Review

Room Temperature Molten Salts: Neoteric "Green" Solvents for Chemical Reactions and Processes

Jaírton Dupont[a], Crestina S. Consorti[a] and John Spencer[b]*

[a]Instituto de Química, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves, 9500, 91501-970, Porto Alegre - RS, Brazil

[b]Thrombosis Research Institute, Emmanuel Kaye Building, Manresa Road, London SW3 6LR, GB

Líquidos iônicos, em particular aqueles derivados do cátion 1,3-dialquilimidazólio, que possuem uma ampla faixa de temperatura em suas fases líquidas, pressões de vapores muito pequenas, baixas viscosidades e elevada estabilidade térmica e química vêm emergindo como uma nova classe de solventes "verdes" para processos de extração e separação, síntese orgânica e catálise. Os principais resultados obtidos com estes líquidos em Química Limpa nos últimos dois anos são objeto deste artigo de revisão.

Ionic liquids, especially those based on the 1,3-dialkylimidazolium cation, with a large range of liquid phase, negligible vapour pressure, low viscosity and high thermal and chemical stability are emerging as a new class of 'green' solvents for extraction and separation processes, organic synthesis and catalysis. The main milestones reached in the last two years, on the use of ionic liquids in green technologies, are reviewed.

Keywords: solvents, catalysis, molten salts, ionic liquids, clean technologies

Introduction

With many chemical transformations taking place in solution, the role of solvents in chemistry is vital. Although, in principle, any liquid could be employed as a solvent, polar organic solvents have been extensively used for both synthetic chemistry and extraction technologies and have largely superseded water, which was widely employed historically. However, the ever-increasing awareness of the detrimental health and environmental effects of some organic solvents has given chemists the impetus to search for 'green' technologies[1].

The obviously ideal situation for a chemical process, from an ecological point of view, involves no solvent[2]. Although many reactions can be performed without solvent, chemistry remains dominated by processes taking place in solution. Note that most of solvents have a significant solubility in the water phase, and therefore must be stripped from the water before it leaves the process, both for economic and environmental reasons. Moreover, if the solvent cannot be effectively recovered for recycle back to the system (reactor, extractor, etc.) then the process will not

be economically viable[3]. Nowadays, there are several alternatives under investigation as solvents including the resurgence of water[4], perfluorinated hydrocarbons[5] and supercritical fluids, in particular CO_2 [6].

Room temperature molten salts (ionic liquids) have been known since the beginning of this century[7] and are emerging as an attractive, alternative, 'green' technology in both organic and organometallic chemistry. This review covers the main achievements on the use of room temperature ionic liquids (RTILs) in the area of green chemistry with special emphasis on the results disclosed over the last two years. The synthesis and physical-chemical properties of molten salts, in particular halo-aluminates derivatives, have been extensively studied and a series of books on this subject is available[8]. The use of ionic liquids as solvents for catalysis and organic synthesis has been recently reviewed[9].

Molten Salts (Ionic Liquids)

Molten salts, or ionic liquids, can be described as liquid compounds that display ionic-covalent crystalline structures. This definition involves pure inorganic compounds (sodium chloride, mp=801 ºC), organic compounds (tetrabutylphosphonium chloride, mp=80 ºC) or even eutectic mixtures of

*e-mail: dupont@if.ufrgs.br

inorganic salts (such as lithium chloride/potassium chloride, 6/4, mp=352 °C) or organo-mineral combinations (triethylammonium chloride/cooper chloride, 1/1, mp=25°C).

Organo-chloroaluminate ionic liquids, especially those resulting from the combination of N-alkylpyridinium chloride or 1,3-dialkylimidazolium chloride and aluminium chloride (Scheme 1), have a broad range of liquid phase down to –88 °C [8].

Scheme 1. Examples of room temperature molten salts.

These liquids have been widely used in electrochemical technologies as solvents for highly charged complex ions, for electronic absorption spectra, for organic synthesis and for catalysis, including Ziegler-Natta reactions[9]. The advent of air and water stable ionic liquids, in particular 1-*n*-butyl-3-methylimidazolium tetrafluoroborate and hexafluorophosphate (BMI.BF$_4$, liquid down to –81 °C) and (BMI.PF$_6$) respectively[10], has led to a broader spectrum of applications involving these liquids (Scheme 2).
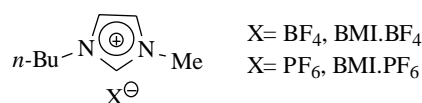
Scheme 2. Air and water stable molten salts.

Moreover, they have a wide electrochemically stable window (up to 7V), negligible vapour pressure, low viscosity, excellent chemical and thermal stabilities and differentiated solubilities with organic compounds (see Table 1)[10,11].

Moreover, the physical-chemical properties of the imidazolium RTILs can be tuned by changing the N-alkyl side chains or the anion. For example, BMI.BF$_4$ is water miscible at room temperature whereas its PF$_6^-$ analogue is much less miscible[11].

It is assumed that 1,3-dialkylimidazolium ionic liquids should not be considered as statistical aggregates of anions and cations but instead as three-dimensional networks of anions and cations, linked together by weak interactions

(mainly hydrogen bonds). In the solid state, this type of supramolecular polymeric structure has been observed several times by X-ray diffraction analysis studies[12]. In the liquid phase, measurements on BMI.PF$_6$ by Recoil spectrometry using rare gas ions on continuously refreshed liquid surfaces *in vacuo* shows neither the imidazolium cation of hexafluorophosphate anion is enriched in the liquid surface[13]. It has also been demonstrated that even in solution this type of supramolecular structure is maintained at least in solvents with low dielectric constants such as chloroform[14]. Moreover, voltammetric studies on these imidazolium ionic liquids suggested that nano–inhomogeneity can be generated by the addition of controlled amounts of water[15]. For example, although BMI.PF$_6$ is essentially insoluble in water it can absorb a considerable amount of water resulting in changes of the physical-chemical properties such as ion diffusion. The coefficient diffusion of representative redox systems such as the oxidation of tetramethylphenylediamine or the reduction of cationic methyl viologen or hexacyanoferrate(II) increases by one order of magnitude with the addition of water compared to the that of neutral species in the ionic liquid. This behaviour has been attributed to the presence of a "nano-structure" in the wet ionic liquid, which allows neutral molecules to reside in less polar regions and the ionic species in the more polar or wet regions. Wet ionic liquids (in the presence of water from other "solvents") may not be regarded as homogeneous structures (solvents), but have to be considered as nano-structures with polar and non-polar regions. It is interesting to note that this type of nano-inhomogeneity is also encountered in some liquid crystalline or concentrated surfactant media[16].

Extraction Technologies

Ionic liquids can be considered, in the majority of cases, as polar phases with their solvent properties being mainly determined by the ability of the salt to act as a hydrogen-bond donor and/or acceptor and the degree of localization of the charges on the anions. In most of the cases, imidazolium-based ionic liquids are highly ordered hydrogen-bonded solvents and can have strong effects on chemical reactions and processes[9b].

Table 1. Physical-chemical properties of selected ionic liquids at 30 °C.

Ionic liquid	η^a (Poises)	d^b (g mL^{-1})	k^c (10^{-2} S cm^{-1})	T_g^d (°C)	Solubility^e			
					H$_2$O	Hex.^{g}	Ar^h	Alc.^{i}
BMI.BF$_4$	2.33	1.17	0.864	-81	Yes	No	Yes	Yes
BMI.PF$_6$	3.12	1.37	0.656	-61^j	No	No	Yes	Yes
BMI.AlCl$_4$	2.94	1.23	2.413	nd	^{f}	No	Yes	^{f}

^{a}Viscosity (1P = 0.1 kg m^{-1} s^{-1}); ^{b}density, ^{c}electrical conductivity at 60 °C; ^{d}glass transition; ^{e}50% by weight solutions; ^{f}unstable, ^{g}hexanes, ^{h}aromatics, ^{i}methanol and ethanol, ^{j}Tg=-61 °C, mp = 10 °C.

In this context, BMI.PF$_6$ ionic liquid can be viewed as a classical solvent and is suitable for liquid-liquid extraction processes[17]. The partitioning data of various organic solutes (aniline, benzene, phthalic acid, etc.) between BMI.PF$_6$ and water show a close correlation with partition coefficients of the same solutes between 1-octanol and water. Although the distribution coefficients for the ionic liquid-water system are, in general, an order of magnitude lower than those for the 1-octanol-water system, these values are suitable for practical purposes.

Reversible pH-dependent liquid-liquid partitioning in RTILs has recently been demonstrated and this approach thereby offers potential for the replacement of the ubiquitous and toxic volatile organic compounds (VOCs) as solvents. In this particular study the authors used thymol blue, which is a dye with two distinct ionization potentials, 1.6 and 8.9. At low pH, the protonated red form could be found uniquely in the RTIL phase, whereas when the pH of the medium was increased beyond 12 the now blue, phenolic, form was quantitatively partitioned in the aqueous phase. By the impressive fine tuning of this process, they were not only able to use the recyclable gases CO$_2$ and NH$_3$ to adjust the pH of the media but they also demonstrated the use of ionic liquids at slightly elevated temperatures (1-decyl-3-methylimidazolium derivative, Scheme 3, mp=38 °C) which upon cooling to room temperature crystallized enabling removal of the dye by a basic wash[18].
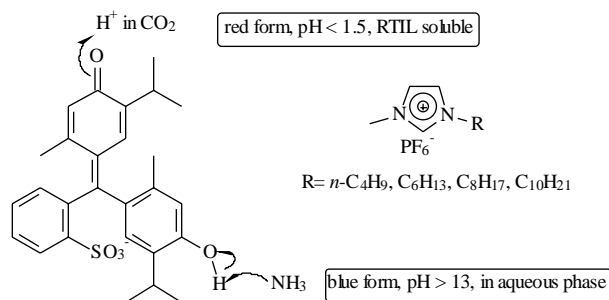

Scheme 3. A proton switch in a RTIL/water mixture.

New Materials

The ionic liquid BMI.PF$_6$ can solubilize complex polar molecules such as cyclodextrins and glycopeptides and due to its wetting ability and viscosity it can be coated onto fused silica capillaries. Therefore this ionic liquid can be used as a stationary phase for gas chromatography (GC). Using reverse phase GC the nature of this ionic liquid and its interactions with a variety of organic compounds have been recently examined[19]. This ionic liquid displays dual behaviour: it acts as a low-polarity stationary phase to non-polar compounds, whereas molecules with strong proton donor groups are tenaciously retained. These "unusual" properties of this, and other ionic liquids, could lead to beneficial applications in many areas of separation science and technology.

1-Alkyl-3-methylimidazolium tetrafluoroborate or hexafluorophosphate ionic liquids (Scheme 4) containing short alkyl chains (n = 2-10) are isotropic materials, whereas the longer alkyl chains are low melting mesomorphic crystalline solids which display an enantiotropic smectic A mesophase[20]. The thermal range of the mesophase is dependent on the length of the alkyl chain and the mesophase range is *ca.* 150 °C for the C18 methylimidazolium tetrafluoroborate ionic liquid crystal.
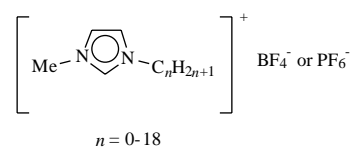
Scheme 4. 1-alkyl-3-methylimidazolium ionic liquids.

Ionic liquids have been also been employed to great effect as media for the preparation of ionic liquid-polymer gel catalytic membranes[21]. Such membranes have been prepared by mixing Pd on activated carbon with a gas-permeable ionic liquid polymer gel composed of BMI.PF$_6$ and poly(vinylidene fluoride)-hexafluoropropylene copolymer. This system was tested for the hydrogenation of propene and the gradual rise in catalytic activity was attributed to uniform Pd/C particles throughout the ionic liquid polymer structure.

RTILs can be also used as effective solvents for the preparation of aero-gels and this process has several benefits compared to more conventional methods (Scheme 5); long aging times, no shrinkage (due to the low vapor pressure), increased rate of aggregation due to the high ionic strength and the use of mild conditions. Highly stable aero-gel structures can be made without the need of supercritical drying processes, which are usually necessary when using classical solvents and a simple acetonitrile extraction will remove the RTIL without cracking the monolith[22].
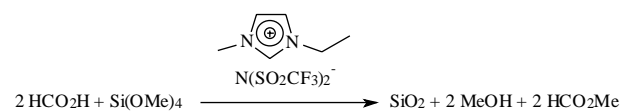

Scheme 5. A sol-gel process in a RTIL.

Ionic liquids are also being extensively exploited for the generation of high conductivity materials[23]. In this

respect highly polymeric electrolytes have been prepared by the polymerization of vinyl monomers in RTIL's or from the polymerization of alkylimidazolium molten salts. Moreover, ionic liquids have been exploited as media for the conversion of polyethylene to light alkanes indicating a possibility to generate fuels from olefin polymeric materials[24] and also as catalyst for the direct epoxidation of propene[25].

Organic Synthesis

There are two major applications of ionic liquids in organic synthesis depending on the nature of the RTIL. The first one involves the use of organo-aluminate ionic liquids in reactions promoted by Lewis acids taking advantage of the controlled acidity of such melts[8]. A mixture of $AlCl_3$ with 1-ethyl-3-methylimidazolium chloride leads to ionic liquids whose Lewis acidity is controlled by the amount of added aluminum compound. Indeed, these compounds have been used as solvents and Lewis catalysts for Friedel-Crafts acylations, alkylations, isomerisation of alkanes, and the alkylation of isobutane with butene[9b]. For example, simple aromatic compounds, such as toluene, anisole or chlorobenzene are easily acetylated in these organo-aluminate molten salts in yields equal to the best literature values (obtained under classical conditions)[26]. Moreover, organometallic compounds, such as ferrocenes, are also easily acetylated by anhydrides or acid chlorides and the selectivity in mono or bis(acetylated) ferrocenes is a function of the Lewis acidity, *i.e.*, the amount of $AlCl_3$ (Scheme 6)[27].

x= 1	0%	0%
x= 1.2	89%	0%
x= 3	16%	40%
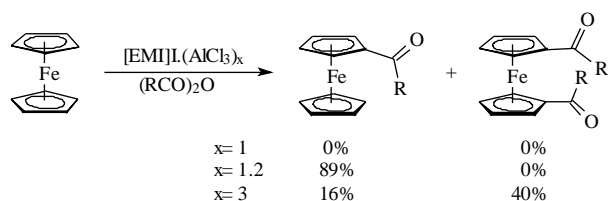
Scheme 6. Acetylation of ferrocene.

Moreover, 1-ethyl-3-methylimidazolium halogeno-aluminate ionic liquids have been successfully employed as reaction media for the acylative cleavage of a series of cyclic and acyclic ethers (Scheme 7)[28].
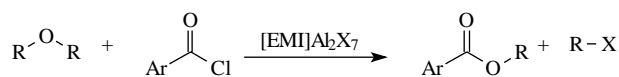
Scheme 7. Acylative cleavage of ethers in RTILs.

In applications involving Lewis acid ionic liquids, it is assumed that these type of media facilitate the generation and stabilization of organic cations (such as the benzoyl cation). It is also evident that other reactions involving carbocations should proceed equally well in these media.

The second application in organic synthesis is related to the use of the RTILs as "neutral" solvents. These solvent properties were nicely exemplified in a study of the Diels-Alder reaction between cyclopentadiene and methyl acrylate[29] for which the influence of the organic solvent is well understood. The reaction performed in $BMI.BF_4$ (Scheme 8) displayed a strong *endo* selectivity (*endo/exo* = 86:14) which is similar to that observed in polar organic solvents and slightly higher than those observed in non-polar solvents (diethyl ether, 74:26). The *endo* selectivity follows the same trend observed in conventional organic solvents, *i.e.*, decreases with increasing reagent concentration and reaction temperature.
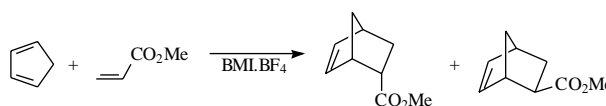
Scheme 8. Diels-Alder reaction in $BMI.BF_4$.

In most of the cases, Diels-Alder reactions in ionic liquids lead to significant rate enhancement and high yield and selectivity[30]. The use of these ionic "solvents" could replace the best alternative, lithium perchlorate-diethyl ether, avoiding the generation of lithium perchlorate-based wastes and avoiding significant safety problems (diethyl ether and pressure reactions).

Seddon's group recently showed that the $BMI.PF_6$ system is also an alternative clean medium to classical dipolar aprotic solvents for the alkylation of ambident nucleophiles[31]. Thus, 2-naphthol and indole, dissolved in this ionic liquid, were selectively O- and N-alkylated respectively, by a series of alkyl halides using solid KOH as base. The products were quantitatively extracted by diethyl ether and the recovered ionic liquid was recycled many times without any noticeable decrease in yield or regioselectivity (Scheme 9). The same group disclosed an impressive electropositive metal-mediated selective low-pressure hydrogenation of poly-aromatics using the $EMI.AlCl_4$ (EMI = 1-ethyl-3-methylimidazolium cation) system (Scheme 9)[32].
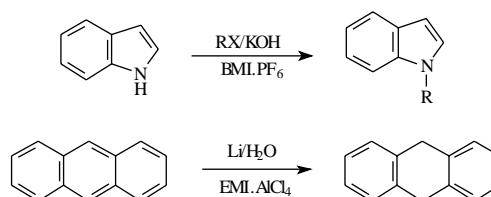
Scheme 9. Selective alkylations and reductions in imidazolium molten salts.

Biphasic Catalysis

The field of biphasic catalysis in ionic liquids is attracting increasing interest. Transition-metal catalyst precursors are often soluble and stable in BMI.BF$_4$ and BMI.PF$_6$ ionic liquids, whereas many organic compounds are either insoluble or easily separated by decantation, and the recovered ionic catalytic solution can be reused[9b]. One asset of biphasic catalysis in ionic liquids is that it allows, in various cases, the direct transposition of known homogeneous one-phase reactions to two-phase systems without the synthesis of specially tailored ligands and/or complexes. Moreover, in various cases, ionic liquids have been shown to promote reactions which are difficult or do not occur in classical organic solvents. RTILs can be divided in two major classes: (i) organo-aluminate molten salts that are particularly suitable for Ziegler-Natta type reactions and (ii) "neutral" ionic liquids containing generally BF$_4$ and the PF$_6$ anions.

Organo-aluminate molten salts derived from 1-alkyl-3-methylimidazolium or N-alkylpyridinium cations, whose Lewis acidity can be tuned by the amount of aluminum salt added were amongst the first to be used in biphasic catalysis. The immobilization and activation of nickel catalyst precursors, used in the oligomerisation of α-olefins, was ingenuously developed by Chauvin *et al.*[32-36]. One of the most impressive results reported so far involves the immobilization of the nickel complex (Scheme 10) in slightly acidic 1-*n*-butyl-4-methylpyridinium chloro-aluminate molten salts for the selective dimerization of 1-butene[37].
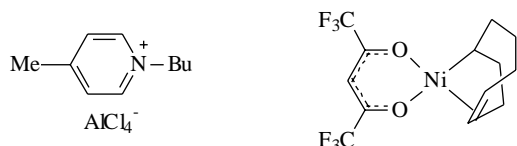
Scheme 10. Pyridinium molten salt and Ni catalyst precursors used in the dimerisation of 1-butene.

This nickel derivative was the most active catalyst precursors dissolved in organic solvents for the dimerization of 1-butene giving turnover frequencies of up to 500 h^{-1} with 85% selectivity in octenes. However, the use of the pyridinium organo-aluminate molten salt as solvent led to turnovers of 2100 h^{-1} with 98% selectivity in linear dimers. Moreover, this biphasic mode of operation allows easy catalyst recovery and recycling, without the use of organic solvents.

However, in terms of biphasic catalysis and green processes the RTILs BMI.BF$_4$ and BMI.PF$_6$ are by far the most popular solvents.

In the field of hydrogenation almost all of the classical Ru, Rh, Co and Pd catalytic systems have been successfully transposed to biphasic conditions. For example, arene hydrogenation can be performed by [H$_4$Ru$_4$(η^6-C$_6$H$_6$)$_4$] [BF$_4$]$_2$ dissolved in BMI.BF$_4$ in a typical biphasic reaction with catalytic turnovers similar to those obtained by the same catalyst dissolved in water under the same reaction conditions[38]. More interestingly, it was found that RuHCl(CO) (PCy$_3$)$_2$ dissolved in BMI.BF$_4$ is able to selectively reduce NBR (acrylonitrile-butadiene rubber) to HNBR (hydrogenated acrylonitrile-butadiene rubber) under mild reaction conditions[39]. The selectivity and catalytic activity achieved in molten salts are clearly superior to those obtained under homogeneous or heterogeneous conditions. Another interesting property of biphasic catalytic systems is the possibility of extracting the primary products formed during the reaction (due to the different miscibility of the products) and thus enabling the modulation of the product selectivity. In ionic liquids this property has been used to modulate the selectivity in mono-hydrogenated olefins from the hydrogenation of dienes promoted by transition metal complexes[40]. For example, the hydrogenation of methyl sorbate by Pd(II) compounds dissolved in BMI.BF$_4$ produces, as the primary product, mono hydrogenated diene (Scheme 11) which can be recovered almost quantitatively before further hydrogenation can take place.

**Scheme 11.** Selective hydrogenation of methyl sorbate.

Not surprisingly, palladium catalyzed C-C and C-heteroatom bond forming reactions can be performed in RTILs and in most of the cases the ionic liquid has a strong beneficial effect on the reaction rate and selectivity. For instance, allylic alkylations and aminations in BMI.BF$_4$ have been recently reported (Scheme 12)[41]. Poor catalyst separation and leaching hampered catalyst recycling, although the deployment of P(*m*-C$_6$H$_4$SO$_3$Na)$_3$ meant that the organic product could be toluene extracted.
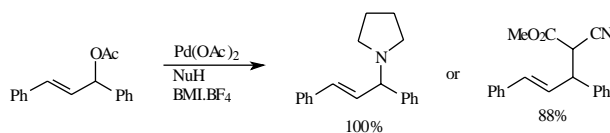
Scheme 12. Palladium catalyzed reactions in molten salts.

Hermann reported Heck reactions where even bromo-benzene could be vinylated, with impressive turnovers (up to 1,000,000), in molten ammonium salts using a

cyclopalladated phosphine catalyst precursor (Scheme 13)[42]. In this case the formation of NaBr as by-product causes an increase in viscosity of the medium. The ionic catalytic phase could be re-used up to six times and thereafter metallic palladium was formed.
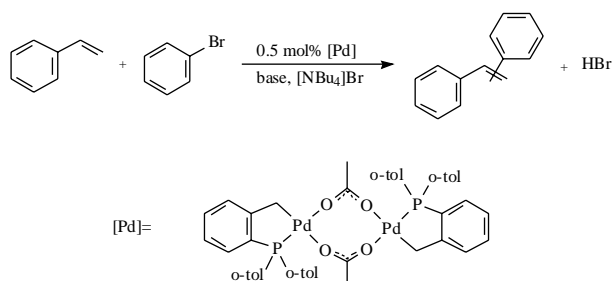
Scheme 13. Cyclopalladated complex catalyzes the Heck reaction in molten salts.

However, the salt by-product can be easily removed from ionic solution using Pd(II) and Pd(0) compounds dissolved in BMI.PF$_6$. In this particular case, the palladium compounds are retained in the ionic phase, the products extracted by hexanes and the salt by-product removed by washing with water. Since BMI.PF$_6$ is not miscible with water and hexane, a typical triphasic system is formed[43].

Very recently it was shown that during Heck-type reactions, catalyzed by palladium acetate in ionic liquids such as 1-*n*-butyl-3-methylimidazolium bromide, catalytically active species are stabilized by the formation of palladium-carbene complexes (Scheme 14)[44].
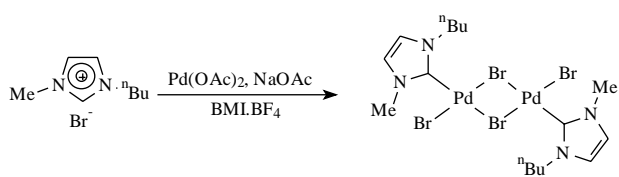

Scheme 14. Formation of palladium-carbene complexes in molten salts.

It was also observed that palladium compounds dissolved in RTILs such as BMI.BF$_4$ can cause the de-alkylation of the imidazolium cation (Scheme 15)[45]. These results clearly indicated that ionic liquids do not act as simple solvents but can also induce and actively participate in the formation of new compounds.
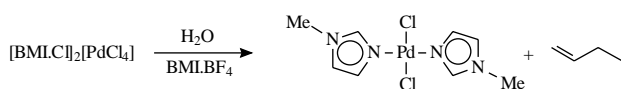
Scheme 15. De-alkylation of the imidazolium cation in BMI.BF$_4$.

Ionic liquids improve the activity, selectivity and stability of palladium-catalyzed Trost-Tsuji couplings in biphasic media. In an elegant study, C. de Bellefon and co-workers showed that palladium chloride associated with triphenylphosphine trisulphonate, dissolved in 1-*n*-butyl-3-methylidazolium chloride, promoted the selective coupling between ethyl cinnamyl carbonate and ethylacetoacetate (Scheme 16)[46]. The molten salt catalytic system has definitive advantages over an aqueous catalytic phase such as faster reaction rates and selectivity and common organic layers can be used for product extraction without catalyst deactivation.
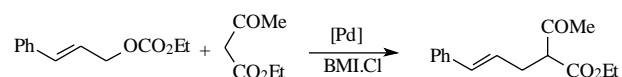
Scheme 16. Allylic alkylation catalyzed by Pd dissolved in BMI.Cl.

Although the exploration of ionic liquids as solvents is still very much in its early days, they have proved to be an excellent medium, especially for biphasic reactions as varied as asymmetric catalysis[10a,47], hydroformylations[10a,48-50], olefin telomerizations and oligomerisations[45], although these remain out of the scope of this review.

Conclusions

In most of the applications described above the organic compounds can be easily separated from the ionic solution by decantation or distillation. In some cases until very recently, only liquid-liquid extraction using organic solvents, resulting in cross-contamination, could be used. However, non-volatile organic compounds, at least aromatic compounds, can now be removed by using another environmental benign solvent - supercritical carbon dioxide[51]. This process was investigated using BMI.PF$_6$ as ionic liquid and naphthalene as a low-volatility model solute. Spectroscopic analysis indicated the quantitative recovery of the solute in the supercritical solvent phase without ionic liquid contamination.

The possibility of modulating the hydrophilic or hydrophobic character of ionic liquids leads to several potential applications in extraction technologies[17], in the generation of new materials (liquid-polymer gels[21], stationary phases for gas chromatography[19], liquid crystals[20], electrochemical gas phase reactors and gas sensor systems[15], etc.), and in two-phase catalysis where separation phenomena are crucial, in particular for the design of green processes.

We anticipate the increasing importance of ionic liquids in industrial processes as well as their association with other green technologies, such as supercritical CO$_2$, for future

clean synthetic and extraction processes. For a general paper concerning the role of catalysis (in particular two-phase catalysis) in the design, development, and implementation of green chemistry see ref 52.

Much of the work covered herein has been published over the last decade, demonstrating the impact of green chemistry and it is clear that ionic liquid "science" will have many future applications. Further studies on the physical properties of ionic liquids and their design will lead to even more efficient and applied green solvents and industrial applications should follow[53]. Indeed, the industrial implications of such an impressive technology are now apparent, with IFP (France) using the $BMI.AlCl_4$ system in a nickel-catalyzed butene dimerization process[54]. Moreover various patents have appeared in the last five years claiming the beneficial effects of ionic liquids on the substitution of classical organic solvents[55].

Acknowledgments

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