantitative" remotion of contaminants, even when in some cases a 1:1 ratio (IL/hydrocarbons) is required, it is, their extractive properties are very poor.
- The Nernst partition coefficient (K_N) favors extraction of most aromatic components of the fuel oil and this can be a limitation of the extractive method.
- In many cases, the studies have been carried out with model feeds under laboratory scale. These obtained results are far from those under real conditions. The results should be validated at higher scale and with real samples.
- The most efficient ILs for desulfurization are water sensitive, Lewis acid ILs, which can be used in only one extraction cycle because they suffer decomposition after being used.
- In these extractive processes volumetric lost of hydrocarbons are produced, due to is difficult to achieve a exhaustive separation between phases, partial hydrocarbon dissolution in the ILs and because to a difference of HDS, in these extractive processes, the carbon and hydrogen atoms contained in the SCs are separated from the hydrocarbons feeds.
- The efficiency of the extraction of SCs for ODS procedures is high, however the synthetic process for the preparation of several efficient catalysts are generally

complicated and these catalysts are not commercially available. Very high volume of the oxidant and additional equipments are required.

Very recently, Kulkarni and Afonso published a critical review about deep desulfurization of diesel fuels using ILs were some additional references of this topic can be found (Kulkarni & Afonso, 2010).

3.3 Denitrogenation of gasolines

Another extractive process for increasing the efficiency of HDS process is the remotion of nitrogenated compounds before the charges will be introduced in the HDS process to obtain ultralow sulfur hydrocarbons. Is well known that the selective removal of nitrogen compounds from the feeds before HDS strongly enhanced the further deep desulfurization, and increase the catalyst time of live because nitrogen compounds in the fuel and NH_3 produced from them during hydrocarbon reforming process are poisons to the catalysts in hydrocarbon process and fuel cells; thus, the development of new approaches to reduce the nitrogen content in transportation fuel oils in order to meet the need of ultra-clean fuels for environmental protection and H_2 production. (Laredo et al., 2001 and 2003).

The applications of ILs as extractants of N-containing compounds have also been studied for several researchers. Eβer et al. and Zhang et al., described for the first time in 2004, the ability of some ILs to remove nitrogenated compounds from hydrocarbons (Eβer et al., 2004, Zhang et al., 2004). Eβer et al. determined a high partition coefficient (K_N) of 34 mg(N) kg(IL)$^{-1}$/mg(N) kg(oil)$^{-1}$ for a experiment with model oil containing 1000 ppm of N as indole in n-dodecane using [BMIM][OcSO$_4$], while K_N were 0.7 and 2.9 for piperidine and pyridine, respectively.

Zhang et al. evaluated the adsorption capacities of N-containing saturated and non-saturated heterocyclic compounds and probed the extractive removal of both organonitrogen and organosulfur compounds for a model fuel (MF) consisted of n-C$_{12}$ with either DBT, pyridine, or piperidine, the IL removed 12% S (DBT) in n-C$_{12}$, 45% N (pyridine) in n-C$_{12}$, and 9% N (piperidine) in n-C$_{12}$ using [BMIM]BF$_4$ (ratio IL/MF: 1/5). The amount removed from each model fuel is much less than the absorption capacity for the corresponding pure model compound by the ionic liquid, reflecting a partitioning of the model compounds in both the ionic liquid and the dodecane phases. The most effective extraction was the pyridine whose is fully miscible in the IL.

On the contrary of S-containing compounds, N-containing compounds can be very efficiently removed with chloride base-ILs (Fist geneartion ILs), which can be obtained in one-step synthesis, as have been demostrated by Xie et al. (Xie et al. 2008 a and b)

In 2008, Xie et al. synthesized and evaluated four ILs with different carbon chain length and saturation of N-substituent groups: 1-butyl-3-methylimidazolium chloride (BMImCl), 1-allyl-3-methylimidazolium chloride (AlMlmCl), 1-benzyl-3-methylimidazolium chloride (BzMImCl) and 1-octyl-3-methylimidazolium chloride (OcMImCl). The distribution coefficient of carbazole (CAR) and dibenzothiophene (DBT) between the ILs phase and the model fuel phase and the extraction selectivity of the ILs for CAR and DBT were determined using a dibenzothiophene and carbazole solution in toluene and n-decane as a model fuel. The results show that CAR has higher distribution coefficient than DBT in these ILs phases. The CAR distribution coefficients in BMImCl and AlMImCl are 46 and 14, and the selectivity of CAR/DBT is 125 and 38, respectively (c Xie et al., 2008).

Huh, et al reported on the use of Zn-containing imidazolium-based ILs bearing an alkylsulfate anion for the extraction of nitrogen compounds present in hydrocarbon mixtures at room temperature. The denitrogenation process was studied using a model oil containing 5000 ppm of quinoline and 20000 ppm of *n*-octane as internal standard in *n*-heptane. The performance of dialkylimidazolium alkyl sulfate IL for the extraction of basic nitrogen compounds, such as quinoline and acridine, was significantly improved up to more than 2 times.

Theoretical investigation on the interactions of $ZnCl_2(EtSO_4)^-$ and $EtSO_4^-$ with quinoline and indole were carried out at the B3LYP level of theory using Gaussian 03. Computational studies show that active Zn-containing anionic species, such as $[EMIm]ZnCl_2(EtSO_4)$ and $[EMIm]ZnCl(EtSO_4)_2$, can be generated from the interaction of $ZnCl_2$ with $[EMIm]EtSO_4$, and thus, the extraction of quinoline can be facilitated through the coordination of quinoline to the Zn center. The bonding mode of ethylsulfate ligand in $ZnCl_2(EtSO_4)^-$ is changed from bidentate to monodentate for the coordination of quinoline, thereby retaining a tetrahedral environment around Zn.

The regeneration and reuse of the ILs was also investigated. Diethyl ether was found to be an efficient back extractant for the regeneration of $[EMIm]EtSO_4-ZnCl_2$, used for the denitrogenation of quinoline from the model oil, and to recover trapped quinoline in the IL (Huh et al., 2009).

Another strategy for separation of organic nitrogen compounds was by means supported liquid membranes based on 1-alkyl-3-methylimidazolium and quaternary ammonium salts ILs. Matsumoto et al. in 2006 showed the potential of these membranes for the separation process of organic nitrogen compounds and heptane. The organic nitrogen compounds selectively permeated the membranes.

The main difficult for this strategy is that when nitrogenated compounds are absent in the fuel HDS catalyst might start to deeply hydrogenate the feed, with the consequent high hydrogen consumption (Prins, 2001).

3.4 Separation of aliphatic/aromatic hydrocarbons

Aromatic compounds are other important contaminants in hydrocarbons mixture products. The feed stream of naphtha crackers may contain up to 25% aromatic hydrocarbons, which must be removed. In general these compounds are very toxic by inhalation and their evaporation into the atmosphere produce detrimental effects on the environment and human health. The presence of aromatic compounds in the feed to the cracker also has a negative influence on the thermal efficiency and tends to foul the radiation sections and the Transfer Line Exchangers.

The separation of these environmental pollutants (benzene, toluene, ethyl benzene and xylenes) from aliphatic hydrocarbon mixtures is challenging since these hydrocarbons have boiling points in a close range and several combinations form azeotropes.

The conventional processes for the separation of these aromatic/aliphatic hydrocarbon mixtures are liquid extraction, when the aromatic range is 20-65 wt.%, extractive distillation for 65–90 wt.% of aromatics and azeotropic distillation for more than 90 wt.% of aromatic content. Typical solvents used for the extraction are polar components such as sulfolane (Choi et al., 2002), *N*-methyl pyrrolidone (NMP) (Krishna et al., 1987), ethylene glycols (Al-Sahhaf et al., 2003) and propylene carbonate (Ali et al., 2003). A step of distillation for separating the extraction solvent is required.

For their negligible vapor pressure and low toxicity, ILs are, in theory, an excellent alternative for being used for the extraction of aromatic compounds by means an environmental friendly procedure and where the distillation step is not required. In 2001, Azko Novel patented a procedure for the extraction of an aromatic compound from an aliphatic phase using ILs (Shyu et al, 2001). To this point many papers have been published about studies of liquid-liquid equilibrium in mixtures of aliphatic and aromatic hydrocarbons (Letcher et al., 2003, Letcher et al., 2005) and in the last years spanish researchers have focused in these equilibria and in physicochemical aspects of two ternary systems comprising aliphatic/aromatic/ILs compounds (a-e. González et al., 2010, a- b. Pereiro et al., 2009, a-c. Arce et al., 2009, a-b. Arce, 2008, Alonso, 2008, a-b. García et al., 2008, García et al., 2010, a-b. Pereira, et al., 2010).

In 2005, Meindersma et al., found that several ILs are suitable for extraction of toluene from toluene/heptane mixtures. The toluene/heptane selectivities at 40 °C and 75 °C with ILs like [MeBuPy]BF$_4$, [MeBuPy]CH$_3$SO$_4$, [BMIM]BF$_4$ (40 °C) and [EMIM]Tosylate (75 °C), are a factor of 1.5-2.5 higher compared to those obtained with sulfolane (S$_{tol/hept}$ = 30.9, D$_{tol}$ = 0.31 at 40 °C), which is the most industrially used solvent for the extraction of aromatic hydrocarbons from a mixed aromatic/aliphatic hydrocarbon stream, being [MeBuPy]BF$_4$ the most suitable, because of a combination of a high toluene distribution coefficient (D$_{tol}$ = 0.44) and a high toluene/heptane selectivity (S$_{tol/hept}$ = 53.6). Therefore, with [MeBuPy]BF$_4$ also extraction experiments with other aromatic/aliphatic combinations (benzene/n-hexane, ethylbenzene/n-octane and m-xylene/n-octane) were carried out, obtaining similar selectivities (Meindersma et al., 2005).

Also Meindersma & Haan presented a conceptual process design for the separation of aliphatic/aromatic hydrocarbons, in which the authors concluded that ILs which show a high aromatic distribution coefficient, D_{arom} = 0.6 m/m, with a reasonable aromatic/ aliphatic selectivity, $S_{arom/alif}$ = 40, could reduce the investment costs of the aromatic/aliphatic separation to about M€ 25 to 30 and the annual costs to M€ 16 to 17 respect to total investment costs in the typically applied sulfolane extraction process (Meindersma & de Haan, 2007).

In 2006, Domanska et al. published a paper about the liquid-liquid equilibria in binary mixtures that contain a room-temperature IL and an organic solvents as [MMIM][CH$_3$SO$_4$], or [BMIM][CH$_3$SO$_4$] with an aliphatic hydrocarbon (n-pentane, or n-hexane, or n-heptane, or n-octane, or n-decane), or a cyclohydrocarbon (cyclohexane, or cycloheptane), or an aromatic hydrocarbon (benzene, or toluene, or ethylbenzene, or propylbenzene, or o-xylene, or m-xylene, or p-xylene) measured at normal pressure by a dynamic method from 270 K to the boiling point of the solvent and liquidus curves were predicted by the COSMO-RS method. For [MMIM][CH$_3$SO$_4$], the COSMO-RS results correspond. According with their results the solubilities of [MMIM][CH$_3$SO$_4$] and [MMIM][CH$_3$SO$_4$] in alkanes, cycloalkanes and aromatic hydrocarbons decrease with an increase of the molecular weight of the solvent and the differences of the solubilities in o-, m-, and p-xylene are not significant. By increasing the alkyl chain length on the cation, the upper critical solution temperature, UCST decreased in all solvents except in n-alkanes (Domanska et al., 2006).

In 2007, Cassol et al., found that the selectivity on the extraction of a specific aromatic compound is influenced by anion volume, hydrogen bond strength between the anion and the imidazolium cation and the length of the 1-methyl-3-alkylimidazolium alkyl side chain. The interaction of alkylbenzenes and sulfur heterocyles with the IL is preferentially through CH-π hydrogen bonds and the quantity of these aromatics in the IL phase decreases with the

increase of the steric hindrance imposed by the substituents on the aromatic nucleus. Competitive extraction experiments suggest that benzene, pyridine and dibenzothiophene do not compete for the same hydrogen bond sites of the IL (Cassol et al., 2007).

The more relevants structural aspects of ILs (González et al., 2009 and a. González et al., 2010, Pereiro & Rodríguez, 2010), effect of the chain length of the aromatic ring (b. González et al., 2010), effect of the size of aliphatic hydrocarbures (c. González et al., 2010), and isomer effects (Arce et al., 2010) for their performace as aromatic extractants have been studied.

Very recently, a systematic studiy about the influence of structure of ILs on selectivity and capacity for aromatic/aliphatic hydrocarbons separation problem and n-hexane/hex-1-ene separation problem were reviewed. Analysis of cation and anion structure of the ILs and effect of the temperature on the selectivity and the capacity for aliphatics/aromatics and n-hexane/hex-1-ene separation problems was made. ILs based on imidazolium, pyridinium, pyrrolidinium, sulfonium, phosphonium and ammonium cations were taken into consideration. Analysis was made on the basis on activity coefficients at infinite dilution because this parameter is helpful for characterizing the behaviour of liquid mixtures, estimation of mutual solubilities, fitting the excess molar energy (G^E) model parameters (e.g. Wilson, NRTL, UNIQUAC), predicting the existence of an azeotrope, analytical chromatography, calculation of Henry constant and partition coefficients, development of thermodynamic models based on the group contribution methods such as mod. UNIFAC. All the data utilized in this work were obtained from published literature available at the end of September 2009 and analysed by means a linear regression. According with the results the highest values of selectivity show ILs with less aliphatic character of the anion and the cation, e.g. based on following cations [MMIM]+, [EMIM]+, [ePy]+, [Et$_3$S]+ and with –CN group in the structure, like [CN-C$_3$MM]+. Unfortunately always when the IL reveals high values of the selectivity, the capacity takes low values. The highest values of capacity have [NTf$_2$]– and [FeCl$_4$]– anions. As was shown most of ILs with high values of both selectivity and capacity is based on [NTf$_2$]– anion. Details of specific structures and correlations of the ILs can be reviewed in this reference (Marciniak, 2010).

3.5 Remotion of naphthenic acids from crude oil

Naphthenic acids are mixture of several cyclopentyl and cyclohexyl carboxylic acids, which are natural constituents in many petyroleum sources. The main fraction contains carboxylic acids with a carbon backbone of 9 to 20 carbons. The naphtha fraction of the crude oil is oxidized and yields naphthenic acid. The composition differs with the crude oil composition and the conditions during raffination and oxidation (Walter et al., 2002).

The presence of naphthenic acids in crude oil has a great influence tend to cause operational problems on petroleum refiners, such as foaming in the desalter or other units and carrying cations through the desalting process, which can cause deactivation of catalysts and corrosion problems.

Typically naphthenic acids are effectively removed from crude fractions by aqueous base washing (Varadaraj & Savage, 2000, Sartori et al., 2000), but serious emulsion problems are presented.

Chinese researchers proposed in 2008 a novel method to separate naftenic acids from highly acidic crude oil by forming ILs. In this method, the basic character of imidazole heterocycle is utilized to prepared Brønsted ILs by acid-base reaction between imidazole and

naphthenic acids to form naphthenates ILs (Figure 4). Reagent recovery and naphthenic acids refining were also proposed (Shi et al., 2008).
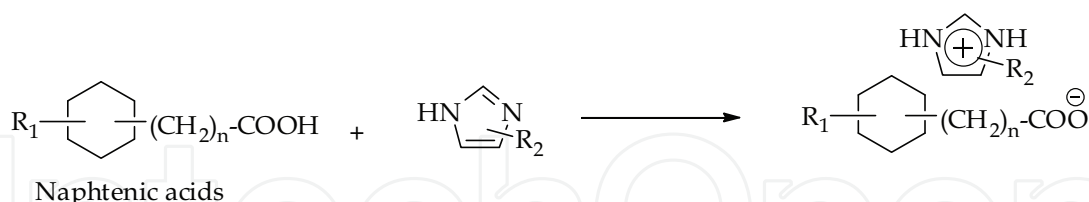

Fig. 4. ILs formation by acid-base reaction between naphtenic acids and alkylimidazole.

The effect of different imidazole derivatives and polar solvents were evaluated. The acid-removal rate was influenced by the 2-methylimidazole content, reagent/oil ratio, reaction time, and reaction temperature, all of which had a positive effect on the acid-removal rate. The reagent/oil ratio had a negative effect on the oil yield rate. High-purity naphthenic acids could be obtained in this process.

4. Ionic liquids in membrane technologies

4.1 Ionic liquids in membranes for selective gases separation

In Petroleum Industry several liquids and gases separations are highly required for gases purifications. Membrane technology can offer a competitive way of the off-gas treatment when the membrane able to work in the conditions of the power plant stack will be developed (Zhao et al., 2008), but maybe the main limitation of this process is the membrane stability especially at high temperatures due to solvent depletion through evaporation and long-term membrane performance.

By their very low vapor pressure, temperature stability, non-flammability and non-corrosively, ILs appear as an excellent alternative for membranes technology.

Efficiently separating CO_2 from H_2 is one of the key steps in the environmentally responsible uses of fossil fuel for energy production. Amines treatment is currently being used for separating CO_2 (Blauwhoff et al., 1984). This process is expensive due to high energy consumption at desorption stage and loss of the amine during the treatment and amine recovery (Rao & Rbin, 2002).

During the present century, a big number of studies have been performed to explore the prospects of ILs for gases separation and for founding the best prototypes for CO_2 capture (Bates et al., 2002, Baltus et al., 2004, Baltus et al., 2005, Shiflett & Yokozeki, 2005, Jacquemin et al., 2006, Hou & Baltus, 2007, . Schilderman et al., 2007, Yokozeki & Shiflett, 2007, Sánchez et al., 2007, Ventura et al., 2008, Shin and Lee, 2008, Shin et al., 2008, Li et al., 2008, Camper et al., 2008, Palgunadi et al., 2009, Soriano et al., 2008, Soriano et al., 2009, Condemarin & Scovazzo, 2009, Heintz et al., 2009, a, b. Carvalho et al., 2009, Kuleman et al., 2010, Shokouhi et al., 2010) and also several discoveries have been patented (Brennecke & Maginn, 2002 and 2003, Davis Jr., 2004, Chinn et al., 2006, Yu et al., 2008).

Oleffin/paraffin separation is other very important separation process in refineries. Propane produced in refinery operations often contains substantial amounts of propylene. Propylene may cause problems through engine and injector deposits when propane is used as a motor fuel. Also, propylene is capable of polymerizing in storage, fuel lines, or vaporizers, and thus may cause plugging by gum deposits. In this case the traditional separation technologies involving distillation (low-temperature and extractive distillation) and catalytic

hydrogenation (Bryan et al., 2004). Both processes are both energy and capital intensive because of the similarity in volatilities between olefins and their corresponding paraffins and by the high demand of hydrogen required in the case of the catalytical hydrogenation process. One of the most interesting strategies in membrane technologies are the Supported Liquid Membranes (SLMs). The first paper describing the application of ILs for SLMs was published in 1995 using quaternary ammonium salt hydrates (tetramethylammonium fluoride tetrahydrate, $[(CH_3)_4N]F \cdot 4H_2O$, or tetraethylammonium acetate tetrahydrate, $[(C_2H_5)_4N]CH_3CO_2 \cdot 4H_2O$, immobilized in films of Celgard 3401® (Quinn et al., 1995) and from this begining a number of papers have increase exponentially in the following years until the present.

SLMs are porous membranes with the pores saturated with a solvent mixture. SLMs suffer significant solvent loss due to volatilization when conventional solvents are employed as supported liquid. The used of ILs as the immobilized phase within the pores of the membranes is the improving in the membrane stability and their performance do not depend of the water presence (a. Scovazzo et al., 2009). Supported ionic liquid membranes (SILMs) increase the efficiency and selectivity of gas separation respect to non-supported liquid membranes because the higher area of contact IL-gases.

Studies in SILMs are principally focused in CO_2 capture especially from methane or nitrogen (For excellent recent reviews see: Hasib-ur-Rahman et al., 2010 and Bara et al., 2010) but also have been proposed for sulphur dioxide, carbon monoxide and hydrogen and olefin/paraffin, and water (dehydration) separation.

Several research group have proposed predictive correlations for gas solubilities in ILs (Camper et al., 2005, Kilaru et al., 2008, Kilaru & Scovazzo, 2008, Zhang et al., 2008, Carlisle et al., 2008, Sprunger et al., 2008, Lei et al., 2009) and gas diffusivities in ILs (Morgan et al., 2005, Camper et al., 2006, Hou & Baltus, 2007, Ferguson & Scovazzo, 2007, Condemarin & Scovazzo, 2009) based on their physico-chemistry properties.

In Table 4 several papers describing the applications of SILMs for gas separation are presented.

Reference	Selective separation studied	IL(s)/support(s) employed	Experimental Conditions	Observations
(Lee et al., 2006)	H_2S/CH_4, CO_2/CH_4	ILs into poly(vinylidene fluoride)(PVDF) matrix.	Three types of feed gas (CO_2, H_2S and CH_4) were permeated, at permeate pressure below 2 mbar, through the new SILMs using GPA-60 at feed P = 2-5 bar and T = 35-65 °C.	The membranes had excellent stability under sever operating conditions. The novel SILMs exhibited very high H_2S, CO_2 permeability and H_2S/CH_4 and CO_2/CH_4 selectivities.
(Zhang et al., 2006)	CO_2 absorption	Tetrabutylphospho-nium amino acid $[P(C_4)_4][AA]$, where	$[P(C_4)_4][AA]$ was loaded in the porous silica ge by	No changes in absorption capacity and kinetics were found after four

Reference	Selective separation studied	IL(s)/support(s) employed	Experimental Conditions	Observations
		AA are amino acids, including glycine, L-alanine, L-β-alanine, L-serine, and L-lysine/porous silica.	dopping method to enhance the absortion rate. CO_2 absorbed was determined bu an analytical balance after absortion equilibrium in dry atmosphere (chemisorption of CO_2).	cycles of absorption/desorption. The CO_2 absorption capacity at equilibrium was 50 mol% of the ILs. In the presence of water (1 wt%), the ILs could absorb equimolar amounts of CO_2. The CO_2 absortion in IL supported on silica is fast and reversible.
(Myers et al., 2008)	CO_2/H_2	bis(trifluoromethylsulfonyl)imide ($[H_2NC_3H_6mim][Tf_2N]$)/ cross-linked nylon	30 mL/min of feed (CO_2 (19.95 mole%), H_2 (20.01 mole%) and Argon (balance). 6-10 mL/min Ar passed of the permeate side of the membrane. Total pressure of 108 kPa for the feed.	Amine-functionalized IL based facilitated transport membrane with a selectivity maximum at 85°C.
(Huang et al., 2008)	Oleffin/ paraffin	$[Ag(olefin)^+ Tf_2N^-]$, olefin: 1-hexene, 1-pentene and isoprene, and Silver(I)/N,NDime-thylbenzoamide $[Ag(DMBA)_2^+Tf_2N]$/ microporous alumina.	Experiments were carried out with IL membranes prepared by dropping 0.5 mL of IL on the top of the microporous alumina support and using a stainless steel permeation cell at 23 °C with an olefin/paraffin mixed gas. The feed pressure was 212 kPa.	$[Ag(olefin)^+Tf_2N^-]$ and $[Ag(DMBA)_2^+Tf_2N^-]$ ILs exhibit excellent performance for olefin/paraffin separation. These ILs provided high permeability and good selectivity. The reversible interaction of olefins and silver ions in the $[Ag(olefin)^+Tf_2N^-]$ was demonstrated.
(Kang et al., 2008)	Oleffin/ Paraffin (propylene /propane	$[BMIM^+BF_4^-]$, $[BMIM^+Tf^-]$, and $[BMIM^+NO_3^-]$ were employed to control	The ILs/Ag composite membranes were prepared by	The effect of ILs on the formation of a partial positive charge on the surface of silver

Reference	Selective separation studied	IL(s)/support(s) employed	Experimental Conditions	Observations
	mixtures)	the positive charge density of the surface of silver nanoparticles.	dispersing Ag nanopowder in ILs. For fabrication of the separation membranes, the mixed solution was coated onto polyester microporous membrane supports (Osmonics Inc., pore 0.1 µm) using an RK Control Coater. Gas flow rates were measured with a mass flow meter.	nanoparticle and its subsequent effect on facilitated olefin transport were inves-tigated. A better separation perfor-mance for olefin/paraffin mixtures was observed with a higher positive charge density of the silver nanoparticles. It was therefore concluded that facilitated olefin transport was a direct consequence of the surface positive charge of the silver nanoparticles induced by ILs.
(Jiang et al., 2007)	SO_2 separation from	[EMIM]BF_4 [BMIM]BF_4 [BMIM]PF_6 [HMIM]BF_4 ([BMIM][Tf_2N]/ hydrophilic polyethersulfone	The SO_2 solubility in ILs in this study was also measured The simulated flue gases were a mixture of N_2 and SO_2 with a SO_2 content of 8 % by volume at ambient pressure and at 40.0 °C. The gas stream was bubbled through about 3.5 g of IL and the flow rate was about 50 mL min^{-1}.	The experimental results show that the SILMs not only offer very good permeability of SO_2 but also provide ideal SO_2/CH_4 and SO_2/N_2 selectivities up to 144 and 223, respectively. When compared to CO_2 in the tested SILMs, there is also over an order of magnitude increase in the permeability and selectivity of SO_2.
(b. Scovazzo, 2009)	H_2O/CH_4	[EMIM][Tf_2N], 1-ethyl-3-methyimidazolium dicyanamide ([EMIM]DCA), [EMIM]BF_4 and butyltrimethylammonium bis(trifluoro-methanesulfonyl)-	Two procedures to investigate membrane performance changes due to H_2O or CH_4 absorption were applied. The first procedure used nominal feed	SILMs have larger permeability coefficients that are constant with relative humidity. The initial evaluation of SILMs for dehumidification is that they are potentially competitive with polymer

Reference	Selective separation studied	IL(s)/support(s) employed	Experimental Conditions	Observations
		amide ([N(4)111][Tf$_2$N])/ hydrophilic polyethersulfone (PES)	absolute pressures of 1 bar (15 psi) and 2 bar (29.4 psi) of nitrogen. The procedure tested a series of feed relative humidities (rHs) from 0% to >90% at both nominal feed pressures. The second used nominal feed absolute pressures of 1 bar and 2 bar of methane for the [Tf$_2$N]-membranes.	membranes. Water permeance does not change with relative humidity (rH). Methane permeance increases with increasing rH with the [Tf$_2$N]-membranes having an increase of 20% and the water miscible [BF$_4$]-membrane having an increase of 110%.
(Park et al., 2009)	CO$_2$/CH$_4$, H$_2$S/CH$_4$	[BMIM]BF$_4$/PVDF (poly vinylidene fluorolide)	Three types of feed gas (CO$_2$, H$_2$S and CH$_4$) were permeated, at permeate pressure below 2 mbar, through the new SILMs using GPA-60 at feed P = 2-5 bar and T = 35-65 °C.	The permeability coefficients of CO$_2$ and H$_2$S were found to be considerably high at 30–180 and 160–1100 barrer, respectively. Moreover, the selectivity of CO$_2$/CH$_4$ and H$_2$S/CH$_4$ were found to be 25–45 and 130–260, respectively.
(Raeissi & Peters, 2009)	CO$_2$/H$_2$	1-alkyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl)imide: [EMIM]NTf$_2$, [BMIM]NTf$_2$	Binary phase behaviour experiments were carried out Cailletet apparatus, which allows the measurement of phase equilibrium according to the synthetic method within temperatures and pressures up to 450 K and 15 MPa,	The experimental results indicated that CO$_2$ solubility is strongly dependent on temperature and pressure, decreasing with temperature and probably having an economically optimum mid-range pressure.Methane and carbon monoxide solubilities in [BMIM][Tf$_2$N] fall in between those of H$_2$ and

Reference	Selective separation studied	IL(s)/support(s) employed	Experimental Conditions	Observations
			respectively.	CO_2, and they have a linear relationship with pressure.
(b. Scovazzo et al., 2009)	CO_2/CH_4 CO_2/N_2	[EMIM][BF$_4$], [EMIM][dca], [EMIM][CF$_3$SO$_3$], [EMIM][Tf$_2$N], and [BMIM][BETI].	Mixed-gas permeances and selectivities for the gas pairs CO_2/CH_4 and CO_2/N_2 using continuous flows of the mixed gases at various CO_2 concentrations (up to 2 bars of CO_2 partial pressure).	Three showed attractive mixed-gas selectivity combined with CO_2-permeability for CO_2/CH_4 separa-tions. In addition, one of the tested membranes is, economically viable for CO_2 capture from flue gas.
(Shishatskiy et al., 2010)	CO_2/N_2, CO_2/H_2	Ammonium compounds obtained by reaction of (3-Aminopropyl)trieth-oxysilane, glycidyl-trimethylammonium chloride in molar ratio of 1:1 (1N$^+$) and 1:2 (2N$^+$), blends with PEBAX® MH 1657, and products form hydrolysis of 1N$^+$ and 2N$^+$ in the presence of TEOS as co-monomer.	The diffusion, permeability and solubility of pure H_2, He, N_2, O_2 and CO_2 in dry membrane samples were measured at feed pressures 0.3–1.7 bar and temperatures 10–120 °C using a constant volume/variable pressure. The transport parame-ters of the same membranes in wet envi-ronment were determi-ned on the constant volume /variable pressure, where feed gas stream was humidified to the water partial pressure close to the dew point at 23 and 60 °C.	1N$^+$ and 12N$^+$ in the form of blends with PEBAX® MH 1657 showed high CO_2 solubility coefficients and high CO_2/N_2 (up to 1500) and CO_2/H_2 (up to 1350) solubility selectivity. At low temperatures CO_2 was irreversibly absorbed in the quaternary ammonium compound and was released only at temperatures higher than 60 °C. Co-hydrolysis with TEOS at 60 °C was found to be an additional transition point giving for H_2, N_2, O_2 and CO_2 break on the solubility coefficient Arrhenius plots.

Reference	Selective separation studied	IL(s)/support(s) employed	Experimental Conditions	Observations
Simons et al., 2010	CO_2/CH_4	The polymerizable styrene-based 1-[(4-ethenyl phenyl) methyl]-3-alkyl-imidazolium bis (trifluoromethane) sulfonamide IL monomers with three different lengths of the alkyl substituent (methyl, n-butyl or n-hexyl)	The separation performance of the poly(IL) membranes was investigated with a temperature-controlled high pressure gas permeation setup using a constant volume-variable pressure method. A constant feed pressure was applied and during the measurement, the permeate side was kept under vacuum.	As opposed to regular glassy polymers, poly(ILs) do not show a minimum in permeation rates for CO_2: the permeability increases continuously with increasing feed pressure. Non-plasticizing methane shows a pressure independent permeability.

Table 4. Papers describing the applications of supported ILs membranes for gas separation.

In 2009 Scovazzo published a significant paper where literature data obtained using the proposed model to predict gas solubility and gas permeability was summarized, along with adding new data, on the SILMs membranes permeabilities and selectivities for the gas pairs: CO_2/N_2, CO_2/CH_4, O_2/N_2, ethylene/ethane, propylene/propane, 1-butene/butane, and 1,3-butadiene/butane, with the object as to serve as guide for future researches in this area.

The data analysis predicts a maximum CO_2-permeability for SILMs and an upper bound for permeability selectivity vs. CO_2-permeability with respect to the CO_2/N_2 and CO_2/CH_4 separations. The analysis recommends a number of future inverstigations including studies into SILMs cast from ILs with smaller molar volumes.

According with Scovazzo's analysis, for CO_2-separations, there are two critical ILs properties that effect SILM performance: molar volume and viscosity. The permeability selectivity is a function of IL molar volume while the CO_2-permeability is a function of viscosity.

In the context of olefin/paraffin separations, the preliminary data is encouraging when considering the use of facilitated transport via silver carriers. Since IL-solvent/solvent interactions dominate interminating the overall SILM performance, past attempts at enhancing solute/solvent interactions via the addition of functional groups to the ILs have not produced SILMs with better separation performance compared to the unfunctionalized ILs. Future research into functionalized ILs needs to consider the changes to the dominant solvent/solvent interactions and not just the solute/solvent interactions (c. Scovazzo, 2009).

Cserjesi and Belafi-Bako have published several papers about ILs membranes, especially for gas separations, which are discussed in details in other chapter of this book.

ILs with appropriated structure can polymerize via the cation and/or anion, forming solid films. This sence, several polyILs have also show a good performace for CO_2 capture (a-d.Tang et al., 2005, Hu et al., 2006, Bara et al., 2007, a, b. Bara et al., 2008, Tang et al., 2009). As example Bara et al. in 2008, after several works in developing polyILs for gas separation membranes, in 2008 published a paper about a second-generation of functionalized polyILs using imidazolium-based monomers containing either a polar, oligo(ethylene glycol) substituent and alkyl-terminated nitrile groups (C_nCN) on the cation of imidazolium-based ILs, which contribute can have pronounced effects on gas separations in polymer membranes for improving CO_2 selectivity. Membranes were prepared via the photopolymerization of IL monomers with additional cross-linker (divinylbenzene) on porous supports. The nature of the polar substituent was significant impacts on the permeability of CO_2, N_2 and CH_4. OEG functionalities, when included in polyILs, produced membranes that were several times more permeable than those with C_nCN functional groups. OEG-functionalized poly(ILs) exhibited CO_2 permeabilities on par with polyILs with n-alkyl groups, but with improved CO_2/N_2 selectivities that exceeded the "upper bound" of the "Robeson Plot". CO_2/CH_4 separation was also enhanced in each of these second-generation polyILs (c. Bara et al., 2008).

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4.2 Ionic liquids in selective liquid separations

ILs membranes are also being studied for the selective separation of liquids. Investigations on aliphatic/aromatic hydrocarbons, sulfur and nitrogen compounds separations have been carried out and will be presented in this section.

As was commented before the separation of benzene and cyclohexane is one of the most challenging processes in the chemical industry.

Because the characteristics of ILs are high surface tension and a lack of detectable vapor pressure, with the advantages of minimum loss of membrane liquid take place by the dissolution/dispersion effect, as well as by evaporation.

Pervaporation is a physical process that involves the separation of two or more components across a membrane by differing rates of diffusion through a thin polymer and an evaporative phase change comparable to a simple flash step. A concentrate and vapor pressure gradient is used to allow one component to preferentially permeate across the membrane. A vacuum applied to the permeate side is coupled with the immediate condensation of the permeated vapors. Pervaporation is considered a forward looking and modern membrane process for separation of various liquids or vapour mixtures.

Pervaporation, in its simplest form, is an energy efficient combination of membrane permeation and evaporation. It's considered an attractive alternative to other separation methods for a variety of processes (Smitha et al., 2004).

The potential of ILs in SILMs for pervaporation of solutes from aqueos mixtures was first demonstrated for Schäefer and coworkers (Schäefer et al., 2001), and Izák and coworkers (Izák et al., 2005, 2006 and 2009), however until now few paper about pervaporations using SILMs with potential applied in oilfield have been published.

With the object of prevent the loss of membrane liquids, Wang, Feng & Peng proposed a novel approach of SILMs in which vapor permeation with an IL filling-type supported liquid membrane replaces solvent extraction. The molecular diffusion coefficient is higher in ILs than in polymers, and the latter are often chosen as dense materials for the separation of organic liquids. According with the authors unlike solvent extraction, only a small amount of liquid is used to form SLMs, and the use of expensive ILs becomes economically possible. In this paper [BMIM][PF$_6$] was studied as a membrane liquid for the separation of toluene/cyclohexane mixture, as a representative of aromatic and aliphatic hydrocarbons and the dehydration of aqueous 1-propanol and aqueous ethanol mixtures was also investigated with vapor permeation through SILMs.

A porous flat membrane made of poly(vinylidene fluoride) (PVDF) with a molecular weight cutoff of 150 kDa was used as the substrate to prepare de SILM. The affinity between the [MMIM][PF$_6$] IL and the hydrophobic PVDF membrane resulted in a strong capillary force to hold the ionic liquid, so that the membrane liquid is stable even when the SLM is used under high-vacuum conditions.

For the separation of toluene/cyclohexane mixtures for a 550-h test, the permeation rate was determined by the aromatic component, and the separation factor reached 15-25 at 40 °C. Owing to the low organic solvent composition in the feed, the fluxes of the organic compounds were relatively small. When the same SLM was used for the dehydrations of aqueous 1-propanol and of aqueous ethanol, water was found to be the preferential permeation component (Wang et al., 2009).

In 2007, the application of the bulk liquid membrane technique is investigated for separation of toluene from n-heptane, using different imidazolium ILs (1-methyl-3-octyl imidazolium chloride, 1-ethyl-3-methyl-imidazolium ethyl sulfate, 1-methylimidazole hydrogen sulfate and 1H-imidazolium, 1-ethyl-4,5-dihydro-3-(2-hydroxyethyl)-2-(8-heptadecenyl) ethyl sulfate). Using silver ion as a carrier in membrane phase, batch wise extraction experiments were also carried out and the permeation rate and separation factor were determined by varying the operating parameters: the contact time, concentration of Ag$^+$, stirring effect, initial feed phase concentration and temperature.

This study demonstrates that the use of [OMIM]Cl as a membrane solvent enables the bulk liquid membrane operation to be used for the separation of toluene from *n*-heptane. Although the permeation rates through the membrane based on [OMIM]Cl is low, the selectivity of toluene is high enough for the separation of toluene from *n*-heptane. Facilitated transport of toluene is also demonstrated using [OMIM]Cl membrane containing Ag$^+$ as the carrier. It has been found that Ag$^+$ concentration, stirring speed, initial toluene concentration in feed phase and temperature have a strong effect on permeation rate and separation factor (Chakraborty & Bart, 2007).

Matsumoto et al. have investigated the SILMs for selective separations since 2005 (Matsumoto, et al., 2005). In 2009, this group studied the vapor permeation of benzene/cyclohexane through SILMs based on 1-alkyl-3-methylimidazolium and quaternary ammonium salts. In this paper, the effects of ILs and the benzene fraction in the feed on the permeation flux and separation factor, and the stability of the SILMs was studied, founding that the sorption step mainly affected the separation factor depending on the hydrophilicity of the IL. The ammonium type IL *N*,*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium tetrafluoroborate showed the highest selectivity of 47.1 for the mixed solution, gave the highest separation factor, 185 for 53 wt.% benzene and 950 for 11 wt.% benzene for the VP, which are superior to the previously reported values obtained by

pervaporation and the SILM was very stable after work over 1 month in steady flux without lot in their selectivity (Matsumoto et al., 2009).

Matsumoto and coworkers have begin to explored the application of SILMs for the selective permeation of organosulfur and nitrogenated compounds. They preliminary studies had demonstrated that SILMs has a good potential for the separation process of organic nitrogen and sulfur compounds from the fuels (Matsumoto et al., 2006 and 2007).

4.3 Ionic liquids in membranes for fuel cells

Liquid-fuelled solid-polymer-electrolyte fuel cells are very promising as electrochemical power sources and have drawn immense attention as high-efficiency and low-emission power sources, for application in portable devices and automotive applications (Li, 2006). Fuel cells are an alternative power sources that could be a future substitutes of the hydrocarbons as energy source.

The performance of a polymer electrolyte membrane (PEM) fuel cell is significantly affected by liquid water generated at the cathode catalyst layer (CCL) potentially causing water flooding of cathode; while the ionic conductivity of PEM is directly proportional to its water content. Therefore, it is essential to maintain a delicate water balance, which requires a good understanding of the liquid water transport in the PEM fuel cells.

At present, the most commonly used humidified perfluorinated ionomer membranes, represented by Nafion, are limited to being used at temperatures lower than 100 °C because of the evaporation of water, which results in a rapid loss of conductivity. Nafion membranes are limited for practical application due to their high cost and high fuel crossover (Adjemian et al., 2002).

The ionic conductivity of PEM is significantly dependent on the membrane hydration. Inadequate membrane hydration results in high electrical resistance as well as the formation of dry and hot spots leading to membrane failure. The electroosmotic transport occurs due to the proton transport. Proton migrations drag water along with it from the anode side to the cathode side that can eventually reduce the membrane hydration and block the active reaction site in the CCL. Water transport process in a PEM fuel cell is a complex phenomenon, hence it is essential to make a delicate water balance for better and optimum fuel cell performance, and prevent material degradation (Das et al., 2010).

The operation of PEM at temperature higher 100 °C is receiving much attention because it could enhance reaction kinetics at both electrodes, improve the carbon monoxide tolerance of the platinum catalyst at the anode, and simplify heat and water managements of the fuel cells.

Many effort have been carried out in developing another polymeric membranes different than Nafion membranes with better performance and low cost and to enhance the water retention (Tezuka et al., 2006, Di Vona et al., 2008, Kim & Jo, 2010), and more resistant materials and with higher thermal stability, like inorganic/polymeric membranes have been evaluated (Triphathi & Shahi, 2008, Okamoto et al., 2010, Umeda et al., 2010, Pereira et al., 2010).

ILs are an interesting alternative for this purpose, due to their negligible vapor pressure, high thermal stability, and ionic conductivity ILs can increase the membrane hydration at higher temperatures and anhydrous proton conduction.

In principle, there are mainly two methods to prepare IL-based polymer electrolytes: one is doping of polymers with a selected IL (Ye et al., 2008, Subianto et al., 2009, Padilha et al.,

2010, Che et al., 2010), and another approach is via *in situ* polymerization of polymerizable monomers in an IL solvent (Susan et al., 2005).

With the main object to delay the release of the ILcomponent, which may affect the long-term stability of the membranes, organic-inorganic composite membranes have been studied (Fernicola et al., 2008, a-b. Lakshminarayana et al., 2010).

Yu et al. reported for the first time the preparation and polymerization of microemulsions that contain IL polar cores dispersed in polymerizable oil comprising surfactant-stabilized IL nanodomains.

They demonstrated the effectiveness of this method with methyl methacrylate, vinyl acetate, and *N,N*-dimethylacrylamide instead of styrene as a polymerizable oil to prepare the microemulsions containing IL polar cores, using a long acryloyloxy functionalized imidazolium type-IL (MAUM-Br). Phase diagrams show that all of these [Bmim][BF$_4$]/vinyl monomer systems can form transparent and stable microemulsions when MAUM-Br (Figure 5) was used as surfactants.

MAUM-Br
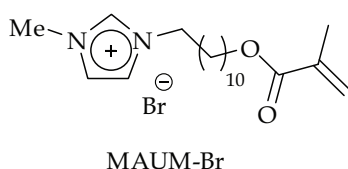
Fig. 5. Polymerizable surfactant used to prepare proton conducting membranes via the polymerization of microemulsions.

Polymerization of these IL-based microemulsions yielded free-standing, flexible, and transparent polymer electrolytes even though the resulting vinyl polymers are incompatible with IL cores. The obtained IL/polymer composites show high conductivity at both room temperature and elevated temperature (Yu et al., 2008).

In 2009, the same research group published the second paper in proton conducting membranes via the polymerization of microemulsions containing nanostructured Protic ILs (PILs) networks. PILs nanostructures formed in the precursor microemulsions could be preserved in the resultant polymeric matrix without macroscopic phase separation, even if the produced vinyl polymers are incompatible with PIL cores.

PLIs were synthesized by mixing of an imidazole derivative with equivalent molar amount of trifluoromethanesulfonic acid using newly the polymerizable surfactantMAUM-Br (Figure 6).

1, R = Me, R1 = H,
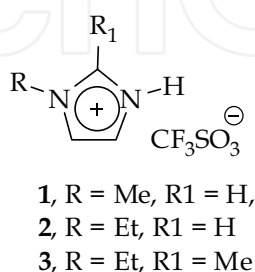**2**, R = Et, R1 = H
3, R = Et, R1 = Me

Fig. 6. Protic ILs employed to prepared proton conducting membranes via the polymerization of microemulsions.

These PIL-based polymer membranes have quite a good thermal stability, chemical stability, tunability, and good mechanical properties. Under nonhumidifying conditions, PIL-based

membranes show a conductivity up to the order of 1×10^{-1} S/cm at 160 °C, due to the well-connected PIL nanochannels preserved in the membrane (Yan et al., 2009).

5. Another applications

5.1 Ionic liquids as corrosion inhibitors

The use of corrosion inhibitors (CIs) constitutes one of the most economical way to mitigate the corrosion rate and to protect metal surface against corrosion and preserve industrial facilities (Sastri, 2008, Revie & Uhlig, 2008). The role of inhibitors added in low concentrations to corrosive media, is to delay the reaction of the metal with the corrosive species in the medium. The CIs act by adsorption of ions or molecules onto the metal surface. They generally reduce the corrosion rate by blocking of the anodic and/or cathodic reaction.

The treatment of mild steel corrosion through organic compounds has resulted in considerable savings to the oil industry. Several families of organic compounds, i.e. fatty amides (Olivares-Xometl et al., 2006 and 2008), pyridines (Abd El-Maksoud & Fouda, 2005, Ergun et al., 2008, Noor, 2009), imidazolines (García et al., 2004, Martínez-Palou et al., 2004, Olivares-Xometl et al., 2009, Liu et al., 2009) and other 1,3-azoles (Likhanova et al., 2007, Popova et al., 2007, Antonijevic et al., 2009) have showed excellent performance as CIs; however, the majority of these compounds are toxic and they are not in according with the environmental protection standards. By this reason, in the last years big efforts have been made by the researchers on this area to develop new environmental friendly CIs (Muthukumar et al., 2007).

ILs present a property structure suitable to absorb on metal surfaces and some compounds of the family had probed that they can form a protective coating over different metal surface again corrosive mediums as aqueous HCl [a-b. Zhang & Hua, 2009, Ashassi-Sorkhabi & Es'haghi, 2009) and H_2SO_4 (Perez-Navarrete et al., 2010, Morad et al., 2008, Saleh & Atias, 2010).

Likhanova et al. have published recently a paper about the inhibitory action of 1,3-dioctadecylimidazolium bromide (ImDC$_{18}$Br) and *N*-octadecylpyridinium bromide (PyC$_{18}$Br) in 1 M H_2SO_4 on mild steel at room temperature was investigated. The effect of the concentration of inhibitor compounds was investigated by electrochemical tests, whereas the surface analysis techniques were performed at 100 ppm for both compounds. In the case of ImDC$_{18}$Br, corrosion products were additionally studied by X-ray diffraction and Mössbauer spectroscopy. The results revealed that ILs act as corrosion inhibitors with 82–88% at 100 ppm to protect the mild steel corrosion in the aqueous solution of sulfuric acid; their efficiencies are increased with the inhibitor concentration in the range 10–100 ppm. ImDC$_{18}$Br provided a better inhibition effect than PyC$_{18}$Br, which may be attributed to the larger esteric body of ImDC$_{18}$Br in comparison to PyC$_{18}$Br, which results in a higher surface coverage area during the chemical adsorption process. These compounds affected both anodic and cathodic reactions so they are classified as mixed type inhibitors. Chemisorption of these inhibitors on the mild steel surface followed the Langmuir's isotherm. SEM-EDX, XRD and Mössbauer analysis indicated the presence of carbon species and iron sulfates in the presence of ILs; whereas corrosion products such as iron oxyhydroxides were present in the absence of the ILs (Likhanova et al., 2010).

The same research group have submitted recently a paper en where five imidazolium-type ILs containing N1-insatured chain and N3-long alkyl saturated chains as cation and bromide as anion were synthesized and evaluated as CIs for acid environment (Table 1). Weight loss test and electrochemical polarization technique were used to test the inhibitory properties of these compounds against AISI 1018 carbon steel corrosion in acidic media. These ILs showed inhibitory properties and the inhibition depends on the long chain size linked to N3, as was also evidenced by SEM/EDS and AFM images (Figure 7) (Guzmán-Lucero et al., 2010).

          (a)   (b)   (c)
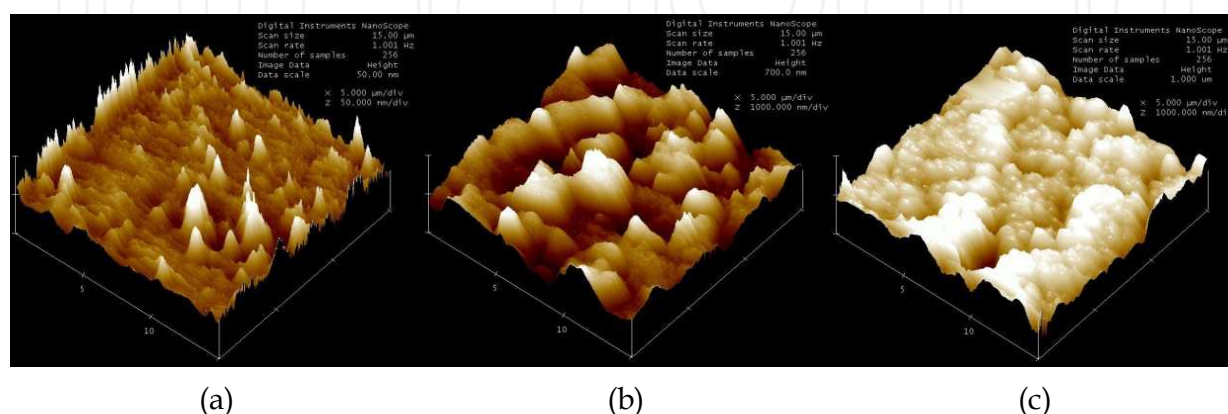
Fig. 7. Three-dimensional AFM images (at *data scale* = 50.0 nm) of (a) coupon after polish, (b) coupon after a 6 hour immersion in the corrosive media without inhibitor (at *data scale* = 700.0 nm), (c) coupon after a 6 hour immersion in the corrosive media containing 6 ppm of IL4 (at *data scale* = 1.0 µm).

ILs have also been employed to prepare a protective aluminium thin layer on carbon steel surface by electroreduction and electrodeposition of 1-butyl-3methyl-imidazolium chloroaluminate (AlCl$_3$/[BMIM]Cl) (Caporali et al., 2008, Yue et al., 2009).

5.2 Ionic liquids as demusifier agents

Crude oil containing brine generally results in the formation of stable water-in-oil (W/O) emulsions when turbulent mixing conditions are encountered during the transportation process. The dispersion of water droplets in oil is facilitated by the presence of interfacial active agents in the crude oil such as asphaltenes, waxes, resins and naphthenic acid (Schramm, 1992). The quantity of these natural emulsifiers is more abundant in heavy than in light crude oils and, thus, the formation of more stable emulsions in heavy crude oils (Kokal, 2005).

The crude oils should be desalted and dewatered before refining because salts produce enormous corrosion problems, they are poison for the catalysts in refining and reduce the efficiency of energy exchanging, and increase the oilflow resistance and even obstruct the pipes.

The process of desalting in Oil Refining Process usually involves addition 1–20% (w.) of wash water to the crude oil, mixing to form a W/O emulsion and then subjecting the emulsion to electrostatic demulsification or hydrocyclone treatment (Goyal, 1993, Varadaraj et al., 2001). Most crude oils that contain asphaltenes and naphthenic acids, especially heavy crude oils form marine environments trend to form stable W/O emulsions, which are complex scattered systems (Kumar et al., 2001).

Chemical demulsification by adding surfactant demulsifiers is still one of the most frequently applied industrial method to break the crude oil emulsions (Sjöblom et al., 2001). This process can be very difficult and non-efficient to demulsify W/O emulsions of heavy viscous crude oils, and it takes a long time.

Commercial demulsifiers are polymeric surfactants such as block copolymers of polyoxyethylene (EO) and polyoxypropylene (OP) (**1**) or alkylphenol-formaldehyde resins (**2**), or blends of different surface-active compounds and polyfunctionalized amines with EO/PO copolymer (**3**, Figure 8) (Kokal, 2005).
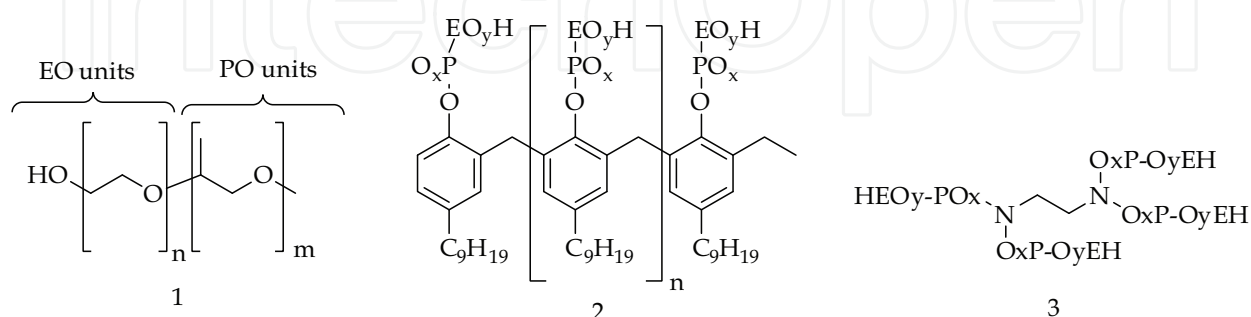

Fig. 8. Demulsifiers to break W/O emulsions.

The application of microwave irradiation to break a W/O emulsion was described for the first time in 1995 (Fang, 1995) and in the last decade has been studied by several research groups (Xia et al., 2002, a-b. Xia et al., 2004, a-c. Nour and Yunus, 2006, Fortuny et al., 2007).

Recently, ILs were described as demulsifier agents for W/O emulsions. In this 2010 paper ten amphiphilic ILs were synthesized and evaluated fas demulsification agents employing three emulsion of Mexican crude oils (medium: 29.59°API, heavy: 21.27 and ultra-heavy, 9.88°API). The ILs studied can act as demulsifiers in medium crude oils and, in some cases, in heavy crude oils at 1000 ppm after 10 hours of heating at 80°C. W/O emulsion from ultra-heavy crude oil was broken only by Trioctylmethylammonium chloride and its performance dramatically increased when it was carried out in conjunction with microwave irradiation (Guzmán-Lucero et al., 2010).

Lemos et al., investigated the role of two type of ILs ([OMIM]BF_4 and [OMIM]PF_6) as demulsifier agents of high stable W/O emulsions in conjunction with microwave irradiation. The stable emulsion was prepared from a Brazileam crude oil (23.3° API) and distilled water or brine solutions ([NaCl] = 50 g.dm^{-3}). The microwave experiments were always much faster and efficient than under conventional heating; however, Black test without ILs have not produce water separation, while the simultaneous use of ILs under microwave hesating allows the demulsification with higher efficiency at shorter time (Lemos et al., 2010).

5.3 Ionic liquids-assisted biodiesel synthesis

Biodiesel is a mixture of fatty acid methyl esters (FAMEs) which are produced from a broad range of crude oil materials, such as vegetable oil, animal fats, and waste oil, via transesterification of triglycerides with methanol or ethanol. Biodiesel has been regarded as a promising fuel to be able to partly substitute for conventional fossil diesel since it is obtained from renewable sources and for their environmental friendly properties like biodegradability and very low toxicity, lower particulate emissions and increased lubricity and provides a means to recycle CO_2 (Kim & Dale, 2005, Ryan et al., 2006).

The traditional route to perform the transesterification of triglycerides from vegetal oils, animal fats with an alcohol under homogeneous chemical catalysis at around 80 °C using a base (usually NaOH or KOH) or acid (generally H_2SO_4) as catalyst, but the application of these synthetic methods present environment problems such as corrosion and emulsification formation, difficulties to separate the catalyst from the final product and the generation of toxic effluents associated with these methodologies (Antolín et al., 2002). Some alternative to minimize these problems have recently been investigated, such as heterogeneous catalysts, enzymatic catalysis, application of organic bases, supercritical fluids, biphasic and multiphasic systems (Helwani et al., 2009).

The ILs could have several applications for biodiesel synthesis as described in Figure 9.

[Earle et al., 2009, Chen et al., 2009, Han et al., 2009, Liang, X. et al., 2009 & 2010]

ILs as catalyst

ILs as solvent

ILs applications in biodiesel synthesis

ILs as support of the catalyst

[Lapis et al., 2008, Neto et al., 2007, Crocker, 2007]

[Muriell et al., 2008]

ILs-assisted enzimatic biodiesel synthesis

Immobilization of metal complexes in ILs

[Rusich et al, 2010, Zhao et al., 2010, Arai et al., 2010]   [Dupont et al., 2000, Neto et al., 2006]

Fig. 9. Applications of ILs in biodiesel synthesis.

Wu et al. showed that some ILs could act as very efficient catalyst for the green synthesis of biodiesel. In this paper the transesterification of cottonseed oil with methanol to biodiesel was carried out in the presence of various Brønsted acidic ILs catalysts. 1-(4-Sulfonic acid)butylpyridinium hydrogen sulfate showed the best catalytic performance, confirmed that the catalytic activity of the ILs is dependent on its Brønsted acidic strength. Increased Brønsted acidity gave improved catalytic activity. Compared with conventional liquid and solid acid catalysts, ILs exhibit many outstanding advantages, such as high catalytic activity, excellent stability, easy product isolation, and environmental benefits. Brønsted acidic ILs have potential application in the production of biodiesel (Wu et al., 2006 and 2007). After this work, some other papers describing the catalytic effect of the ILs have been published as was described in Figure 9.

The catalysis of ammonium-based protic and Brønsted ILs for biodiesel synthesis under microwave dielectric heating has been investigated. Ammonium-based ILs. According with

the results, biodiesel can be obtained very fast and with high purity using these ILs. The application of microwave dielectric heating in conjunction with ILs as catalyst not only reduces considerably reaction time and simplifies the reaction hangling, but also permits the access to an environmental friendly procedure for biodiesel production (Flores et al., 2010).

In addition to the known application of ILs as solvent for chemically catalyzed transesterification, ILs can act as a solvent in ezymatic synthesis to enhance the dissolving of reactants and as an immobilization agent for enzymes, such as lipase. The IL forms a strong ionic matrix, therefore creating an adequate microenvironment for the catalyst to remain active.

Ha et al. screened several types of ILs in a lipase-catalyzed transesterification reaction using soybean oil and methanol. Results indicated that the use of hydrophobic ILs, yielded higher percent conversions as compared to solvent-free systems (Ha et al., 2007).

Very recently Ha et al. studied the continuous production and *in situ* separation of biodiesel using ILs through immobilized *Candida antarctica* lipase-catalyzed methanolysis of soybean oil. A screening of twenty three ILs was carried out, obtaining the best results with [EMIM]TfO after 12 hours at 50 °C. The production yield of 80% was eight times higher compared to the conventional solvent-free system (Ha et al., 2010).

Ruzzi and Bassi introduced the use of methyl acetate as the acyl acceptor in the place of the more commonly used methanol due to the negative effects methanol and the glycerol by-product has on lipase enzyme activity. The results of this research indicated that biodiesel was successfully produced, with an 80% overall biodiesel yield in the presence of [BMIM]PF$_6$, at a 1:1 ratio (v/v) to the amount of oil and the addition of IL facilitated the separation of the methyl esters from the triacetylglycerol by-product (a. Ruzich & Bassi, 2010).

The same authors, had investigated different reactor configurations for biodiesel production from triolein. These included shake flask or 500 mL jacketed conical reactors with two different configurations. Recycling and reuse of the lipase and IL was also examined, as well as the separation of products (b. Ruzich & Bassi, 2010).

Bioethanol is also a biofuel with high perspectives of wide applicacion as non-fossil fuel, since it has a high octane and their use reduces the green house gas emission. Bioethanol can be produced from cellulosic materials. Pretreatment of cellulosic materials is a prerequisite to facilitate the release of sugars from a lignocellulosic biomass prior to fermentation recovery of bio-digestible cellulose from a lignocellulosic byproduct. Recently, some pretreatment methods have been tried with ILs which has showed a considerable increasement hydrolysis rate respect with the process without ILs and to develop an eficient process to recovery of bio-digestible cellulose from a lignocellulosic byproduct (Clark et al., 2009, Nguyen et al., 2010, Jones & Vasudevan, 2010, Bose et al., 2010, Yang et al., 2010, Simmons et al., 2010).

5.4 Ionic liquids as catalyst of alkylation gasolines

One of the most important reactions in the petroleum industry is the isoparaffin-olefin alkylation for producing alkylated gasoline with a high content of isooctane (Albright, 2009). This process is industrially carried out employing an acid catalyst, in most of the cases sulfuric or hydrofluoric acid, because the reaction is quick, clean and with high yield of alkylated gasoline (Olah & Molnar, 1995). The general reaction to obtain alkylated gasolines is showed in Figure 10.
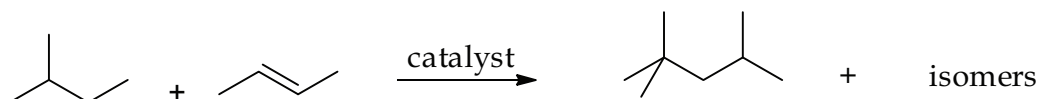
Fig. 10. Scheme of isoparaffin-olefin alkylation reaction.

Alkylated gasoline is a high-quality product from oil industry. The alkylate contains no olefins or aromatics but consists exclusively of isoalkanes. It has a low vapor pressure and a high octane number. In several time this gasoline contains fluoride traces due to inefficient catalyst remotion (Corma & Martínez, 1993).

The HF is a good and cheap catalyst for isobutene alkylation, however its use caused significant concern because its high vapors pressure and tendency to form aerosol. The fluoride anion is highly toxic and ecological problems are generated when fluoride is not completely removed after the alkylation reaction (Weitkamp & Traa, 1999).

Many efforts have been made to introduce new developments relating to established technologies and properly new technologies (Hommeltoft, 2001) and other catalysts have been evaluated as alternative for this process, such as solid materials like zeolites and Lewis and Brønsted acid in different solid supports (Feller et al., 2003, Feller et al., 2004, Feller & Lercher, 2004, Platon & Thomson, 2005, Thompson & Ginosar, 2005, Guzmán et al., 2006), heteropolyacids (Zhao et al., 2000) and Nafion silica nanocomposite (Kumar et al., 2006, a-b. Shen et al., 2010).

ILs being environmentally benign reaction media, open up exciting challenges and opportunities to clean catalytic processes. Since 1994, Chauvin et al. suggested the idea of employ Lewis acidic ILs as an alternative catalyst for alkylation reaction (Chauvin et al., 1994), but after this first effort several paper describing the application of supported and non-supported ILs catalysts have been published (Huang et al., 2004, Yoo et al., 2004, Kumar et al., 2006, Zhang et al., 2007, Tang et al., 2009).

Frech Petroleum Institute has applied acidic chloroaluminates ILs for the alkylation of isobutane with 2-butene or ethylene in a continuous-flow pilot plant operation, showing that [pyridine,HCl]/AlCl$_3$ (1:2 molar ratio) was the best catalyst in the case of ethylene. The reaction can be run at room temperature and provides good quality alkylate (2,3-dimethylbutane is the major product) over a period of 300 h with a Motor Octane Number (MOM) of 90-94 and a research octane number (RON) of 98–101. In the case of butenes, a lower temperature and a fine tuning of the ILs acidity are required to avoid cracking reactions and heavy by-product formation. The continuous butene alkylation has been performed for more than 500 h with no loss of activity and stable selectivity (80–90% isooctanes are obtained containing more than 90% trimethylpentanes (TMP); MON = 90–95; RON = 95-98) (Olivier-Bourbigou, 2005).

Chinesse reserchers from Petrochina and China University of Petroleum, develovep a very efficient process called "*Ionokylation*" for gasoline alkylation using a mixture of chloroaluminate-IL with CuCl as catalyst. The process was compared with the typical processes catalyzed by HF and H$_2$SO$_4$ showing significant advantages and higher RON, MOM and trimethylpentanes content was obtained. Ionikylation was probed at pilot plant scale demonstrated the high stability of this catalyst through 8 months ageing test before 60 days of operation. The alkylation reaction was performed at 15 °C and 0.4 MPa. During the pilot test period, olefin conversion was more than 99%. The C8 yield in alkylate gasoline was higher than 95% and the yield of TMP was 90%.

Another interesting alternative of new environmentally safe for isobutane-olefin alkylation was develop by Olah et al. They developed an immobilized liquid and solid modified HF catalysts. Being ionic complexes of amines and anhydrous HF, the IL compositions are efficient media and HF equivalent catalysts for alkylations. They decrease the volatility of anhydrous HF and as a result, HF release to the atmosphere in case of accidents is decreased allowing easy neutralization. The handling, use, recycling and regeneration of the catalysts are convenient. Both the liquid and solid polymer based poly(hydrogen fluoride) catalysts (Figure 11) in a ratio 22:1 of HF:pyridine can be advantageously applied in alkylation process representing environmentally benign and safer conditions readily adaptable to the existing refinery alkylation units (Olah et al., 2005).
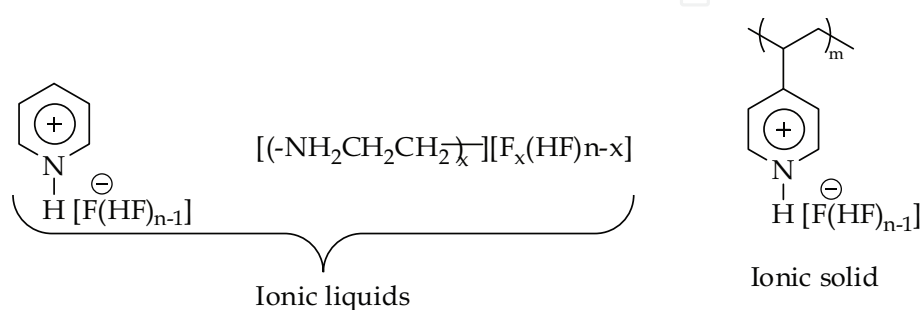

Fig. 11. Structure of liquid and solid polymer based poly(hydrogen fluoride) studied by Olah et al.

More recently the catalytic performance of 1-n-octyl-3-methylimidazolium bromide aluminium chloride ([OMIM]Br-AlCl$_3$) based ILs was investigated for the alkylation of isobutane and 2-butene. The acidity of the IL was modified by addition of water, acid cation exchange resins or 1-(4-sulfobutyl)-3-methylimidazolium hydrogensulfate [(HO$_3$SBu)MIM]HSO$_4$. The activity, selectivity and deactivation behaviour with and without additives were studied in order to find the best catalytic composition. Accroding with their results, the [OMIM]Br/AlCl$_3$/Amberlyst-15 resin (surface acid concentration: 0.11 meq.) catalyst yielded of trimethylpentanes (up to 64%) and thus a high RON up to 96, higher than that with H$_2$SO$_4$ as the alkylation catalyst. Thus, the approach to control the Brønsted acidity by forming superacidic IL species or superacidic species in ILs *via* protic additives is promising. In all cases, the products were separated simply by decantation, and thus the catalyst can be reused. Moreover, the formation of acid soluble heavy hydrocarbons is minimised (Thi et al., 2009).

5.5 Ionic liquids in other catalytic processes

ILs have been explored as solvents and catalysts in different petrochemical processes. Several examples of catalisys in both, homogeneous and biphasic reactions using supported ILs have been published. In Table 3, some recent results described in the scientific literature are showed.

Recently Olivier-Bourbigou published an excellent review about ILs as solvent and catalysts for chemical industry, including petrochemical processes where these topics are discussed in details (Olivier-Bourbigou, 2010).

Reference	ILs employed	Application	Observations
(Atkins et al., 2002)	Chloroaluminate ILs as liquid acid catalyst	Ethylbenzene production. Alkylation of benzene with ethylene	This biphasic alternatives led to the use of chloroaluminate Ils based on imidazolium cation (ex: [EMI][Cl]/AlCl₃ or [HNMe₃][Cl]/AlCl₃ in a 1:2 molar ratio). In a very detailed study based on bench-scale experiments.
(Olivier-Bourbigou & Lecocq, 2003)	Chloroaluminate ILs and Ni(COD)(2) with a Brønsted acid ILs	Biphasic ethylene oligomerization or butene and higher olefins dimerization (Difasol™ process).	These solvents stabilize and activate nickel catalysts, even without ligand, and greatly enhance the reaction activity. The presence of a diimine ligand allows the production of C4-C6 linear olefins with improved alpha-selectivities.
(Zubin et al., 2007)	Three type of Chloroaluminate ILs from hydrochloride of Et₃N, BuPy and BMIM as cation were evaluated as acid catalyst	Olefin reduction in FCC gasoline	The olefin content was reduced in more than 30% after 30 minutes under mild conditions in a ratio IL/oil of 20/100 (w/w).
(Lecocq & Olivier-Bourbigou, 2007)	Chloroaluminate ILs	Biphasic Ni-Catalyzed Ethylene Oligomerization in ILs	Chloroaluminate ILs are highly active catalysts either for the biphasic ethylene oligomerization or for polymerization depending on the bulkiness of the diimine ligand. The activation of Ni(0) with a Brønsted acid in different non-chloroaluminate ILs is also reported. The nickel catalysts are immobilized and stabilized in the Ils and can be recycled.
(Schmidt et al., 2008)	N-butyl-N-methylimidazolium tetracholroaluminate on silica	Olefins disproportionation	Acidic ILs absorbed on silica could potentially catalyze disproportionation reactions more selectively at more favorable conditions.

Reference	ILs employed	Application	Observations
			At low temperatures, silica-supported ILs disproportionated iC_5 attaining up to 65 wt % feed conversion. The optimal temperature operating window was narrow between 80 and 130 °C.
(Magna et al., 2009)	The Brønsted acidity level was evaluated for ILs by means UV: [BMIM] similar to [BHIM] similar to [HNEt$_3$]), whereas changing the nature of the anion of the ionic liquid may lead to very different acidities ([SbF$_6$] > [PF$_6$] > [BF$_4$] > [NTf$_2$] > [OTf]).	Selective Isobutene Dimerization	By an adequate choice of the IL, selectivity for isobutene dimers can reach 88 wt% (at 70% isobutene conversion) with possible recycling of the catalytic system without loss of activity and selectivity. The "acidity scale" was tentatively compared with an "activity scale" obtained for the dimerization of isobutene into isooctenes.
(Gilbert et al., 2009)	EtAlCl$_2$/AlCl$_3$	Olefine dimerization by Difasol™ process, a biphasic analogue of the Dimersol-X™ process	The Difasol™ process produces mixtures of low branched octenes which are good starting materials for isononanol production (intermediates in the plasticizer industry). The reaction takes place with nickel catalyst precursor using chloroaluminate ILs, acting as both solvent and co-catalyst. The best results were obtained from [BMIM][Cl]/AlCl$_3$/EtAlCl$_2$ (1:1.2:0.11) mixtures.

Table 5. Application of ILs in other catalytic processes.

5.6 Ionic liquids as hypergolic fuels

A mixture of two compounds (fuel-oxidixer) is called hypergolic when the propellants ignite spontaneously on contact. The terms "hypergolic propellant" are often used to mean the most common propellant combination, hydrazine/dinitrogen tetroxide or similar. Hypergolic rockets do not need an ignition system.

Hydrazine and its derivatives such as monomethylhydrazine and unsymmetrical dimethyl hydrazine have been extensively studied as hypergolic fuel, but these substances are highly

toxics, corrosives and difficult to handles. For these reasons, it is desirable to replace hydrazine derivatives with greener hypergolic fuels.

The design and synthesis of ILs based on energetic materials provide a powerful methodology in the development of a new type of hypergolic fuel. A variety of multinitrogenated ILs have showed good candidates as hypergolic fuels such as, methylated derivatives of hydrazinium azides (Hammerl et al., 2001), Urotropinium salts with nitrogenated conter ions (Fraenk et al., 2002), triazolium and tetrazolium-based ILs (Galvez-Ruiz et al., 2005, Singh et al., 2006), ILs containing azide and dicyanamide anions (a-c. Schneider et al., 2008,), ILs containing 2,2-dialkyltriazanium cation (Gao et al., 2009), nitrocyanamide deriviaties (He et al., 2010), *N,N*-Dimethylhydrazinium (a. Zhang et al., 2010).

Joo et al., have also synthesized new azide-functionalized ILs like II and III by metathesis reaction from bis(2-azidoethyl)dimethylammonium iodide (I) as candidates to replace the highly toxic hydrazine and its hypergolic derivatives (Figure 11). The relationship between their structures and melting points, thermal stabilities, densities, standard enthalpies of formation, and specific impulse was determined. The high heat of formation of the azide functional group can be used for fine-tuning the energy content, and thus the performance of the hypergolic ILs (Joo et al., 2010).
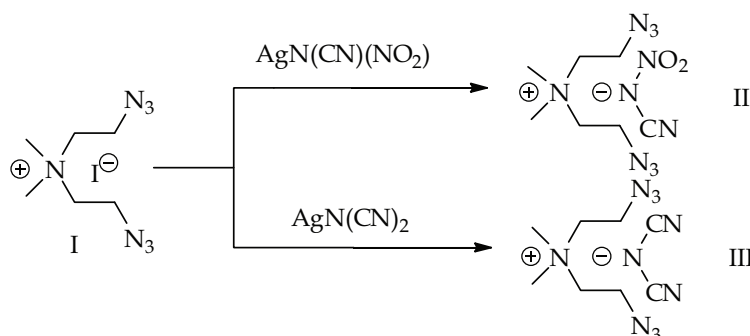
Fig. 11. New azide-functionalized hypergolic ILs.

The interesting properties of the hypergolic ILs have motivated a theoretical studies based on Density Functional Theory (Gao et al., 2007, b. Zhang et al., 2010). Heats of formation coupled with densities can be used further for predicting the detonation pressures and velocities and specific impulses of energetic salts for the rational design of hypergolic ILs.

6. Conclusions y future perspectives

Evidently ILs shows very attractive properties for their application in Petroleum Industry and in renewable energy sources. From this stands ILs have a good chance of becoming the process of choice in the future for different application; however, in many cases a long way is necessary to road for utilizing these technologies in industrial scale.

From an academic point of view, many applications using ILs results very attractive; however, in practice such results are difficult to apply for many reasons, such as economy, product disponibility, ILs stablility, lost of activity during recycling and additional equipments required.

Several factors have made it difficult to introduce a new technology because new equipments and significant process engine changes are required and also because the economically competitive new technology has not been demonstrated. No matter how environmentally friendly or safe a new technology may be, it has to be economically competitive as well as reliable.

For the industrial use of ILs, some major issues must be addressed such as IL synthesis scale-up, purity, stability, toxicity, recycling, disposal and price and may constitute barriers to IL process commercialisation. The IL price must be related to the process performance and to overall economy.

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