

# 1 Ionic Liquid and Petrochemistry: A Patent Survey

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## ABSTRACT

Industrial applications of ionic liquids in petrochemistry have been reviewed through the US and EP granted patents published from 1990 to 2010. A *Chemical Abstracts* search on the STN host retrieved about 300 patents, about 130 of them found relevant and are fully analysed in this chapter. This survey has been divided into six thematic sections: new formulations and methods of fabrication for an improved use of ionic liquids; separation processes using ionic liquids; use of ionic liquids as additives with specific properties; use of ionic liquids as both acidic catalysts and solvents; applications of ionic liquids as solvents of catalytic systems; and ionic liquids and biopolymers. Our study has been complemented by a short description of the emerging areas concerning ionic liquids using the patent applications published during the past five years.

## 1.1 INTRODUCTION

Interest in ionic liquids has been growing rapidly worldwide, as demonstrated by the increasing number of publications and patents these last years. The applications and the prospects for ionic liquids are vast. In the chemical and

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petrochemical industries, numerous applications and benefits of using ionic liquids have been described. However, it is difficult to know which applications have been translated into viable industrial and commercialised processes.

As news releases and scientific publications are a part of company strategic communication, relevant information is difficult to assess. We assumed that granted patents could be one of the most relevant sources of information. From our perspective, companies generally only devote human resources, and pay all the necessary fees to have their patents granted, if they expect an actual industrial development of the claimed invention.

A bibliographic search was performed on the *Chemical Abstracts* database using the STN host. It retrieved about 4000 patent families dealing with “ionic liquids.” Among these patent families, about 500 contain a US or EP granted patent during the period from 1990 to 2010. After a keyword restrictive search to the petrochemicals and oil area, we selected about 300 documents. We then fully analysed the most relevant documents, and these are reported in this chapter.

## 1.2 NEW FORMULATIONS AND METHODS OF FABRICATION FOR AN IMPROVED USE OF IONIC LIQUIDS

In recent patents, improved ionic liquid formulations and new mode of preparations have been disclosed. Some ionic liquids have been claimed as new products. The aim of these inventions is generally to provide either new cations or new anions or both for ionic liquids with higher purity, such as halogen-free ionic liquids. These formulations are claimed to be advantageous when ionic liquids are used as solvents in catalytic reactions. The most cited reactions are hydroformylation, hydrogenation, and oligomerisation or isomerisation. It appeared to be of interest to review here these new ionic liquids and their preparation processes.

### 1.2.1 Alkyl Sulfate Ionic Liquids

Several patents devoted to halogen-free ionic liquid synthesis, mainly based on sulfate anions, have been filed by Merck GmbH or Solvent Innovation. In these patents [1], the use of onium alkyl sulfate ( $[C_nSO_4]^-$ ;  $n = 3 - 36$ ) salts is claimed in various processes, including their use as solvents for catalytic reactions, such as hydroformylation, hydrogenation, oligomerisation, and isomerisation. Sulfate ionic liquids are described as being more friendly than halide ionic liquids, which often lead to corrosion and/or disposal issues. In particular, long chain alkyl sulfate ionic liquids are preferably claimed thanks to their improved stability to hydrolysis compared with the methyl sulfate analogues. Examples give a comparative hydrolysis stability study of 1-butyl-3-methylimidazolium methyl sulfate,  $[C_4mim][C_1SO_4]$ , and 1-butyl-3-methylimidazolium octyl sulfate,  $[C_4mim][C_8SO_4]$ . At 80 °C, the octyl sulfate

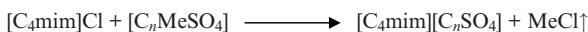
is stable for more than 2 hours, whereas methyl sulfate exhibits rapid degradation. These long chain 1,3-dialkylimidazolium alkyl sulfates are prepared through ion exchange process between 1,3-dialkylimidazolium chloride and sodium alkyl sulfate salts.

New imidazolium and pyridinium ionic liquids bearing anions of general formula  $[\text{Me}(\text{OCH}_2\text{CH}_2)_n\text{OSO}_3]^-$  or  $[\text{Me}(\text{OCH}_2\text{CH}_2)_n\text{SO}_3]^-$  are also reported [2]. These sulfates and sulfonates are claimed to be more stable to hydrolysis than their methyl sulfate analogues, and to have higher thermal stability. Examples show a comparative hydrolysis stability study of 1-butyl-3-methylimidazoliummethyl sulfate and  $[\text{C}_8\text{mim}][\text{Me}(\text{OCH}_2\text{CH}_2)_2\text{OSO}_3]$ . As previously described, these imidazolium sulfates and sulfonates are prepared through ion exchange processes between 1,3-dialkylimidazolium chloride and  $[\text{Me}(\text{OCH}_2\text{CH}_2)_n\text{OSO}_3]^-$  or  $[\text{Me}(\text{OCH}_2\text{CH}_2)_n\text{SO}_3]^-$  salts, respectively. The application of  $[\text{C}_4\text{mim}][\text{Me}(\text{OCH}_2\text{CH}_2)_2\text{OSO}_3]$  to hydroformylation of 1-octene with  $[\text{Rh}(\text{acac})(\text{CO})_2]$  (Hacac = pentane-2,4-dione) pre-catalyst was illustrated.

A new scalable process to prepare high-purity imidazolium or pyridinium alkyl sulfates containing less than 3 ppm of halide contaminant has been granted [3]. This process includes the step of treating a compound of formula  $[\text{cation}][(\text{RO})\text{SO}_3]$  with an alcohol  $\text{R}'\text{OH}$  to give  $[\text{cation}][(\text{R}'\text{O})\text{SO}_3]$ . Compounds of formula  $[\text{cation}][(\text{RO})\text{SO}_3]$  can be prepared by alkylating a tertiary or aromatic amine with a dialkyl sulfate. As described in the examples, dimethyl sulfate can be used to prepare  $[\text{Rmim}][(\text{MeO})\text{SO}_3]$  ionic liquids, which are then treated with  $\text{R}'\text{OH}$  to give  $[\text{Rmim}][(\text{R}'\text{O})\text{SO}_3]$  ionic liquids. A wide variety of  $\text{R}'\text{OH}$  alcohols may be used, such as long alkyl chain alcohols or alkyl chains containing heteroatoms:



Merck GmbH describes an alternative route to onium alkyl sulfates [4, 5] by the reaction of an onium halide with a symmetrical dialkyl sulfate ( $[(\text{C}_n)_2\text{SO}_4]$ ;  $n = 1 - 14$ ) or an asymmetrical dialkyl sulfate ( $[(\text{C}_n)(\text{C}_m)\text{SO}_4]$ ;  $n = 1$  or  $2$ ,  $m = 4 - 20$ ). Halogen can be removed as a volatile haloalkane, leading to low levels of halogen contaminant in the corresponding ionic liquids.



This method has been extended to a large number of reactants: fluorinated alkyl sulfates, alkyl trialkylsilyl sulfates, alkyl acyl sulfates, alkyl sulfonyl sulfates, aryl or alkyl carboxylic acids, and anhydrides [4, 5].

Onium alkyl sulfates have also been used as starting material to prepare other onium ionic liquids. A patent by Wasserscheid et al., granted in 2004 [6], claims the preparation of various onium salts by anion exchange of an onium alkyl sulfate with metal salts. The alkyl sulfates are prepared by alkylation of the corresponding amines or phosphines with dialkyl sulfates.

Patent examples describe the reaction of 1,3-dialkylimidazolium alkyl sulfates with various alkaline salts. The illustrated anions are  $[\text{BF}_4]^-$ ,  $[\text{PF}_6]^-$ ,  $[\text{CF}_3\text{CO}_2]^-$ ,  $[\text{CF}_3\text{SO}_3]^-$ ,  $[\text{C}_4\text{F}_9\text{SO}_3]^-$ , and  $[\text{N}(\text{CF}_3\text{SO}_2)_2]^-$ . The preparation of a pyridinium hexafluorophosphate is also given.

BASF describes the reaction of dialkyl sulfates with 2.2 moles of alkylimidazoles in water or methanol at  $180^\circ\text{C}$  for 6 hours under pressure, to prepare the corresponding 1,3-dialkylimidazolium sulfates in good yields (80–90%). This halogen-free process has been claimed, and broadened to pyridine derivatives [7]. These onium sulfates may react with various metal salts to give a wide range of onium ionic liquids such as ethanoate, tetraphenylborate, dihydrogenphosphate, and ordihydrogenborate.

Phosphonium alkyl sulfates are claimed as new products by Cytec [8]. The preparation process involves the alkylation of trialkylphosphines with a symmetrical dialkyl sulfate without solvent at  $140\text{--}190^\circ\text{C}$  for several hours. This preparation procedure has been broadened to the reaction between trialkylphosphates and trialkylphosphines or alkylimidazoles. The obtained onium phosphates are also claimed as new products.

## 1.2.2 Other Ionic Liquids

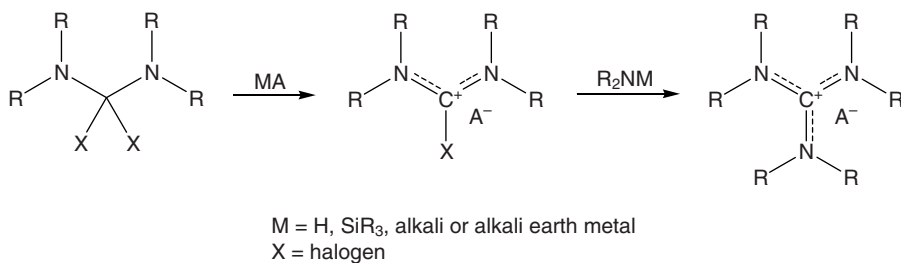
**1.2.2.1 Ionic Liquids with Phosphorus-Containing Anions.** In two patents [9, 10] devoted to perfluoroalkyl phosphorus derivatives, Merck GmbH claims onium bis(perfluoroalkyl) phosphinates and perfluoroalkyl phosphonates as new ionic liquids. These compounds are prepared by anion exchange between an onium halide and the phosphorus-containing acid or its salts. Examples describe the preparation of both phosphonium and imidazolium ionic liquids using such a process.

**1.2.2.2 Alkylpyridinium Dicyanamide.** Lonza claims alkylpyridinium dicyanamides as new products [11]. These compounds are prepared through ion exchange between an alkylpyridinium halide and an alkali dicyanamide. Among the claimed applications of these new ionic liquids is their use as reaction solvents, particularly as solvents for Suzuki reactions.

**1.2.2.3 Ionic Liquids with Cyanoborate Anions.** Oniumtetracyanoborates are described as being more stable than the corresponding tetrafluoroborate salts and thus they may be used as ionic liquids. Merck GmbH claims an effective and economical process for preparing these tetracyanoborates,  $[\text{B}(\text{CN})_4]^-$  [12]. In the first step, an alkali metal tetrafluoroborate is reacted with an alkali metal cyanide in the solid state at  $100\text{--}500^\circ\text{C}$ , optionally in the presence of a

lithium halide. The obtained alkali metal tetracyanoborate is then reacted with an onium halide to give the expected onium tetracyanoborate. Examples include ammonium, phosphonium, imidazolium, and pyridinium tetrafluoroborate preparations. This patent furthermore relates to a process for oniumfluorocyanoborate preparation.

**1.2.2.4 Guanidinium Ionic Liquids.** Merck GmbH claims a simple and inexpensive process for the preparation of guanidinium salts ionic liquids, according to Scheme 1.1 [13]:



**Scheme 1.1** Preparation of guanidinium ionic liquids.

This process gives high-purity salts without using a guanidine as starting material, the synthesis of which is frequently complicated and difficult. In the patent examples, only alkyl R groups are described, with a variety of the following anions: [ClO<sub>4</sub>]<sup>-</sup>, [HSO<sub>4</sub>]<sup>-</sup>, [NO<sub>3</sub>]<sup>-</sup>, [CF<sub>3</sub>COO]<sup>-</sup>, [CF<sub>3</sub>SO<sub>3</sub>]<sup>-</sup>, and [N(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>]<sup>-</sup>.

**1.2.2.5 Ionic Liquids with Lactam Cations.** Deng et al. claim protonated NH-lactams as new room temperature ionic liquids [14]. The preparation process of these compounds involves protonation of the corresponding NH-lactam with a Brønsted acid. These new ionic liquids appear advantageous because starting NH-lactams may exhibit a lower toxicity than pyridines or alkyimidazole bases. Furthermore, some of the lactams, such as caprolactam, are industrially available on a very large scale at reasonable costs.

### 1.2.3 High-Purity Ionic Liquids

Usual ionic liquid preparation methods can lead to products containing acids or halide contaminants, which may be detrimental for some applications. In order to obtain high-purity ionic liquids, several processes have been developed.

ExxonMobil proposes a rather simple process in order to remove acidic contaminants [15]. Ionic liquids are prepared by ion exchange with an onium halide in the presence of inert liquids. Depending on the exchange reaction conditions, a decantation or a filtration is sufficient to give a high-purity ionic

liquid phase. Examples describe dialkylimidazolium chloride exchange with various alkali salts such as tetrafluoroborate, hexafluorophosphate, and bis{(trifluoromethyl)sulfonyl}amide.

BASF claims a process for purifying an ionic liquid which comprises partial crystallisation of the ionic liquid, followed by separation of the crystals from the residual melt [16]. This process can be carried out continuously or discontinuously. Examples describe the application of this method to the recycling of used ionic liquids.

Merck GmbH claims a process for the preparation of onium salts having a low chloride content by reaction of an onium chloride with an aqueous solution of Brønsted acid. The hydrochloric acid formed is bound to 1,4-dioxane and can be separated by azeotropic distillation [17]. Examples describe the application of this process to the reaction of alkylpyridinium or dialkylimidazolium chloride with various acids such as  $\text{HBF}_4$ ,  $\text{CF}_3\text{SO}_3\text{H}$ , and  $\text{H}_2\text{SiF}_6$ .

### 1.2.4 Production of Ionic Liquids under Ultrasonication

Roche claims a process for the manufacture of onium ionic liquids by an anion exchange reaction between an onium halide and an acid or a salt, where the reaction is carried out under ultrasound conditions [18]. Preferred ionic liquids prepared according to this process are pyridinium or imidazolium tetrafluoroborates, hexafluorophosphates, or trifluoromethanesulfonates. According to the examples, ultrasonication allows a significant reduction of reaction time.

### 1.2.5 Immobilised Ionic Liquids

ExxonMobil Research and Engineering Company claims [19] a new range of immobilised ionic liquids. These ionic liquids are based on the reaction between a polymeric supports having hydroxy groups on their surface with ionic liquids. The typical reactions involved anchoring the ionic liquid by condensation reactions or by ring opening reactions or more preferably by hydrosilylation reaction through a terminal alkoxysilane group, such as  $\text{Si}(\text{OEt})_3$ , grafted on the cationic part of the ionic liquid. Another alternative pathway can also be the reaction between a double bond present on the polymeric support and a silane Si-H group. A large range of materials is described, but 1,3-dialkylimidazolium is preferred, with one of the alkyl groups bearing an alkoxysilane function at one end. Such materials are applied for catalytic purposes.

## 1.3 SEPARATION PROCESSES USING IONIC LIQUIDS

### 1.3.1 Introduction

More and more attention is given to the use of ionic liquids for separation processes. Their particular property of having no measurable vapour pressure

makes them ideal for separation by extraction. They do not form azeotropes, as usually observed for more common solvents. Polar and ionic compounds are very soluble in ionic liquids, but alkanes and non-polar organic compounds are generally very poorly miscible. This provides an opportunity for applications involving purification processes. Tuning the cations and the anions can modify the solubility properties. Because of the wide range of possible combinations, ionic liquids offer a large area of investigation.

In this section, we will discuss applications for ionic liquids in separation processes based on granted patents. Reported applications are related to several areas such as:

- separation of olefins from hydrocarbon mixtures
- close-boiling mixture treatment
- acid removal from organic mixtures
- sulfur compound elimination from hydrocarbon streams
- natural gas purification
- oxygen- or nitrogen-containing compound separation

### 1.3.2 Separation of Olefins

There are many streams in petroleum chemistry that include mixtures of various alkenes and alkanes. Separation of these products is difficult because of their close-boiling points. Chevron USA Inc. [20] describes a method for selectively separating mono-olefins from di-olefins. The method implies the use of metal salts, typically silver or copper salts, in ionic liquids. Metal salts, such as silver(I) salts, are known to form complexes with di-olefins. Ionic liquids are used in this case to dissolve, suspend, or disperse the olefin-complexing metal salts. The salt  $\text{Ag}[\text{BF}_4]$  dissolved in 1-butyl-3-methylimidazolium tetrafluoroborate exemplifies these separations. The non-complexed olefin can be separated by decantation or distillation. The alkenes are regenerated by separation from the metal complex by temperature, pressure change, or application of a stripping gas such as an inert gas.

Others patents claim that the ionic liquid itself can be an extracting agent. A simplified process that does not require the presence of a metal complex is described in two patents [21, 22] by Oxeno Olefinchemie and Nova Chemicals Society, respectively. The process is preferably used when the mixtures comprise organic compounds with the same number of carbon atoms, for example, for the extraction of butanes from mixtures of butenes and butanes, or for the separation of propene and propane. Liquid-liquid or gas-liquid extraction can be useful processes. Shell discloses an alternative process type for separating olefins from paraffinic hydrocarbons using a supported ionic liquid membrane [23]. This process can be operated under ambient conditions, thus being highly energy efficient and producing very few waste by-products. The supported ionic liquid membrane is prepared by the immersion of a suitable membrane

in an ionic liquid composition. The ionic liquid is drawn into and held within the pores of the membrane by capillary forces. The ionic liquid composition can comprise a metal salt dissolved, dispersed, or suspended. This metal salt is supposed to form complexes with olefinic hydrocarbons. Examples mainly refer to a polycarbonate membrane and an ionic liquid composition comprising a silver(I) nitrate solution with 1-butyl-3-methylimidazolium nitrate.

### 1.3.3 Close-Boiling Mixtures Treatment

BASF discloses broad patents for using ionic liquids as entraining agents in an extraction process to separate azeotropic or close-boiling mixtures or to perform reactive distillation [24–26]. Ionic liquids appear to be more selective than conventional extracting agents. In principle, it allows the possibility of reducing mass flow, or the number of theoretical plates in the extractive column. Examples concern an azeotropic mixture of trimethylborate and methanol. A 1-ethyl-3-methylimidazolium-based salt is used to break the azeotrope and separate the constituents of the mixture. Several mixtures were investigated, all of them dealing with an alcohol-containing mixture (methanol, ethanol, cyclohexanol, or isopropanol). Recovery of the ionic liquid from the extractive distillation and recycling is also described [27]. An integrated process includes the extraction with the use of the ionic liquid, and the evaporation stage for the regeneration of the ionic liquid. This step is performed at low pressure. An alternative possibility is the use of a stripper that is operated through use of inert gas or steam.

### 1.3.4 Acid Removal from Organic Mixtures

**1.3.4.1 Recovery of Hydrochloric Acid.** Ionic liquids are not miscible with certain organics. BASF takes advantage of this property and claims a simplified process to remove acids from reaction mixtures [28]. Examples of reactions in which the process of the invention may be applied include alkylations, silylations, phosphorylations, and sulfurisations, or whatever process produces an acid as a by-product. Usually, an auxiliary base is added and forms a salt by reaction with the acid. Salts are generally insoluble and precipitate, so that they form suspensions that are more difficult to handle and separate. BASF has commercialised a process to remove HCl by adding a specific compound such as an alkylimidazole. The reaction between the alkylimidazole and HCl leads to the formation of an alkylimidazolium chloride salt ionic liquid. This salt is liquid above 100 °C and is immiscible with the organic phase. A liquid–liquid phase separation is simple from a process-engineering point of view. BASF commercialises this technology, called BASIL™, offering the supply of the 1-alkylimidazole for many reactions where acid scavenging is needed, and offering to recover the used alkylimidazolium salt for recycling. Higher yields are claimed when using this separation technology.

Alternatively, the ionic liquid itself can be a separating agent due to its affinity with the hydrogen chloride. It has been investigated more specifically



for the separation of HCl from phosgene. For example, BASF claims a process [29] in which at least part of the hydrogen chloride is dissolved by contact with an ionic liquid and then separated off. A process scheme illustrates the separation of HCl from phosgene,  $\text{COCl}_2$ , in a tray column and the regeneration of the ionic liquid before returning to the column. The recycling is based on an evaporator stage, where hydrogen chloride is driven off from the solvent. One or more evaporation stages can be used in which different pressure levels can prevail. This case utilises the miscibility property of the 1-ethyl-3-methylimidazolium chloride with HCl over phosgene, the HCl presumably forming the stable  $[\text{HCl}_2]^-$  anion in this process.

Solvay applies a similar approach for the preparation of  $\text{COF}_2$ , organic acid fluorides, or phosphorus(V) fluoride. All these products are useful as raw materials [30]. Hydrochloric acid, produced as a by-product, is usually removed with acid scavengers like amines. The invention is based on the fact that HCl (or HF) is retained in the ionic liquid while  $\text{COF}_2$ ,  $\text{PF}_5$ , or acid fluorides are not. Any suitable device able to favour the contact area can treat the gas mixture. A mixture of ionic liquids is preferred. Cations are chosen from imidazolium derivatives, and anions are chosen between triflate and tosylate anions. Higher selectivity is evidenced using ionic liquids over ethanenitrile solvent. The constituents retained in the ionic liquid can be recovered in a reconditioning treatment, by application of a vacuum, heating, or passing inert gases through the ionic liquid. The desorption temperature is preferably not higher than  $100^\circ\text{C}$ . In the case of a vacuum, 1 mbar is a preferred limit. Depressurisation and heating can be combined to emphasise the desorption efficiency.

**1.3.4.2 Recovery of Sulfuric Acid.** HaldorTopsoe A/S claims [31] a process for recovering a sulfuric acid stream. An ionic liquid is used as an adsorbent with the adsorption process occurring by counter current between the ionic liquid and the sulfuric acid and/or  $\text{SO}_3$ -containing stream. Then the sulfuric acid is separated in a further separation step from the ionic liquid, the latter being recycled to the absorption step. Claimed ionic liquids are preferably based on the hydrogensulfate,  $[\text{HSO}_4]^-$ , anion, and  $[\text{NH}_4]^+$ , or alkali cation as a countercation. This process is useful for treating exhaust gases from metallurgical operations and from the combustion of hydrogen-containing fuels (petrochemical alkylation, petroleum coke,  $\text{H}_2\text{S}$ , etc.)

### 1.3.5 Sulfur Compound Elimination from Hydrocarbon Streams

Ionic liquids can be used to reduce the sulfur content in fuels for reducing  $\text{SO}_2$  emissions. The deep desulfurisation is a major problem in the production of fuel. Merck has disclosed the extraction of the sulfur-containing impurities from fuels by means of ionic liquids, in order to comply with the regulatory requirements [32]. By several extraction steps the residual sulfur content can be reduced. Efficiency of the method is illustrated for the removal of a model stimulant, such as dibenzothiophene dissolved in dodecane, and for real fuels.

Ionic liquid recycling is claimed. Examples of possible processes can be steam distillation, sublimation, absorption, and purification using active charcoal or zeolite. Similarly, Extractica discloses a process for extracting sulfur-containing compounds from gasoline and fuels with an ionic liquid [33]. These compounds can be partially oxidised to sulfoxides and/or sulfones to increase their solubility in ionic liquids. A desulfurisation technology based on liquid–liquid extraction sounds attractive over conventional hydrotreating technology, since generally mild conditions would result in lower capital and operating costs. The pathway and its operating conditions for recycling the ionic liquid are not disclosed, although the step is claimed.

IFP [34] obtained a granted patent dedicated to the elimination of sulfur compounds by alkylation reaction, the alkylation agent being dissolved in an ionic liquid. It appears from the literature that the final desulfurisation of gas oils makes this finishing process necessary, to transform the sulfur-containing molecules that are particularly refractory to standard hydrodesulfurisation precursors. Instead of oxidation, alkylation is described in the IFP patent. Here, the charged sulfur-containing derivatives, such as the sulfonium derivatives formed through the alkylation process, have an increased solubility in ionic liquids. For example, extraction of butanethiol is achieved with trimethylxonium tetrafluoroborate in the ionic liquid  $[\text{C}_4\text{mim}][\text{NTf}_2]$ .

More recently, a way to improve the hydrodesulfurisation process is described by UOP LL [35]. A treatment of a diesel fuel with an ionic liquid such as  $[\text{C}_4\text{mim}][\text{HSO}_4]$  is efficient for denitrogenation and allows a reduction of the amount of the catalyst used in the subsequent hydrodesulfurisation process. Similarly, the life time of this catalyst can be increased by up to about 50%, to about 100%, when compared to desulfurisation without performing denitrogenation. An integrated process with two steps of denitrogenation (by extraction), two regenerators for the liquid ionic recovery by steam stripping, and the subsequent desulfurisation zone is proposed.

### 1.3.6 Natural Gas Purification

Carbon dioxide and hydrogen sulfide from natural gas are usually removed thanks to the use of amines. Amines have a natural affinity for both  $\text{CO}_2$  and  $\text{H}_2\text{S}$ , allowing this to be an efficient process. However, amine treatments present several main issues and challenges, such as their intensive energy requirement, corrosivity of the amine, and its possible degradation. Use of a physical solvent (such as *N*-formylmorpholine) is an alternative option, which requires less energy for regeneration but tends to have lower  $\text{CO}_2$  capacities and co-solubilises the hydrocarbon in some extent.

Chevron Texaco Company claims a new process for removing  $\text{CO}_2$  from hydrocarbon containing streams using an ionic liquid absorbent [36]. The new method provides several advantages, such as high  $\text{CO}_2$  capacity and low hydrocarbon solubility, and requires low energy for regeneration of the ionic liquid absorbent.  $\text{CO}_2$  loading curves in solvents, evidence that ionic liquid behaviour

can be adjusted to a chemical solvent (such as methyldiethanolamine) or a physical solvent (such as water) by changing the anion. Physical solvents dissolve  $\text{CO}_2$  into the liquid without any chemical forces and have low volumetric  $\text{CO}_2$  loading, while chemical solvents reversibly bind  $\text{CO}_2$  as hydrogen carbonates species and have a high volumetric  $\text{CO}_2$  loading. 1-Butyl-3-methylimidazolium ethanoate ionic liquid shows loadings that are intermediate between the aqueous amines and physical solvents. Thus, the patent claims the use of an ionic liquid comprising a cation and an anion having a carboxylate moiety.

IFP discloses three complementary patents [37–39] for processing natural gas with a solvent that removes the acid compounds such as hydrogen sulfide and carbon dioxide. The ionic liquid is brought into contact with the purified gases or/and with the acid gases (obtained after regeneration of the charged solvent) in order to trap the residual content of solvent from these streams. The solvent can be a mixture of water, methanol and diethanolamine. The contact of gases (either purified stream or acidic stream) with 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]amide enables methanol and water contained in gases to be recovered. Methanol contained in the solvent acts as an antihydrate compound. Compounds selected from alcohols, glycols and glycol ethers compounds can be useful to prevent the formation of hydrocarbon hydrates during transportation and storage.

### 1.3.7 Oxygen- or Nitrogen-Containing Polar Compound Separation

Polar compounds in organic mixtures can be successfully extracted with ionic liquids by taking advantage of the immiscibility between the ionic liquid and the organic phase. The traditional liquid-liquid separation would not be possible for the separation of a cycloalkanol and a cycloalkanone from a cycloalkane because all of them would dissolve in conventional solvents. The oxidation of cyclohexane, and its subsequent separation, is a key-step in the manufacture of adipic acid and caprolactam. Invista Technology [40] claims a separation process by contacting an ionic liquid with a mixture comprising a non-polar solvent and at least one of an alcohol and a ketone. Similarly, BASF describes a general method using ionic liquids for extracting impurities selected from a wide range of polar compounds such as phenols, alcohols, amines, and acids. These impurities can be removed with good efficiency from hydrocarbons. Removal of water is described using 1-methylimidazolium sulfate. A drying process using this technology could be envisaged [41].

### 1.3.8 Other Applications

In addition to the above examples, we can find the use of ionic liquids to improve purification processes. Arkema [42] discloses a hydrogenation process to convert chlorolactams to the corresponding lactams in presence of a metal catalyst, such as palladium deposited on carbon. Chlorolactams are impurities that impact the properties of the polymers prepared from lactams (especially

the colour), and must be removed. The reaction is performed in an ionic liquid that avoids the deactivation of the catalyst and improves the yield of the reaction.

Similarly, ionic liquids are used as additive solvents for the selective hydrogenation of block copolymers (typically triblock copolymers formed from polystyrene, polybutadiene and polymethylmethacrylate). The presence of the block comprising olefinic double bonds renders them sensitive to light, oxidising agents and to heat. Arkema [43] describes a process for the selective hydrogenation of the olefinic double bonds of block copolymers using a catalyst based on a metal from Group 8–10 in a medium comprising an organic solvent and a water-immiscible ionic liquid. In the process according to the invention, the catalyst is dissolved in the ionic liquid and the copolymer to be hydrogenated in an organic solvent. After the reaction, the hydrogenated copolymer can be isolated by precipitation, by introducing the reaction medium into a large amount of a non-solvent for the hydrogenated copolymer or, when there are two phases, by decantation and subsequent isolation of the copolymer. The yield is enhanced by the dissolution of the catalyst in the ionic liquid, such as  $[\text{C}_4\text{mim}][\text{PF}_6]$ .

## 1.4 USE OF IONIC LIQUIDS AS ADDITIVES WITH SPECIFIC PROPERTIES

Beyond the typical reactions where ionic liquids are expected to be applied, some companies seem to have developed some very specific knowledge where ionic liquids are involved in physical processes rather than pure chemical interactions.

### 1.4.1 Ionic Liquids as Lubricants

UT-Battelle LLC and University of Tennessee Research Foundation claim [44] the use of an ionic liquid made of tertiary ammonium with long alkyl linear chains (preferred octyl) and bis{(perfluoroalkyl)sulfonyl}amide (preferred with  $\text{CF}_3$ , viz.  $[\text{NTf}_2]^-$ ) anions that displays excellent lubrication performances, alone or in combination, between two metal surfaces (such as aluminium), thanks to the excellent thermal stability of the ionic liquid and its low affinity with water. Thirty per cent of extra performance can be therefore achieved compared with conventional oil in applications such as car engines.

### 1.4.2 Ionic Liquids as Antistatic Agents in Polymers

Evonik Goldschmidt claims [45] the use of ionic liquids as a solvent for alkali metal salts, the latter providing antistatic polymers properties. This addresses the issue of poor solubility of antistatic additives in the polymer matrix. A special focus deals with polyurethane. Although a large number of cations and anions are claimed, preferred compositions involve 1,3-dialkylimidazolium

cations with alkyl sulfate anions in combination with sodium or potassium dicyanamide or thiocyanate salts. An alternative combination involves a third solvent based on adiol such as glycol.

### 1.4.3 Ionic Liquids as Additives for Oil Drilling/Oil Wells

Schlumberger Technology Corporation claims [46] new fluids for stimulation of hydrocarbons wells, more specifically for a technique called “matrix acidizing,” which consists of injecting acids that dissolve a small portion of the formation and create alternate paths for the oil. An acidic ionic liquid, such as one based on a chloroaluminate as an anion, is used as a retarding agent to produce HCl after reaction with water while using the exothermic reaction resulting from the ionic liquid formation to improve solubility and therefore lower melting points of the material. The kinetics of dissolution can be therefore much better adjusted, with the possibility of drilling much deeper. Also, this reduction in kinetics has a significant advantage regarding corrosion, and in overcoming most of the issues encountered during matrix treatment, such as organic deposits and avoidance of costly additives.

Schlumberger Technology Corporation also claims [47] a drilling fluid that combines a non-aqueous feature of an ionic liquid with an enhancement in electrical conductivity that is very important for telemetry purposes. The fluid contains hydrocarbons and a portion of water-stable ionic liquid.

### 1.4.4 Carbon Nanotubes

In the nanotechnology area, Fuji Xerox Co. [48] claims the production a film of carbon nanotube by dropping a composition of ionic liquid and carbon nanotube onto a liquid surface. Preferred ionic liquids for this application are hydrophobic ones, such as 1,3-dialkylimidazolium as a cation and hexafluorophosphate as an anion.

### 1.4.5 Fine Particles Recovery

Japan Science and Technology Agency [49] claims an original method for recovering fine particles below 300 nm of different natures: polyacetylene, polydiacetylene, oxides (titanium oxide), and metals (silver, gold). The originality of the patent lies in a very specific (and narrow) ratio between the concentration of the particles and the quantity of ionic liquid to be added for a complete recovery. Ionic liquids made of typical 1-butyl-3-methylimidazolium cation and hydrophobic perfluorinated anions, such as hexafluorophosphate, seem to be preferred.

### 1.4.6 Anionic Surfactants

Procter & Gamble Company claims the use of compositions of ionic liquids for surface treatment, including soft surfaces such as textiles and hard surfaces

such as dishware, floors, and glassware. The ionic liquids are made of an amine oxide cation such as  $[R_1R_2(OR_3)NOH]^+$  and an anion made of an alkyl aryl sulfonates [50], or of mid-chain length, branched alkyl sulfates or of mid-chain length polyoxyalkylene sulfates [51].

### 1.4.7 Pressure-Sensitive Compositions

In the field of surface-protecting films obtained in the form of sheets or tape, Nitto Denko Corporation claims a pressure-sensitive adhesive composition with good antistatic properties that can prevent electrification of the surface to be protected upon peeling. Different patents [52–55] cover compositions that include an ionic liquid, and different combinations displaying a polymer containing as a monomer, a methacrylate ester, and an ethylene oxide group. These patents claim the use of ionic liquids with nitrogen-, sulfur- or phosphorus-containing onium salts. Examples include the use of ionic liquids made of 1-butyl-3-methylimidazolium chloride and lithium bis((trifluoromethyl) sulfonyl)amide.

## 1.5 USE OF IONIC LIQUIDS AS BOTH ACIDIC CATALYSTS AND SOLVENTS

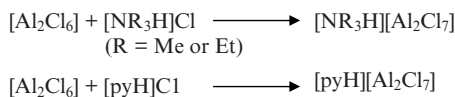
### 1.5.1 Introduction

The most catalytically interesting ionic liquid acid catalysts are those derived from ammonium halides and Lewis acids. Among the Lewis acids reported, aluminium(III) chloride is the most commonly used. Acidic chloroaluminates are the most claimed ionic liquids acid catalysts to be used in petrochemical processes.

Mixtures of alkylpyridinium chloride [56] or alkylimidazolium halides [57, 58] with aluminium(III) chloride form fused chloroaluminates salts that were described in earlier patents for their applications as electrolytes. More recently, their use as solvents in catalytic reactions was disclosed [59].

Liquid clathrates composed of a mixture of aluminium(III) chloride, a quaternary ammonium or phosphonium salt, and at least one aromatic compound were also described as useful reusable aluminium(III) chloride catalysts for Friedel–Crafts reactions [60].

Mixing of a metal halide solid (such as aluminium(III) chloride) and an alkyl (most commonly methyl or ethyl) or aromatic ammonium halide solid salt can form ionic liquid compositions at low temperatures:



These can be suitable for use as acidic catalysts in some transformations.

It seems that imidazolium halides, while largely described, are not so well used or popular for industrial applications in the petrochemical field because their price is too high. An economical method for the production of commercial amounts of these ionic liquids is needed.

Due to their ease of preparation, the commercial availability of their components, and their low costs, Lewis acidic ionic liquid have been advantageously used for carrying out many acid-catalysed processes such as:

- olefin oligomerisation for lube base stock manufacture
- olefin–paraffin alkylation for alkylate oil production for fuel
- aromatic alkylation
- paraffin carbonylation
- liquid phase fluorination process

These reactions will be detailed below. Chevron Chemical has been very active in this field. Chloroaluminate(III) ionic liquids are used to replace aluminium(III) chloride. One main advantage of using ionic liquid catalyst is that it forms a separate phase from the organic phase, which contains the reaction products and the residual olefin feed. The reaction products can then be easily separated by conventional means, such as decantation or distillation, and the ionic liquid that remains after recovery of the products may be recycled. Methods to regenerate the used ionic liquids are also largely disclosed.

### 1.5.2 Economical Preparation of Chloroaluminate(III) Ionic Liquids

Considering the usefulness of these low temperature ionic liquids, an economical method for manufacturing them has been especially disclosed [61]. This method is performed in two steps. In a first step an alkylamine, such as the triethylamine, is contacted with a hydrogen halide, such as HCl, in the gaseous state in the presence of a hydrocarbon diluent. Then, in a second step, the metal halide is added, as a solid or as a slurry. This two-step process avoids the difficult handling of the alkylammonium halide salts. It is interesting to note that the composition of the ionic liquid (molar ratio of the metal halide to the alkylammonium halide salt ranging from 1.5 to 1.9) can be determined simply and quickly from a correlation to the ionic liquid specific gravity, which is determined with a hydrometer tube.

### 1.5.3 Applications of Acidic Ionic Liquids: Catalysts and Solvents

**1.5.3.1 Olefin Oligomerisation.** In years before 2000, ionic liquid acid catalysts were described to catalyse the oligomerisation of olefins, such as 1-decene, to produce polyalphaolefins (PAOs) having a viscosity index of at least 120 and a pour point of  $-45^{\circ}\text{C}$  or less [62]. It has been found now that it is also possible to make PAOs, used as lube base stock, with higher viscosity



using the ionic liquid catalyst in the absence of solvent [63]. In these processes, olefin feeds can originate from dehydrogenated Fischer–Tropsch paraffinic feedstock [64] or from Fischer–Tropsch dehydrated alcohols [65]. Because ionic liquids can be quite costly for this application, there was a need for a method to increase their efficiency for improving the economics of the process. This was achieved by the introduction of a control amount of dioxygen in the catalytic reaction headspace zone while controlling the water content of the olefinic feedstock [66]. The examples illustrate the impact of the concentration of dioxygen added: an increase in dioxygen concentration leads to an increase in olefin conversion and product viscosity.

**1.5.3.2 Alkylation of Paraffins.** In the field of petrochemical catalysis, alkylation reactions of alkanes and olefins, such as isobutane and butenes, are important industrial processes to produce alkylate oil, mainly composed of branched octenes. These processes are catalysed by strong, highly corrosive acids, such as concentrated sulfuric or hydrofluoric acids. In recent years, most of the studies have focussed on the search of new solid acid catalysts and technologies in order to solve the problem of equipment corrosion and pollution. However, the problem with the new solids was still their quick deactivation, and none of these solid acids have been put into practice at commercial refineries. Another challenge of these processes is to improve the C8 content in the alkylate products and the trimethylpentene (TMP) to dimethylhexene (DMH) molar ratio in the C8 fraction. The use of acidic chloroaluminates as alternatives to strong liquid acids was disclosed several years ago for this application [67–70]. The more recent patents disclose improved processes. In particular, the ionic liquid is a composite consisting of a cation coming from alkylammonium or pyridinium chlorides, and an anion coming from two or more metal compounds [71]. The preferred metal compounds are aluminium(III) chloride, and a copper and/or a nickel salt. Continuous manufacturing of alkylate oil in a static mixer reaction apparatus was also described, with a reaction temperature of 30°C and a ratio of isobutane to butene in the reactor of 10:1. The olefin conversion can be up to 98 wt%, with a C8 content in the alkylate oil of 76 wt% and a TMT/DMH ratio of up to 6.7.

Another interest in using chloroaluminates ionic liquids versus conventional acids is their ability to catalyse the alkylation of isoparaffins (such as isopentane) with ethylene, which is not possible in the existing processes. In this case, it was shown that pyridinium- or imidazolium-based chloroaluminates were more effective than aliphatic ammonium chloroaluminates in terms of ethylene conversion. The preferred ionic liquid was composed of 1-butylpyridinium chloride and aluminium(III) chloride (1:2 molar ratio). To maintain high ethylene conversion, HCl needs to be co-fed into the reactor. In that specific case, in a continuous run, ethylene conversion can be around 95 wt%, with a selectivity for the C7 fraction of up to 79 wt% [72]. Haloalkanes, such as chloroethane, have also been disclosed to be good promoters of chloroaluminates and can be used instead of HCl [73, 74]. In that case, the alkylate



produced can contain a high amount of organic chloride. To dechlorinate the product, a conventional hydrotreatment can be applied [75]. The ethylene/isopentane alkylation process has been integrated in a refinery for the production of high-quality gasoline blending components from low value components, such as fluid catalytic cracking (FCC) off-gas and isopentane [76].

A novel way to reduce the concentration of double bonds in the olefinic hydrocarbon effluent, and at the same time enhance the quality of the fuel or lubricant, was provided by performing the alkylation reaction of a stream comprising at least one C8+ olefin with an isoparaffin (e.g., isobutane) with an acidic chloroaluminate in the presence of a Brønsted acid such as HCl [77], or by subjecting the alkylation effluent to a hydrogenation step.

**1.5.3.3 Alkylation of Aromatic Ring.** Aromatic hydrocarbon alkylation with an olefin catalysed by acidic chloroaluminates was disclosed in earlier patents [78]. More recently, Chevron disclosed the alkylation of non-hydroxyl-containing aromatic compounds with olefin oligomers coming from light olefin oligomerisation in the presence of an ionic liquid. The olefinic oligomers are typically propylene oligomers (C12+). The acidic ionic liquid used for olefin oligomerisation and aromatic alkylation with the olefin may be the same, based on a trialkylammonium cation and a chloroaluminate(III) anion [79].

Aromatic alkylation of the ring of anilines or alkylated aniline derivatives is also of interest, in order to improve the solubility of anilines in hydrocarbons. Prior art in this field related an improvement of the ring alkylation selectivity by using acidic zeolites. Chemtura Corporation disclosed the use of ionic liquids as both solvents and acid catalysts, with the advantage of permitting a convenient separation of the alkylated anilines from the reaction mixture. The ionic liquids preferably used are acid chloroaluminates based on quaternary ammonium or 1,3-dialkylimidazolium cations, and the olefin can be either an alpha olefin or branched olefins. The inventors claim that the ionic liquid may be recycled by simple phase decantation and that the ionic liquid can be reused by itself or in combination of additional fresh one [80].

**1.5.3.4 Carbonylation of Aromatic Hydrocarbons and Paraffins.** The carbonylation of aromatic hydrocarbons (the Gatterman–Koch reaction) to form alkylaromatic aldehydes has been described in the presence of acidic ionic liquids (Hammett acidity value less than  $-10$ ) based on Lewis acids such as aluminium(III) chloride or gallium(III) chloride [81–83]. After the reaction, the aromatic aldehyde is normally present as a complex with the acid present in the system. The use of ionic liquids can provide for more convenient separation of the aldehyde products. This process can be applied on a mixture of *ortho*-, *meta*-, and *para*-xylenes. *m*-Xylene is the most reactive, and produces 2,4-dimethylbenzaldehyde with selectivity depending on the conversion. The difference in conversion rate of the different xylenes may be used to separate *p*-xylene (the least reactive) from *m*- and *o*-xylenes. After separation of the products, the alkyl aromatic aldehydes can be subjected to an oxidation

reaction to form the corresponding acids. This claimed method could be applied to the reaction of toluene to form terephthalic acid, but is not exemplified.

The carbonylation of saturated hydrocarbons to give oxygenated saturated hydrocarbons is known to be more difficult to perform, and is generally catalysed by liquid super acids such as  $\text{HF-BF}_3$ . UOP LLC [84] disclosed the use of ionic liquids for the replacement of these liquid superacids, with the aim of being more environmentally friendly. In this reaction, the ionic liquid serves both as the catalyst and the solvent. 1-Butylpyridinium chloride–aluminium(III) chloride ionic liquid was exemplified to catalyse the carbonylation of isobutane to methyl isopropylketone with very high selectivity but very low conversion (<10%).

**1.5.3.5 Isomerisation.** *Exo*-tetrahydrodicyclopentadiene is a high energy fuel that is usually obtained from synthetic reactions through an isomerisation of *endo*-tetrahydrodicyclopentadiene. This isomerisation is catalysed with strong acids, such as aluminium(III) chloride, but side reactions can occur such as ring-opening degradation and polymerisation, with the formation of many undesired by-products. Chinese Petroleum Corp. [85] discloses a novel method for producing *exo*-tetrahydrodicyclopentadiene with the use of acidic chloroaluminate(III) ionic liquids. Different cations are related, based on 1-alkylpyridinium, tetraalkylammonium, or 1,3-dialkylimidazolium. High conversions and selectivities can be reached (>99%). The ionic liquid may be recyclable, but no example is given.

In a similar way, CPC Corporation relates the production of adamantane by isomerising *exo*-tetrahydrodicyclopentadiene [86].

**1.5.3.6 Fluorination of Halogenated Compounds.** Arkema discloses a patent [87] using a particular ionic liquid for liquid phase fluorination catalysis. The ionic liquids results from the reaction of a halogenated Lewis acid, based on titanium, niobium, tantalum, tin, or antimony. These liquids can be used in liquid phase fluorination, using hydrogen fluoride (HF), of saturated or unsaturated compounds containing C–Cl groups. Examples evidence the use of 1-butyl-3-methylimidazolium chloride associated with an antimony salt for the liquid phase fluorination of dichloromethane or trichloroethylene.

**1.5.3.7 Polyamide Hydrolysis.** Invista North America S.A.R.L. claims [88] a process of hydrolysis with water of polyamide made of a diamine and a dicarboxylic acid such Nylon 6,6. The process is carried out at relatively low temperature (100°C) with an ionic liquid based on hydrogensulfate  $[\text{HSO}_4]^-$  or hydrogenphosphate  $[\text{HPO}_4]^-$  and preferably a phosphonium cation. A complete process is claimed including the separation of the aqueous phase comprising the products of hydrolysis, such the diamine and the dicarboxylic acid, and a process of regeneration of the ionic liquid with either  $\text{H}_2\text{SO}_4$  or  $\text{H}_3\text{PO}_4$ , depending on the nature of the anion used.

### 1.5.4 Regeneration of Chloroaluminate(III) Ionic Liquids

One of the unsolved problems impeding the commercial use of chloroaluminate(III) ionic liquid catalysts has been the inability to regenerate and recycle them. Chevron has provided different processes for regenerating the used and deactivated acidic chloroaluminates.

For example, in alkylation reactions, one of the major catalyst deactivation mechanisms is the formation of by-products known as “conjunct polymers,” which are unsaturated cyclic or acyclic molecules formed by acidic side reactions, such as polymerisation, cyclisation, or hydride transfer. These conjunct polymers proved to be a cause of deactivation of acidic chloroaluminates by weakening their acidity.

Hydrogenation of these conjunct polymers to remove them from the chloroaluminate(III) ionic liquids has been disclosed. The hydrogenation can be operated over a metal, such as aluminium [89] in the presence of a Brønsted acid (such as HCl), or over a supported transition metal (such as nickel) [90], a metal alloy [91], or a homogeneous catalyst [92], under dihydrogen. The saturated polymeric compounds can then be separated in a second upper phase, leaving a denser ionic liquid phase that can be recovered and reused after filtration.

## 1.6 APPLICATIONS OF IONIC LIQUIDS AS SOLVENTS FOR CATALYTIC SYSTEMS

### 1.6.1 Introduction

The patents in this field can be classified according to the catalytic applications claimed. With our strategy of research, the main related applications can be divided into the following:

- olefin oligomerisation, co-dimerisation, and dimerisation
- olefin hydroformylation and hydrogenation
- alcohol carbonylation
- olefin metathesis
- hydrosilylation

In these varied applications, the use of ionic liquids may increase reaction rates and yields. It could permit the recovery, and sometimes the reuse, of catalytic systems. The use of ionic liquids as solvents is also usually claimed to reduce environmental impacts and to lead to more energy-efficient separation. Ionic liquids may appear as novel solutions to chemical industry. However, it is still very difficult to deduce from these patents if the ionic liquids have been really translated into viable industrial processes. This information is generally not made public.

### 1.6.2 Transition-Metal Catalysed Olefin Oligomerisation

At the beginning of the 1990s, IFP found that the mixture of an alkyl aluminium chloride and a quaternary ammonium or phosphonium chloride, such as a 1,3-dialkylimidazolium chloride, formed a liquid at low temperature (below 80 °C), and that these mixtures can be used as novel solvents for transition-metal catalysis [93]. Nickel-catalysed olefin oligomerisation is one of the main applications described in chloroaluminate ionic liquids. The reaction is performed in a two-phase medium consisting of (1) the ionic liquid, where the nickel catalyst is dissolved, and (2) a hydrocarbon upper phase, where the reaction products are separated. IFP described a process for carrying out the nickel-catalysed olefin oligomerisation in two catalytic steps of different types: in a first step, it undergoes catalytic oligomerisation without an ionic liquid, then the effluent of this first step is sent to a second reaction zone in which oligomerisation is carried out in a two-phase medium containing the ionic liquid [94].

Different nickel-catalysed compositions have been claimed to be active in chloroaluminate ionic liquids. One can mention the use of a nickel compound that contains at least one heterocyclic mono- or bi-carbene ligand [95]. The nickel compound can be activated not only by alkyl aluminium derivatives but also by methylaluminumoxane [96].

A novel nickel catalyst composition that consists of a mixture of a nickel(0) compound, a Brønsted acid, a nitrogen ligand, and an ionic liquid has been discovered. In this case the ionic liquid is preferably based on a weak coordinating anion such as  $[\text{SbF}_6]^-$  or  $[\text{NTf}_2]^-$ , and the ligand is preferably a diimine [97].

### 1.6.3 Hydroformylation

The hydroformylation reaction of olefinic compounds is a reaction of great industrial importance. Industrial processes use homogeneous catalysts based either on cobalt or rhodium complex. One of the main challenges is the separation of the reaction products, and the recovery and reuse of the catalyst. Many solutions have been claimed in patents. The use of ionic liquids in this reaction was first described by IFP and then by Celanese. In order to retain the metal in the ionic phase, ligands carrying ionic function must be added to the catalytic composition. Nitrogen [98] or phosphorus ligands are claimed [99].

It has been discovered and claimed by IFP that, when using cobalt as the metal in presence of an ionic liquid, recycling of the metal is improved when a Lewis base is present, and when a depressurisation step is realised before decantation and separation of the products. The Lewis bases are preferably chosen from the family of the pyridines [100]. In order to improve the reaction rate and the cobalt recovery, a new implementation of the system has been described. It consists of a hydroformylation stage carried out in the presence

of the cobalt, the ionic liquid, and a Lewis base as the ligand. This stage is followed by depressurisation and decantation stages, and then a recycling stage wherein the ionic liquid phase, which contains the cobalt, is sent back to hydroformylation first stage. An improvement can be achieved by adding some ligand in the post-reaction stage [101].

Celanese [102] disclosed that ionic liquids can act as solvents, but also as ligands, forming complexes with rhodium. Surprisingly, the reaction can be performed with a large excess of ligand, which can stabilise the active species and leads to a reduction of noble metal losses. One example of the “ligand liquid” is a sulfonated or carboxylated phosphorus triester. The use of ionic liquids based on organic sulfonates or sulfate anions, associated with sulfonated arylphosphines and a rhodium compound, has also been disclosed by Celanese [103]. These ionic liquids appear to allow a better retention of the rhodium in the ionic phase.

### 1.6.4 Carbonylation of Alcohols

The carbonylation of alcohols, more specifically methanol for the production of ethanoic acid, is extensively operated industrially. All the commercial processes are performed in liquid phase and are catalysed with a homogeneous catalyst system comprising a Group 8–10 metal, such as rhodium, and an iodine-containing compound. The separation of the volatile reaction products and starting materials from catalyst components is still a main issue for these processes. There is a need for a process that provides simple product separation while maintaining a stable catalyst environment, and giving high reaction rates with efficient heat removal from the reaction zone.

Eastman Chemical Company [104] describes a new continuous process in which vapour phase reactants, methanol, iodomethane, and water, are contacted with a non-volatile rhodium or iridium catalyst solution that comprises an ionic liquid. The ionic liquid is preferably based on iodide anions, and an organic cation such as 1-butyl-3-methylimidazolium.

At the same time, IFP [105] disclosed a process for carrying out the carbonylation of alcohol in the liquid phase, in which the homogeneous catalyst system, based on rhodium or iridium, is stabilised in an ionic liquid. At high methanol conversion (>99 wt%), the selectivity for ethanoic acid can be high (>95 wt%). After distillation of the products, the ionic liquid containing the catalyst can be recycled. WackerChemie [106] described a process for the continuous carbonylation of methanol with carbon monoxide in the gaseous phase in the presence of a rhodium catalyst supported in an ionic phase confined on a support such as silica gel. The reaction is preferably performed at 180°C and 20 bar using 1-butyl-3-methylimidazolium iodide as the ionic liquid and a dicarbonyldiiodorhodate(I)anion,  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ , as the catalyst. The observed products are ethanoic acid, methyl ethanoate (major product), and dimethyl ether. This catalyst technology is sometimes referred to as supported ionic liquid-phase (SILP) technology.

### 1.6.5 Metathesis

The first patent that described the use of ionic liquids for metathesis made use of a tungsten catalyst dissolved in chloroaluminate ionic liquids [107] and was applied to mono-olefin cross-metathesis. Bayer [108] later disclosed a process for preparing cyclic and/or polymeric compounds by ring closing metathesis of the starting alkenes or alkynes that contain at least two functional groups. The metathesis is performed in ionic liquids, preferably chloroaluminates, with a metal-carbene transition metal catalyst. The preferred catalyst precursors are ruthenium or molybdenum imido carbene complexes.

In 2000, Chevron [109] filed a patent that related to a process for manufacturing fatty acid nitrites and fatty amines by cross-metathesis, followed by hydrogenation of normal alpha olefins and acrylonitrile in the presence of a transition metal catalyst, preferably a Schrock molybdenum type catalyst. In a preferred embodiment of the invention, the reaction is performed in an ionic liquid such as [C<sub>4</sub>mim][PF<sub>6</sub>]. The ionic liquid containing the catalyst can be reused after separation of the reaction products, but nothing is disclosed about the leaching of the metal into the organic phase.

The combination of ionic liquids and compressed carbon dioxide has been described in a patent filed by Boehringer Ingelheim International, in 2006, for continuous olefin ring closing metathesis of both liquid and solid reactants. The carbon dioxide acts as solvent for the reactants and for the product obtained, while the ionic liquid acts as the metal catalyst solvent and support. The preferred catalyst is a ruthenium carbene complex, and a continuous process is exemplified. A particular application of homo-metathesis in the presence of at least one ionic liquid and a metal catalyst has been used for the co-production of olefins and diesters from unsaturated fats [110]. Ruthenium catalysts are preferred. Recycling experiments are described with bis((trifluoromethyl)sulfonyl)amide ionic liquids.

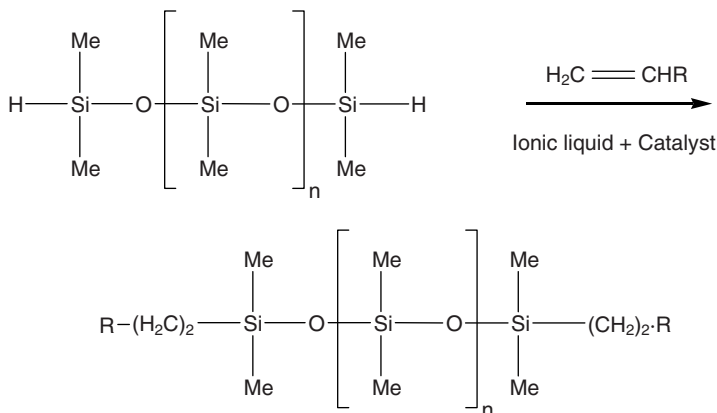
### 1.6.6 Hydrosilylation

Among processes for producing and for modifying organopolysiloxanes, hydrosilylation in the presence of transition metal catalysts is of particular importance since it permits a variety of Si-C linkages (Scheme 1.2).

In order to make it possible for the hydrosilylation catalyst to be recycled in a simple fashion, Goldschmidt-Degussa (now Evonik) proposes the use of ionic liquids [111].

This patent claims a process for preparing organomodified polysiloxanes which comprises reacting a SiH-containing polysiloxane with a compound that contains carbon-carbon multiple bonds in the presence of transition metal catalysts, wherein (1) the reaction is carried out in the presence of an ionic liquid, and (2) after the reaction is completed, the ionic liquid containing the dissolved catalyst is separated from the reaction mixture.

Preferred ionic liquids are imidazolium or pyridinium salts and more specifically 1,2,3-trimethylimidazolium methylsulfate as well as pyridinium



**Scheme 1.2** Hydrosilylation for modification of organopolysiloxanes.

tetrafluoroborates. Typical examples describe the reaction of  $\alpha,\omega$ -(Si-H)-polydimethylsiloxane (20 to 50 silicon atom chain length) with a 1.3 molar equivalent of a multiple bond containing compound (such as unsaturated polyether 400–500 g M<sup>-1</sup> molecular weight) in the presence of a platinum catalyst dissolved in the ionic liquid at 80–100 °C for a period of 5 hours. After cooling to room temperature, the polyethersiloxane (free of metal, according to ICP determination) is separated from the ionic liquid catalyst phase by decantation or filtration. Preferred platinum catalysts used are hexachloroplatinic acid or  $\mu$ -chlorodichlorobis(cyclohexene)diplatinum(II).

### 1.6.7 Synthesis of Polymers

Polytrimethylene ether glycol and polytetramethylene ether glycol are used in various applications including fibres, films, or moulded products. A series of patents concerning preparation of such polymers in the presence of an ionic liquid has been granted to E.I. duPont de Nemours.

Use of ionic liquids for this process provides several advantages: the produced polyol polymer can be recovered in a separate phase from the ionic liquid and catalyst, and the polyol polymer molecular weight may be tuned thanks to appropriate choice of the ionic liquid.

Polytrimethylene ether glycols are prepared through polymerisation of 1,3-propanediol (or its oligomers) with an acid catalyst in the presence of an ionic liquid [112–114].

Preferred acid catalysts are polyfluoroalkylsulfonic acids. The patent claims contain a large number of compounds, but preferred ionic liquids are typical onium ionic liquids bearing a perfluoroalkylsulfonate anion, or specifically designed 1-(2-*N,N,N*-trialkylaminoalkyl-5-methyl)pyrrolidinium salts with a sulfonic acid. Separation of the ionic liquid phase containing the acid catalyst



from the polymer phase through decantation and its recycling are also claimed. A typical example describes reaction of 1,3-propanediol with 1,1,2,2-tetrafluoroethanesulfonic acid in the presence of 1-butyl-3-methylimidazolium 1,1,2,2-tetrafluoroethanesulfonate at 160 °C for 9–10 hours. After cooling to 75 °C, the acid-containing ionic liquid phase is separated from the obtained polymer through decantation.

Polytetramethylene ether glycols are prepared through polymerisation of THF with an acid catalyst in the presence of an accelerator and an ionic liquid [115,116]. The preferred acid catalyst is polyfluoroalkylsulfonic acids and preferred accelerators are carboxylic anhydrides, acid chlorides, or carboxylic acids. The patent claims contain a large number of compounds, but preferred ionic liquids are classical onium ionic liquids containing a perfluoroalkylsulfonate anion, or a specifically designed 1-(2-*N,N,N*-trialkylaminoalkyl-5-methyl)pyrrolidinium salt with a sulfonic acid. A typical example describes the reaction of tetrahydrofuran with 1,1,2,2-tetrafluoroethanesulfonic acid and ethanoic anhydride in the presence of 1-butyl-3-methylimidazolium 1,1,2,2-tetrafluoroethanesulfonate at room temperature for 1 hour. The acid-containing ionic liquid phase is separated from the obtained polymer through decantation.

### 1.6.8 Microwave-Assisted Chemical Transformations with Ionic Liquids

A Swedish company (Personal Chemistry i Uppsala) claimed a method for performing a microwave-assisted chemical transformation, wherein an ionic liquid is used as solvent [117]. Ionic liquid preparation under microwave irradiation is also claimed. Although the patent claims do not limit the scope of the chemical transformations involved, examples only illustrate the cases of alcohol or amine alkylation with an organic halide.

The main advantage of microwave irradiation is a dramatic reaction time reduction when compared to the same reaction carried out under more conventional conditions (several minutes vs. several hours).

### 1.6.9 Methane to Methanol

California Institute of Technology [118] claims a process for the conversion from methane to methanol in presence of  $\text{H}_2\text{SO}_4$  and a catalyst made of platinum dissolved in an ionic liquid. Rates are rather modest at high pressure and at 220 °C. 1,3-Dialkylimidazolium ionic liquids are preferred, but not with a butyl substituent, as this substituent can be oxidised during the reaction.

### 1.6.10 Fluorination

RhodiaChimie [119] claims a new fluorination method with KF as a fluorinating agent and a tetraalkylphosphonium halide (preferably bromide), possibly in combination with a polar solvent, as reaction medium to undertake nucleo-



philic substitution reactions (F/Cl exchange). Different organic substrates are claimed, but the focus seems to be primarily on 1,3,5-trichlorobenzene and to a lesser extent phenylchloroform,  $\text{PhCCl}_3$ , as raw materials.

### 1.6.11 Aldol Condensation

Aldol condensation is claimed in a patent from ExxonMobil Research and Engineering Company [120]. The use of an ionic liquid as a reaction medium allows a much better design of the selectivity in terms of the number of additions. Neutral ionic liquids, such as those based on hexafluorophosphate or tetrafluoroborate anions, are claimed and used in combination with a catalyst, NaOH or KOH.

### 1.6.12 Acylation

Institut Universitari de Ciència i Tecnologia claims [121] the use of an ionic liquid made up of the trifluoromethylsulfonate anion and, preferably, with 1,3-dialkylimidazolium as a cation to perform Friedel–Crafts acylation with, for example, anisole as a Friedel–Crafts substrate and carboxylic anhydride acids as an acylating agent. The reaction is performed without any other solvent, the ionic liquid playing both roles of solvent and catalyst. Reaction is carried out around 100°C and the *ortho*-/*para*-selectivity is 100%.

### 1.6.13 Hydrocarbon Stream Drying

HaldorTopsoe A/S claims [122] a process for drying a hydrocarbon stream. The process is carried out by putting a wet hydrocarbon stream in contact with an ionic liquid, such as trialkylammonium triflate, and removing the water from the ionic liquid in a separate phase before recycling.

### 1.6.14 Photolysis

Fuchigami and Nisshinbo Industries claim [123] a process for photolysing organic matter by placing the waste water in contact with an ionic liquid in order to solubilise the organic matter of the waste stream into the ionic liquid phase, then treating this phase with a photocatalyst such as  $\text{TiO}_2$  under conditions of light irradiation. The ionic liquid claimed is made up of a bis{(trifluoromethyl)sulfonyl}amide as anion and a quaternary ammonium cation.

### 1.6.15 Preparation of Alkoxyamines

Atofina claims [124] a biphasic process to prepare  $\alpha,\beta,\beta$ -trisubstituted hydroxylamines from nitroxide that can be used as radical polymerisation initiators. The biphasic medium comprises an ionic liquid containing a metal salt as a

catalyst and an organic solvent that is immiscible with the ionic liquid. Preferably, ionic liquids are made of 1,3-dialkylimidazolium chloride or bromide, the catalyst is copper based, and the organic solvent is an aromatic hydrocarbon. The alkoxyamine can be then recovered from the organic phase and the ionic liquid phase can be recycled.

## 1.7 IONIC LIQUIDS AND BIOPOLYMERS

Biopolymers are polymers produced from biomass. They can be used as plastics, replacing the need for polystyrene or polyethylene-based plastics. The feedstocks for polymers derived from petrochemicals will eventually run out. In contrast, biopolymers are renewable, sustainable, and can be carbon neutral. Biopolymers have the potential to cut carbon emissions and reduce CO<sub>2</sub> quantities in the atmosphere: this is because when the CO<sub>2</sub> released when they degrade can be reabsorbed by crops grown to replace them.

Ionic liquid have now found a place in this field as a solvent for these biopolymers, helping dissolution, and helping processing and regeneration of used biopolymers.

### 1.7.1 Dissolution and Processing of Cellulose

Cellulose is the most abundant biorenewable material, and cellulose-derived products have been used in all cultures from the most primitive to highly developed modern technological society. Apart from the use of unmodified cellulose-containing materials, modern cellulose technology requires extraction and processing of cellulose. Cellulose and its derivatives can be substituted as a source for a number of chemicals. For example, oil feedstocks can be substituted with cellulose to prepare polymers for applications in paints, plastics, and other formulation materials. Cellulose is a major fraction of plant biomass, which is the feedstock for future “biorefineries” with the potential to replace the conventional petrochemical refineries.

Cellulose can be used unchanged, or after physical or chemical treatment. In the latter two cases, it is advantageous for cellulose to be preferably dissolved in a solvent. However, cellulose is insoluble in most solvents.

Ionic liquids have been known to be cellulose solvents for a very long time. Pioneering work [125] by Graenacher described cellulose dissolution in benzyl- or alkyl-pyridinium salts in the 1930s.

It was found at the University of Alabama [126] that cellulose can be dissolved in solvents described as ionic liquids that are substantially free of water. Cellulose displays high solubility in these ionic liquids. Viscous, liquid crystalline solutions are obtained at high concentrations, *ca.* 10–25 wt%. For example, fibrous cellulose was dissolved at 25 wt% in 1-butyl-3-methylimidazolium chloride by microwave heating to provide an optically clear, viscous solution.

The solubility of cellulose in ionic liquids can be controlled by changes in the anion and cation. The requirement for a small anion is indicated by the high solubility of cellulose in chloride-containing ionic liquids, with reduced solubility in the bromide systems and no solubility in tetrafluoroborate and hexafluorophosphate systems.

The solution of cellulose in ionic liquids can be processed simply, and cellulose can be regenerated from the ionic liquid solution by adding water. The recovered cellulose exhibits different physical properties, especially an amorphous structure evidenced from X-ray powder diffraction (XRD) measurements. This may indicate a slow breakdown of the polymer chains with time. The high crystallinity of primary cellulose renders it recalcitrant to hydrolysis aimed at producing glucose (the feedstock for producing fuels and chemicals). A pretreatment including the total or partial dissolution of the cellulose and the subsequent recovery of an amorphous state of cellulose allow a high enhancement of the saccharification [127], according to the University of Toledo. To accomplish the hydrolysis, enzymes such as cellulase are preferred; hydrolysing enzymes and water must penetrate the crystalline fibrils. The resulting amorphous regenerated cellulose is more accessible for the reaction and the yield is thus highly enhanced.

BASF discloses two related patents [128,129] in this area. The dissolution of cellulose in a very large list of possible ionic liquids is described, and the presence of 6–30 wt% of a nitrogen-containing base is claimed.

The ability of ionic liquids to dissolve cellulose has been described then for several applications:

1. Fabrication of nonwovens for textile applications [130] claimed by Fraunhofer-Gesellschaft. The particular properties of the nonwovens result in numerous possibilities for use in medicine for hygiene products, bed sheets, gauze, and so on.
2. Description of an absorbent paper sheet for tissue or towel [131] by Georgia Pacific Consumer Products LP, comprising 1–30 wt% of regenerated cellulose microfibrils prepared from an ionic liquid mixture.
3. Procter & Gamble Company discloses a patent [132] for the sulfatation or sulfonation of cellulose and cellulose ethers in an ionic liquid. The resulting products are suitable in detergent compositions for fabric care, surface care, and air care applications.

### 1.7.2 Starch and Ionic Liquids

Similar to cellulose, starch is a natural biopolymer. A large number of organic starch esters have been prepared and described in the literature, but few are manufactured and used commercially. Practically, these are starch ethanoates and, to a smaller extent, starch succinates. Depending on their degree of substitution (the measure of average number of hydroxyl groups), they are used in applications such as the food area, paper industry, or packaging.

Kemira OYJ is a company interested in this field, and discloses the two following patents. According to the company, ionic liquids can dissolve starch to allow subsequent transformations such as esterification [133]. Both steps can be assisted by applying microwave irradiation and/or pressure. It has also been discovered that the contact between the ionic liquid and starch leads to its depolymerisation [134]. The depolymerisation of starch is achieved after dissolution in an ionic liquid, and treatment by agitating at a temperature and for a period of time, to obtain the desired depolymerisation products.

### 1.7.3 Other Biopolymers

Apart from cellulose and starch examples, Procter & Gamble Company discloses the use of ionic liquids for the dissolution of other biopolymers [135]. Certain biopolymers that are insoluble in water or conventional organic solvents can be extracted from their biological sources with ionic liquids. The concerned biopolymers are chitin, chitosan, elastin, collagen, keratin or polyhydroxyalkanoate. The process comprises the subsequent step of adding an effective amount of nonsolvent to the substantially anhydrous composition to reduce the solubility of the polymer and recover it. The biopolymer can easily be separated from the recoverable composition by known separation methods, such as centrifugation, sedimentation, crystallisation, decantation or filtration.

## 1.8 CONCLUSIONS AND PERSPECTIVES

Granted patents between 1990 and 2010 describe numerous applications of ionic liquids in separation and purification technologies, various catalytic processes, polymer and biopolymer synthesis, and transformation, and also as additives and fluids with very specific properties. The recovery and recyclability of the ionic liquids is not often disclosed in all these new technologies, even if it appears to be a key issue in obtaining economically viable ionic liquid processes.

Granted patents can be relevant indicators of the state of the art of a current industrial technological area. However, because of the time needed to secure a patent, granted patents are not always representative of the last new developments. Patent applications are published 18 months after the invention has been filed, and may be more relevant documents in order to access the most promising future developments. To complete our study, we thus decided to focus on the emerging areas described in the recent open literature on ionic liquids, and we look for the patent applications published during the last five years in these areas. Here we list the topics in which patent applications are the most numerous.

Concerning **enzymes and biomass valorisation**, about 60 patent applications using both ionic liquids and enzymes have been published since 2005 with a

significant yearly increase from three publications in 2005 to 13 publications in 2010. These documents can be divided into two categories. About half of them deal with applications in which ionic liquids are used as solvents for the enzymes to produce fine chemicals with asymmetric synthesis being involved in most of the chemical transformations. The second half concerns processes in which ionic liquids and enzymes are used in two separate consecutive steps. The large majority of these documents deal with ionic liquids lignocellulosic biomass pretreatment, followed by enzymatic hydrolysis to produce glucose solutions as intermediates for biofuels.

Concerning biofuels and chemicals production from lignocellulosic biomass, about 40 other patent applications can be found in which ionic liquids are used to transform biomass into synthons. A large number of companies are found among these patent application assignees, but two main actors, Bioecon and Furanix, can be identified concerning the use of ionic liquids for biomass treatment or transformation.

The need to reduce the inventory of ionic liquids used in catalytic processes, and to go towards heterogenisation of the catalysts, can be detected by the numerous applications concerning **SILP** (supported ionic liquid phase) technology. About 50 patent applications concerning SILP have been published since 2005, with a significant yearly increase from two publications in 2005 to 15 publications in 2010. Various compounds are used as supports for ionic liquids, including minerals (activated carbon, silica, alumina, zeolite, etc.) and polymers. The obtained solids are described to be usable in various applications including the refining and petrochemical area. About half of these documents are Chinese applications. The applications have been filed by a large diversity of companies, including SudChemie, ConocoPhillips, Total, Johnson Matthey, BASF, and CPC.

**Nanomaterials** also emerge as a new area in the field of ionic liquids. About 30 patent applications concerning the use of ionic liquids as solvents to prepare nanomaterials have been published since 2005, with a significant yearly increase from two publications in 2005 to eight publications in 2010. Various compounds can be thus prepared, such as zeolites, minerals, polymers, metals, and hybrid materials, and yet very few data concerning their applications are found. About 60% of these documents are Chinese applications and their assignees are nearly all from academia. Thus, the actual industrial developments in this area could be doubtful.

**Desulfurisation** of oil remains a dominant application area for ionic liquids, with about 30 patent applications published since 2005, with a significant yearly increase from two publications in 2005 to eight publications in 2009, and six in 2010. About 60% of these documents are Chinese applications, and among the other assignees most of the oil industry majors can be found with one or two patent applications each.

About ninety patents applications concerning the use of ionic liquids as **lubricants** have been published since 2005, with a significant yearly increase from seven publications in 2005 to twenty-four publications in 2010. Ionic

liquids are used as lubricant for engines, but they have found application also in the electronic industry. About half of these documents are Japanese applications, and the two main actors may be identified, NSK and the Chinese Lanzhou University.

Surprisingly, especially if we compare to the open literature, only 10 applications are found concerning the use of ionic liquids for carbon dioxide capture, with a rather constant number each year since 2005. Thus, the industrial interest in this application appears doubtful.

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