

Are ionic liquids a proper solution to current environmental challenges?

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It is well known that ionic liquids (ILs) possess extraordinary characteristics, making them greener solvents with unique properties, which allow processes that would otherwise be difficult or impossible with common solvents to be carried out. In this review, we describe and discuss, in the light of possible future large scale applications, some fundamental studies showing the efficacy of ILs in several “hot” fields, from dissolution and transformation of biopolymers to extraction and capture of important inorganic components (metals) or pollutants (CO₂).

Introduction

The human population has grown exponentially over the past century (from two to seven billion) and it is expected to increase to over nine or ten billion by the year 2050. This growth has been accompanied by an accelerated depletion of natural resources. Fossil fuels are generally quoted as the most essential commodities that will become scarce during the coming decades,¹ and petroleum depletion implies not only the necessity of finding other energy sources, but also dangerously restricted access to most chemicals used in the synthesis

of compounds employed everyday worldwide. Furthermore, several minerals and metals have only limited availability.² On the other hand, if the supply of some natural resources is unlikely to keep pace with the increasing demands of a growing population, the concomitant waste production is the other important challenge of our society. Conserving resources, as well as managing materials and waste, are nowadays absolute priorities that are well within the scope of green chemistry.

Ionic liquids (ILs), novel “greener” solvents with unique properties, have been found to be able to dissolve and favour the transformation³ of organic, inorganic and polymeric materials, thus overcoming some technological barriers and allowing a more efficient use of renewable resources or waste materials. In this context, we report here on some fundamental studies showing the efficacy of ILs in addressing the following current challenges: (i) dissolution of cellulose, as well as

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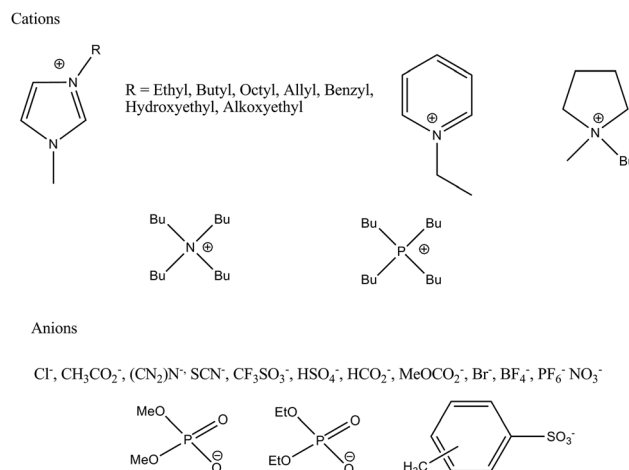
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other biopolymers, under relatively mild conditions to develop new processing strategies in material sciences and fuels; (ii) depolymerisation of non-natural polymers for recycling of waste plastics; (iii) recovery of rare earth elements and extraction of metals from waste, and (iv) capture of CO₂ (and other gases) produced by the burning of fossil fuels and other industrial activities. In particular, we will describe and discuss the principal drawbacks that limit large scale application of ILs at the moment, while also taking into account that, independent of the system employed, the enormous quantity of the raw or waste materials to be treated is one of the principal problems to be solved.

Ionic liquids

The term ionic liquids identifies a very large class of chemical compounds, constituted exclusively of ions (generally an asymmetric organic cation and a polyatomic organic or inorganic anion), which are liquid at, or close to, room temperature. Their ionic nature imparts unique properties to these liquids. Generally, they have high conductivity, high thermal stability, low flammability and very low (if any) volatility. This latter property reduces explosion risks and toxic effects for workers, two dangerous features that are normally associated with the use of volatile organic solvents (VOCs). The often-stressed “green” character of ILs is indeed largely related to their negligible vapour pressure and inability to produce air pollution. However, ILs can spill in water or soil, where they can exert toxic effects: the acute toxicity and eco-toxicity of ILs towards aquatic organisms, described⁴ for several commonly employed ILs, is an important issue extensively discussed and, in recent times, widely investigated. Fortunately, the composite picture emerging from these studies shows that ILs toxicity strongly depends on cation–anion structure: careful design or selection of the IL anion and cation should always be able to guarantee both high process performance and sustainability.⁵ It is noteworthy that the main advantage of ILs relies on the possibility to modify all their properties (*e.g.* viscosity, conductivity, hydrophilicity, hydrophobicity, polarity, hydrogen bond ability) through the selection of appropriate anion and cation combinations (Scheme 1) or through the introduction of specific functional groups on cation or anion.⁶

The peculiar interactions characterizing each IL provide a unique environment, which is able to dissolve even solutes having a significantly different nature.⁷ Anion and cation heads generally represent the “polar” moiety of ILs, dominated by Coulombic interactions, which provide a medium-range charge ordering. Depending on charge distribution and steric effects, the interaction between oppositely charged species can, however, be more or less relevant,⁸ affecting the possibility of substrate insertion into this “polar” region and the ability of the single components (cations and anions) to interact with the dissolved compound. It is noteworthy that, beside the dominance of the ionic interactions in terms of their absolute energy contributions, weaker and directional forces (hydrogen bonding, dipole–dipole, dipole–ion interaction) may also affect the dissolution process.⁹ Furthermore, in ILs



Scheme 1 Selection of widely used cations and anions.

characterized by strong anion–cation interactions, the presence of sufficiently long hydrophobic alkyl chains on the cation or anion can generate dynamic three-dimensional structures with “polar” and “apolar” domains.¹⁰ Hydrophobic substrates can interact exclusively with the apolar regions.¹¹ However, it should be taken into account that these domains are not necessarily present in every IL¹² and, when present, they undergo dynamic changes; the timing of these phenomena probably plays a fundamental role in many processes occurring in ILs. Finally, the presence of specific functional groups on the cation or anion can add further interaction sites favouring dissolution, and sometimes strong binding, of appropriate substrates.

Due to the complexity of the interactions between the solute and the ionic components,¹³ macroscopic parameters, such as the relative permittivity (ϵ , determined as the zero-frequency limit of the frequency-dependent dielectric dispersion),¹⁴ are generally not useful in describing the polarity of ILs, being unable to take into account the multiple specific interactions occurring between the IL components and the solute. Indeed, the ϵ values determined for several ILs classify these media as solvents of moderate–low polarity. On the other hand, microscopic parameters determined using solvatochromic probes give a completely different picture.¹⁵ For example, on the basis of the Kamlet–Taft parameters, expressing polarity in terms of polarizability–dipolarity (π^*), hydrogen bond acidity (α) and hydrogen bond basicity (β), ILs appear as polar solvents, characterized by a significant hydrogen bond acidity and/or basicity, depending on cation and anion structure.¹⁶ α and β parameters have been used with success to rationalize organic reactivity in ILs, in particular when hydrogen bond interactions dominate.¹⁷ The development of additional parametric scales able to describe other important features of ILs, such as Lewis acidity and basicity or coordination ability, might surely be useful to obtain further information about solubility of other species, such as metal cations or metal oxides.

Cellulose dissolution

Cellulose, hemicelluloses and chitin are underutilized sources of renewable feedstocks. The potential of these biopolymers has not yet been fully investigated, principally owing to the free availability of fossil materials that has characterized our society from the 1940s, but also due to the inability of common solvents to solubilise many natural polymers. However, from 2002, when Rogers *et al.* published¹⁸ a foundational paper dealing with the possibility of dissolving and regenerating cellulose, without activation or pretreatment, in a common IL, 1-butyl-3-methylimidazolium chloride ($[\text{C}_4\text{C}_1\text{im}]\text{Cl}$), activity in this field has grown exponentially.

The ability to dissolve cellulose, a peculiarity of only some anion-cation combinations, was initially attributed to the ability of the IL anion to hydrogen bond with the carbohydrate hydroxyl groups.¹⁹ Chloride, acetate, formate and alkylphosphonate are generally considered the most promising anions, and fairly good correlations between the Kamlet-Taft β parameter and cellulose dissolution have been reported.²⁰ However, the possible²¹ participation of the IL cation in the dissolution process has also been invoked²² and a mechanism has been proposed.²³ In this regard, it is noteworthy that the difference between hydrogen bond basicity and acidity, $\beta-\alpha$ ("net basicity"), rather than β alone, has been recently proposed²⁴ as the best parameter to predict cellulose dissolution in ILs. Since the α parameter is mainly related to the IL cation, this component must necessarily play a role. Finally, although it has been reported²⁵ that the presence of an acid function on the IL cation reduces cellulose solubility, as this acidic group competes with the solute, some protic ILs arising from the reaction of a strong base (tetramethylguanidine²⁶ and 1,8-diazabicyclo[5.4.0]undec-7-ene²⁷) with a weak acid (*i.e.* acetic or propionic acid) have recently been used to dissolve cellulose (Scheme 2).

These latter ILs, although often unable to reach the efficiency levels of the generally employed "neutral" imidazolium salts, have the great advantages of being easy to synthesize, inexpensive and retrievable by distillation of the regenerated precursors under appropriate conditions.

On the other hand, the presence of water and alcohols also decreases the solubility of cellulose in ILs,²⁴ probably through

a similar mechanism (water or alcohols compete with cellulose in the interaction with IL anion), and dissolved cellulose in ILs can be reconstituted by adding these protic "anti-solvents". Regeneration of cellulose can be explained similarly to dissolution in terms of $\beta-\alpha$; typically, it occurs at values lower than 0.35. Differences between dissolution and regeneration have been found,²⁴ however: some ILs are very sensitive to water during the dissolution process, but, unfortunately, the same ILs tolerate water during the regeneration process.

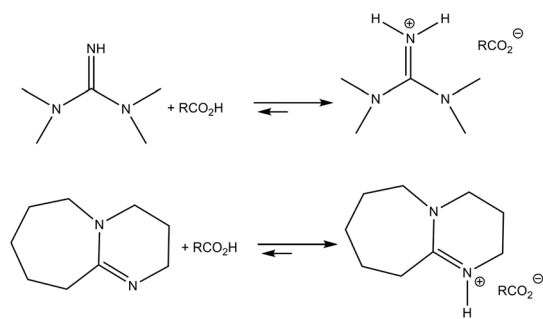
It is noteworthy that, depending on the nature of the IL, process conditions and cellulose type, the reconstituted material can have significantly different properties from the original one: in particular, a considerable reduction of cellulose crystallinity can be observed in certain ILs.

Generally, the anti-solvent precipitates cellulose from the solution, with water (or alcohol) and IL forming a single phase. Cellulose can be recovered by filtration or centrifugation and washed to remove excess IL. However, particularly when water is added, the formation of a gel phase, which can impede cellulose separation, is often observed at high biomass loads and in the presence of ILs characterized by bulky cations. In these cases, a water-acetone (1 : 1, v/v) solution is often employed to avoid gel formation.²⁸

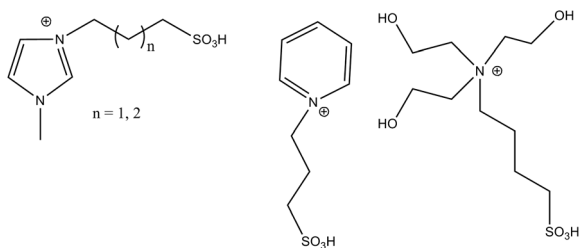
The use of an anti-solvent normally allows a good recovery of cellulose from paper/wood waste (see below). However, this approach requires considerable amounts of water to precipitate carbohydrate rich materials and to extract the residual IL. The energy subsequently required to remove water and recover the IL is consequently high and advanced engineering solutions to address this issue are thus necessary, since this step can negatively affect the large scale application of ILs in these processes.

When the dissolution of cellulose is used in sugar production for biofuels, it might be more convenient to hydrolyze cellulose directly in IL, owing to the enormous amounts of material to be treated. It is well known that both acidic and enzymatic catalysis can be used for this purpose. However, despite the fact that novel and more efficient fungal bio-refinery processes²⁹ or bioengineered enzymes (cellulases)³⁰ are under development, biocatalyzed processes³¹ for large scale applications are still hindered by the high costs³² of the related procedures (processes generally characterized by low reaction rates and carried out at high dilution). Consequently, acid hydrolysis is often considered a simpler approach to obtain sugars from cellulose. Different mineral acids have been tested as catalysts, achieving 81% liberation of total reducing sugars (TRS) in $[\text{C}_4\text{C}_1\text{im}]\text{Cl}/\text{HCl}$.³³ The use of Brønsted acidic ILs of the type reported in Scheme 3, which are able to dissolve cellulose (up to 20%) and to act as catalysts, has also been reported.³⁴

The best results (62% yield of reducing sugars) have been obtained by heating the mixture for 1.5 h at 70 °C, after addition of water. Analogously, sulfonate resins (Amberlyst) in $[\text{C}_4\text{C}_1\text{im}]\text{Cl}$ favour cellulose depolymerization to celooligomers which, if the process is terminated at the proper time, can be isolated and subsequently degraded to sugars.³⁵ Finally, an



Scheme 2 Protic ILs formed from tetramethylguanidine or 1,8-diazabicyclo[5.4.0]undec-7-ene and an acid.



Scheme 3 Brønsted acidic IL cations used for cellulose dissolution and hydrolysis.

efficient cellulose depolymerization has been obtained³⁶ using catalytic amounts of metal chlorides. In this case, while single metal chloride showed much lower activity with respect to mineral acids, paired metal chlorides (in particular, $\text{CuCl}_2/\text{PdCl}_2$) were particularly active in the hydrolytic cleavage of the 1,4-glycosidic bond. However, acid catalyzed hydrolysis cannot be considered a simple process. Indeed, reaction conditions need to be carefully controlled to avoid a decrease in efficiency or the formation of unwanted black tars.

Furthermore, regardless of the catalyst, all these processes present two critical points: the separation of hydrolyzed sugars from the aqueous IL and the recovery of the IL. For this purpose, the use of boronic acids to extract mono and disaccharides from ILs as sugar boronic complexes, which are soluble in organic solvents, has been reported in a recent patent.³⁷ Despite the claimed efficiency, the sustainability of this method appears to be limited, however, whereas the mentioned future developments based on the use of boronic membranes could be more promising.

For large scale applications, it might also be interesting to investigate the recently proposed³⁸ recovery of sugars (maximum yields: 53% glucose, 88% xylose) using the ability of hydrophilic imidazolium based ILs to give phase separation upon addition of an aqueous alkaline solution.

The development of appropriate molecular and engineering technologies to perform these processes (sugar separation and IL recovery) in a cost-effective and ecological way that is competitive with current production technologies remains, in our opinion, the main challenge for large scale application of ILs in cellulose transformation to sugars.

Of course, dissolution of cellulose in ILs is not necessarily restricted to obtaining sugars and biofuels. A variety of cellulose-based materials or composite products, which are often easier to recover from ILs than sugars, have been developed over the last few years by mixing cellulose and other compounds in ILs. Bioactive supports, membrane sensors and cellulose/polymer blends can be obtained using this strategy.³⁹

Starting from the aforementioned results related to cellulose dissolution, the application of various hydrogen-bond basic ILs has been recently extended to degradation of lignocellulosic biomass. Wood is, however, a more complex system: a porous micro-structured composite consisting mainly of cellulose, hemicellulose and lignin, and its dissolution in ILs is controlled by various factors. Water content and wood particle

size (ball-milled wood powder > sawdust \geq thermomechanical pulp (TMP) fibers \gg wood chips) cause large changes in the dissolution efficiency. Also, in this case, a correlation between the hydrogen-bond basicity of the IL and the ability to swell and partially dissolve wood chips (in particular pine chips) has been observed.⁴⁰ The role of ILs in deconstruction and fractionation of lignocellulosic biomass, commonly called pretreatment, has been recently and thoroughly discussed in a critical review by Welton *et al.*²⁰

The tunability of ILs and the information collected in the last years on the factors affecting cellulose dissolution should allow the design and synthesis of low cost ILs, having net-basidity (β - α) associated with high biodegradability and low ecotoxicity (three parameters that can be optimized mainly by modifying IL cation), as well as a modular hydro-compatibility. In other words, ILs that, in contrast with those generally used,²⁴ can tolerate the presence of water during the dissolution of (wet) biomass, but that, after water addition, easily regenerate the cellulose fraction. This latter feature, which is most likely adjustable by changing the temperature, might significantly increase the applicability of these media in large scale processes. However, since extremely large amounts of biomasses must be processed for biofuel production, the optimization of the IL alone is probably not sufficient to solve this generally neglected problem. New engineering technologies assuring continuous processes and higher biomass loading should be developed, together with new improved ILs. Related to this topic, it is noteworthy that the combined use of extruders and ILs as pretreatment reactors of biomasses has been recently reported,⁴¹ showing that this approach requires a significantly lower amount of IL to dissolve cellulose. Further development in this area could favour IL application in large scale operations.

Chitin and keratin dissolution

After the discovery of the ability of ILs to dissolve cellulose, a large number of investigations were carried out on the ability of these solvents to dissolve other biomacromolecules.³⁸ Silk fibroin, wool keratin and shrimp shell chitin have been dissolved by up to 20–25% in several chloride and acetate based ILs. In these cases, solubility depends not only on IL structure and process conditions (for example, temperature, stirring and so on) but also on polymer source. It is noteworthy that, in contrast with cellulose dissolution, a more limited set of IL structures has been investigated for these biopolymers (many investigations are related to the use of $[\text{C}_4\text{C}_1\text{im}]\text{Cl}$, $[\text{C}_4\text{C}_1\text{im}][\text{OAc}]$ and 1-allyl-3-methylimidazolium chloride, $[\text{C}=\text{C}_2\text{C}_1\text{im}]\text{Cl}$). The IL choice has probably been affected by results obtained in wood and cellulose dissolution, since the breaking of the hydrogen bonds among macromolecules is thought to be the driving force in every case,¹² in spite of the differences between these compounds.

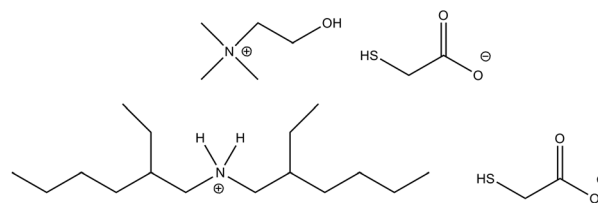
Chitin, which is the most abundant and renewable polymer in the world after cellulose, constituted of *N*-acetyl-D-glucosamine and present in crustaceans, insects and fungi, has been dissolved⁴² in $[\text{C}_4\text{C}_1\text{im}]\text{Cl}$ after heating at 110 °C for 5 h (10%)

or in $[C_2C_1im][OAc]$ after heating at 110 °C for 19 h (20%). The dissolution process is generally followed by regeneration of the biopolymer into different forms (films, fibers and gels), affording new materials. For example, by combining the excellent mechanical properties and biocompatibility of chitin with the electrical conductivity of carbon nanotubes, it has been possible to obtain conducting chitin nanocomposite scaffolds simply by mixing them in an imidazolium based IL ($[C_2C_1im][OAc]$).⁴³ High molecular weight chitin fibers were produced by electrospinning chitin directly from an extraction solution of 2.0 wt% shrimp shell loading in $[C_2C_1im][OAc]$.⁴⁴

Recently, attempts have also been made to obtain N-containing molecules from *N*-acetyl-D-glucosamine by applying transformations similar to those performed on monosaccharides. Under optimized conditions, 3-acetamido-5-acetylfuran (60% yield) was obtained from the dehydration of *N*-acetyl-D-glucosamine in $[C_4C_1im]Cl$ in the presence of boric acid.⁴⁵

Keratin is a fibrous protein that is found in feather, wool, human hair, finger nails and animal horns. This biopolymer is plentifully available as a by-product of the poultry production and textile industries, and is produced in both cases in such large amounts that it causes environmental disposal problems. Although only marginally investigated, wool keratin films have recently been obtained,⁴⁶ starting from a solution of “cleaned” wool fibres in 1-allyl-3-methyl imidazolium chloride ($[C=C_2C_1im]Cl$) or $[C_4C_1im]Cl$. $[C=C_2C_1im]Cl$ appears to be a better solvent than $[C_4C_1im]Cl$, being able to dissolve up to 21% of wool in about ten hours at 130 °C. X-ray diffraction (XRD) data shows a β -sheet structure in the regenerated film, along with the disappearance of the α -helix structure. Analogously, only a few investigations have been carried out on bird feathers. In this case, however, not only $[C=C_2C_1im]Cl$ and $[C_4C_1im]Cl$ have been tested as dissolution media, but also other functionalized ILs. In particular, a hydrophobic IL, 1-hydroxyethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide, $[HOC_2C_1im][Tf_2N]$, has been used⁴⁷ to try to overcome recovery problems due to the solubility of keratin in water (which is the anti-solvent generally used for biopolymer separation from the IL). This solubility, which is probably related to the fragmentation of keratin during the dissolution process, often drastically reduces the polymer recovery when water soluble ILs are used. (Unfortunately, this important parameter – recovery – is rarely reported in the original papers!) In contrast with cellulose, this hydrophobic IL appears to be able to dissolve keratin, although the maximum yield (expressed as a percentage of the total weight of dried feathers) was only 21%, even though quite a large mass ratio of IL to feather, 40:1, was employed at 80 °C for 4 h (in the presence of $NaHSO_3$ 1:1 mass ratio with keratin); in other words, it was possible to solubilize and recover *ca.* 5 mg of keratin using 1 g of IL! Considering that $[Tf_2N]^-$ based ILs are significantly more expensive than chloride based ones, the large scale application of this procedure appears to be unsuitable at the moment.

Recently, the ability of two ILs possessing a reducing thiol function on the anion ($[choline][thioglycolate]$ and $[bis(2-$



Scheme 4 Thiol functionalized ILs used for keratin dissolution.

ethylhexyl)ammonium][thioglycolate]) to dissolve and regenerate keratin from turkey feather has also been evaluated⁴⁸ in comparison with $[C=C_2C_1im]Cl$, $[C_4C_1im]Cl$. Despite their hydrophilic nature, $[C=C_2C_1im]Cl$, $[C_4C_1im]Cl$ and $[choline][thioglycolate]$ were able to dissolve up to 45% turkey feather keratin by weight (at 130 °C for 10 h), while also allowing recovery of around 50% of the water insoluble fraction. In this case, it has been reported that, using 1 g of IL, it was possible to recover *ca.* 270 mg of keratin (Scheme 4).

ATR-FTIR (attenuated total reflectance–Fourier transform infrared), XRD and solid state NMR spectra showed, moreover, that dissolution occurs without major change of the polypeptide chain conformation, even though it probably involves breakdown of the polymer chains into smaller segments and loss of some α -helix structure. $[Choline][thioglycolate]$ appears to only accelerate to some extent the dissolution process, while simultaneously causing a greater degree of fragmentation into unwanted water soluble oligopeptides. This fragmentation is probably due to the presence of the thiol function, which reduces disulfide bridges that are responsible for the high degree of crosslinking in the polypeptide chains. The reducing moiety on the IL has therefore been considered a useful, but not determinant, component for keratin dissolution.

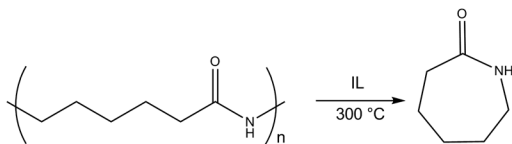
Recovery of keratin and fibroin (and probably chitin as well) through the use of ILs seems to be, for the moment, an interesting target with potential applicability, however much more fundamental research is required to elucidate the mechanisms that determine dissolution, degradation and polymer recovery and to provide the basis for a rational assessment of exploratory technologies.

Depolymerisation of non-natural polymers from the recycling of waste plastics

The chemical recycling of waste plastics is a challenging process, since the conversion of polymers into the corresponding monomeric material generally requires harsh conditions that provoke unwanted side-reactions and by-product formation.

An efficient depolymerisation of nylon-6 using a hydrophobic IL, *N*-propyl-*N*-methyl-piperidinium bis(trifluoromethanesulfonyl)amide ($[C_3C_1pip][Tf_2N]$), was reported⁴⁹ for the first time in 2007. The reaction, carried out at 300 °C for 4–5 h, furnished the corresponding ϵ -caprolactam in 86% yield (Scheme 5).

Subsequently, depolymerisation of nylon-6 has also been reported in a less expensive $[C_4C_1im]Cl$ -water mixture at



Scheme 5 Nylon-6 depolymerisation.

170 °C for 8 h, although the caprolactam was isolated in lower yield (*ca.* 31%).⁵⁰ The hydrolysis of nylon-6,6 to hexamethylenediamine and adipic acid in hydrophobic ILs (in the presence of water and H₂SO₄, at temperatures ranging preferably from 50–100 °C) has also been described by Seddon *et al.* in 2009 in a patent.⁵¹

More recently, Kamimura *et al.* have investigated⁵² the depolymerization of more complex systems, in particular fibre-reinforced plastics (FRP, a composite material widely used in bathtubs, boats, and so on, which consists of inorganic fibres, polystyrene and polyesters) in [C₃C₁pip]Tf₂N]. FRP and unsaturated polyesters were readily depolymerized at 340 °C (2 min, using microwaves). The monomeric material, phthalic anhydride, was isolated by distillation at reduced pressure in >90% yield, whereas the inorganic fibres were recovered in almost pure form in 51% yield, and the IL was recycled and used a further two times without purification.

Finally, a 2013 patent reports⁵³ the use of hydrophobic ILs to dissolve rubber tires. Disposal of waste tires is an important and enormous problem, which nowadays occurs essentially through incineration or discarding in landfills.

With respect to biopolymer dissolution in ILs, research in this area is unfortunately extremely scarce and fragmented, owing to the diverse compositions of materials based on non-natural polymers. To establish the potential impact of ILs in this area, extensive and coordinated investigations are therefore essential.

Recovery and extraction of metals

Metal treatment generally requires high energy consumption and generates large amounts of waste. Furthermore, since the quantity of high quality raw materials is progressively decreasing, the recovery of an increasing number of metals, not only rare earths, from waste products, which is widely employed in several fields and technologies, has become a promising approach not to be rejected *a priori*.

Conventional methods employed nowadays to recover and purify metals use either volatile organic solvents, non-reusable absorbents or harmful chemicals (sulfuric acid and cyanide) or combinations of these.⁵⁴

Starting from the first pioneering works,⁵⁵ several studies have shown that ILs are interesting candidates for performing metal extraction from mineral matrices⁵⁶ or spent nuclear fuel,⁵⁷ as well as for electrodeposition and electrowinning of metals. Metal processing is intrinsically complex, owing to the diverse sources of the starting materials (metals, oxides, sulphides, carbonates, phosphates, complex slags, alloys), which determine the methodology to be applied to obtain a specific

product. ILs have been used in several processes involving dissolution, extraction and recovery of metals, although by far the most work has been carried out in the field of extraction. A critical review on the potential efficacy of these methods has been published recently.⁵⁸ ILs bearing Lewis base anions (mainly chloride and bromide), or less coordinating anions (for example, bis(trifluoromethanesulfonyl)imide) with added halides to increase metal cation solubility, have been used⁵⁹ to process metals. Solubility of metals in ILs has also been increased by adding ligands commonly used in biphasic extractions (for example, crown ethers,⁶⁰ calixarenes,⁶¹ diti-zone,⁶² or, very recently, a neutral thione⁶³) or introducing specific functional groups on the IL cation or anion (thioether or thiourea to favour Hg²⁺ and Cd²⁺ ion solubility,⁶⁴ whereas nitrile and disulfide functional group have been employed to extract⁶⁵ Ag⁺ and Pd²⁺ or Hg²⁺ and Cu²⁺, respectively).

However, despite extensive investigations, in the case of metal recovery several technical aspects must also be addressed before ILs can be applied for large scale processes. The application of ILs as solvents for the extraction of metal ions from water, as stated by Binnemans *et al.*,⁶⁶ has until now only partially met the high expectations for it. Several problems, which are related to the hydrophilicity of ILs generally used for this purpose or to the extraction mechanism that (depending on IL structure) occurs with ion exchange,⁶⁷ should be overcome in order to increase the process efficiency, in particular when unfunctionalized ILs are used. The employment of hydrophobic phosphonium⁶⁸ ILs may represent a promising approach to avoid water contamination by ILs. Moreover, the use of appropriate task-specific ILs and/or ligand–solvent combination should surmount the problem caused by transfer of the IL cation or anion into the aqueous phase.⁶⁶

It is noteworthy that, in the case of processes occurring completely in ILs (electroreduction, cementation), several problems arising from properties of these liquids, such as high viscosity, relatively low conductivity or thermal stability, must also be overcome in order to favour their application. Optimization of the structures of the ILs also requires, in this case, a deeper knowledge of the correlation between IL structure and metal solubilisation mechanisms, and/or metal coordination and speciation.

Despite the problems that must yet be resolved, some studies have recently reported the application of ILs to recover metals from waste, such as municipal and industrial waste water,⁶⁹ discarded printed circuit boards⁷⁰ and phosphor powders in discarded fluorescent lamps.^{71,72} In particular some extraction experiments, carried out for the first time on real samples,⁷⁰ showed that the presence of specific functional groups on ILs (ILs based on quaternary ammonium and phosphonium cations associated to thiol- thioether-, hydroxyl-, carboxylate- and thiocyanate-functionalized anions were screened in this investigation) was not the only factor responsible for metal partition. The physico-chemical properties of ILs (such as viscosity and hydrophilicity) as well as the composition of the matrix (in particular, particles present in waste water may

acts as competitive adsorbent) play an important role. In the same paper, the authors also suggested the necessity of developing appropriate IL immobilization strategies to avoid the water miscibility and effective back extraction phenomena that prevent the reuse of ILs.

Regarding the extraction of rare earth elements from phosphor powders arising from fluorescent lamps, the possibility of using both task specific ILs, prepared from Aliquat336 and commercial organophosphorous acid extractants,⁷² or a common IL, [C₄C₁im][Tf₂N], associated to a new developed extractant, *N,N*-dioctyldiglycolamic acid,⁷³ has recently been demonstrated. In the latter case, it was possible to obtain almost total recovery, after acid leaching, of Y, Eu, La, Ce from metal impurities (Fe, Al, Zn).

Finally, metals and glass fibers were obtained from waste printed circuit boards “simply” by dissolving the bromine epoxy resins in [C₄C₁im][BF₄] at 260 °C.⁷¹

Metals, together with other compounds such as PCB, PAH, dioxins, are moreover well known contaminants of soil, due to improper waste disposal practices, and the remediation of contaminated soils is another great challenge in which ILs could play an important role. The application of ILs in this field is still limited to a few studies, however. Extraction of contaminants from soils and sediments with ILs requires not only an optimization of the IL, but also an appropriate development of the related engineering technologies, considering the exceedingly large mass of solid materials to be treated and the necessity to perform the process *in situ*. Analogous problems also affect the use of ILs for extraction of bitumen from oil sands. Although it has recently been shown⁷⁴ that ILs are able to promote the separation of bitumen from sand in a facile manner on a laboratory scale, the results do not yet provide the basis for a commercial process: on the basis of the published data, the production of a barrel of oil requires roughly two tons of oil sands, six tons of IL and four tons of toluene!

In conclusion, the extensive work carried out in the last ten years to understand how metal ions are partitioned between water and ILs, the metal complex speciation and extraction mechanisms (metal extraction, cation and anion exchange) have provided a solid basis for the possible application of ILs in this sector (metal extraction from water and water waste). In contrast, the extraction processes from solid matrices, requiring appropriate sample pretreatments (depending on the solid matrix) and proper devices and technologies, have scarcely been investigated and much more specialized research in this field is necessary to evaluate the potential of such a process.

CO₂ capture

The emission of CO₂ from fossil fuels has caused worldwide concern, since its increase in the atmosphere is strictly related to the increasing global energy demand and, at the same time, it is one of the greenhouse gases generally thought to be responsible for global warming and climate change. Although the development of new emission-poor energy sources must be the long term goal of our society, in the near future the development of efficient CO₂ capture and storage/recycling

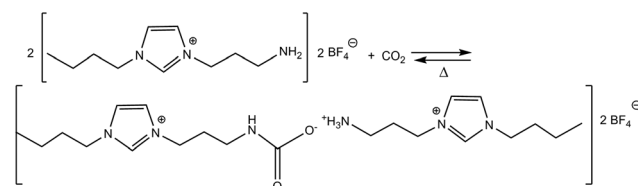
technologies is probably the sole strategy available to control the CO₂ level.⁷⁵

From the first experiments demonstrating the ability of many ILs to dissolve by physical absorption significant amounts of CO₂,⁷⁶ ILs have been proposed as alternative and useful media for CO₂ capture. Moreover, ILs have been evaluated for their use in supported ionic liquid membrane based CO₂ separations.⁷⁷ The non-volatility of ILs avoids solvent evaporation during the absorption and regeneration processes, thus preventing the contamination of the purified gas stream. Moreover, the low enthalpy (about 20 kJ mol⁻¹) of CO₂ physical absorption by ILs requires less energy to release the absorbed CO₂ during regeneration. On the other hand, the absorption capacity of CO₂ under atmospheric pressure by common ILs is up to only 3 mol%, a value that surely has to be improved to develop an efficient technology, otherwise, the application of ILs might appear limited to circumstances where CO₂ is present at high concentrations and high pressures.

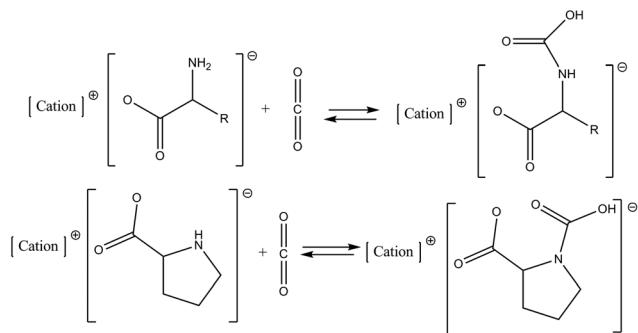
In the last ten years, a new strategy based on chemisorption has been described to increase the CO₂ capture performance of ILs and specific functional groups the on cation or anion of ILs have been introduced. In 2002 Davis *et al.* reported⁷⁸ the first example of CO₂ chemisorption by a task-specific IL having an amino group on the cationic alkyl chain. In this work, 0.5 mol of CO₂ was captured per mol of IL under ambient pressure (Scheme 6).

Despite such positive results, this IL and the subsequently synthesized⁷⁹ derivatives have not found application in industrial processes, since their use presents some drawbacks. In particular, amino-functionalized ILs are highly viscous and their CO₂ adducts are intractable tars. Furthermore, their production requires several synthetic and purification steps and they are not cost-competitive with commodity chemicals already used for this purpose (such as monoethanolamine, MEA). A significant improvement in atom efficiency has been obtained more recently by “simply” tethering the amine group to the anion.⁸⁰ In this way, 1 mol of CO₂ was captured per mol of IL under ambient pressure (100 mol%), since the amine on the anion disfavours the carbamic acid salification, probably owing to the instability of the putative dianion. Furthermore, considering that this behaviour is more pronounced when the negative charge centre and amine are in close proximity, several ILs having amino acids as counteranions have been synthesized (Scheme 7).⁸¹

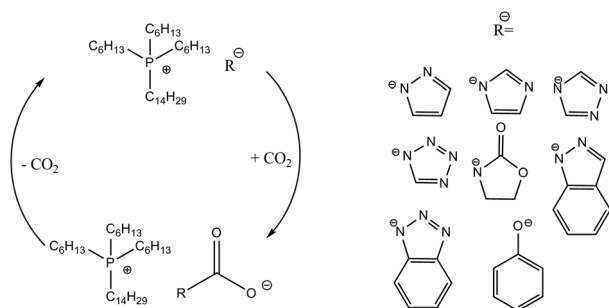
If chemisorption by amino acids guarantees a high CO₂ capture, unfortunately, high energy is generally required for the subsequent CO₂ release from this kind of ILs.



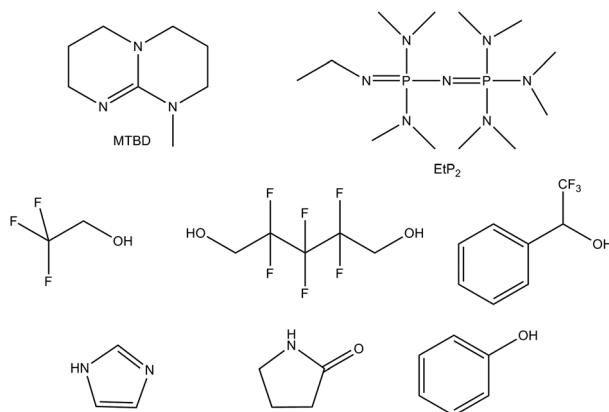
Scheme 6 Chemisorption of CO₂ by task-specific ILs.



Scheme 7 Mechanism for CO₂ absorption by amino acids.



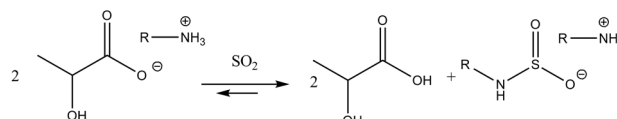
Scheme 8 Structure of anions and cations and mechanism for CO₂ capture in tailored ILs.



Scheme 9 Selected superbases such as fluorinated alcohols, imidazole, pyrrolidone and phenol used as building blocks of superbase-derived protic ILs.

To at least partially overcome these problems, recently highly stable ILs with desirable absorption enthalpies and high capacities have been prepared by neutralizing weak proton donors with phosphonium hydroxide (Scheme 8),⁸² or superbases (MTBD or Et-P₂) with weak acids, including partially fluorinated alcohols imidazole, pyrrolidone or phenol (Scheme 9).^{83,84}

The pK_a of the organic acid constituting the IL anion is generally considered the most suitable parameter for identifying promising systems to bind acid gases at low temperatures



Scheme 10 Proposed mechanism of the absorption of SO₂.

(it must be higher than that of the acid gas to be captured). Suitable ILs have thus been used not only to capture CO₂, but also SO₂, another gas arising from the burning of fossil fuels that is responsible for serious environmental problems.⁸⁵ The proposed mechanism for SO₂ (and CO₂) chemisorption is reported in Scheme 10.

It is noteworthy that these ILs are usually prepared by simple neutralization reactions (synthetic costs are thus drastically reduced), and since it is necessary to use organic acids having pK_a higher than sulfurous or carbonic acid, strong bases are required in order to shift the equilibria completely (>99%) towards the corresponding ionized species (the expected IL). On the other hand, ILs based on carboxylic anions associated with imidazolium cations have also been recently proposed⁸⁶ as promising systems for CO₂ absorption. Their chemisorption ability, due to the formation of a carboxylate at the imidazolium ring (the proton at C2 is sufficiently acid to be removed by a suitable base), can be improved by adding 20 wt% of DBU. It is noteworthy that an important role in all these processes may also be exerted by the water content, a fundamental parameter in IL chemistry, as stressed in a recent patent on separation of gases.⁸⁷

Finally, it is worth mentioning the alternative approach for CO₂ capture based on mixtures of common ILs and commercial alkanolamines.^{88,89} IL-amine mixtures offer many advantages over the corresponding aqueous mixtures, especially with respect to the energy required in the process. ILs are generally not volatile, so there is not an energy loss associated with evaporation during amine regeneration. Furthermore, carbamates are not soluble in some ILs and this feature can be thus usefully employed to develop more efficient processes with respect to those carried out in aqueous solution.⁹⁰

The wide and well-focussed activity in this sector has provided in a short time important information for the future development of IL based systems for CO₂ capture at fossil fuel power plants. In contrast, to the best of our knowledge, no data have been reported about the possibility of transforming CO₂ *in situ* in chemicals or materials of worldwide interest, a promising approach recently discussed⁹¹ by W. Leitner, T. E. Müller *et al.*, which could favour the application of ILs in this field.

Conclusions

The large number of publications on ILs and their applications in several “hot” fields demonstrate that these substances allow processes to be carried out that are otherwise difficult or impossible with common solvents. Among these we include

the dissolution and transformation of largely available biopolymers (cellulose, chitin and so on), as well as the extraction and capture of important components (metals) or pollutants (CO₂) from waste. The unique solvent power of ILs, sometimes associated with catalytic effects, provides chemists with a potent tool to address some of the important challenges of this century, at least at the laboratory scale. Of course, for some applications, experiments performed on the laboratory scale show that the structure of the IL must be adjusted to the specific requirements of the application in order to fulfil expectations. Physical properties, toxicity and cost of ILs must be optimized to obtain suitable solvents having all the requirements for sustainable industrial applications. However, the principal concern related to the processes described in this review is, in our opinion, the extremely large amount of materials (raw or waste) to be treated, often *in situ*, and the correspondingly large amounts of ILs that are required on the basis of laboratory scale experiments. This aspect is fundamental from a practical point of view and should be considered in more detail. Nevertheless, the complexity and heterogeneity of some solid matrices must also be considered. New and appropriate molecular and engineering strategies and technologies must be developed to allow the treatment of billions of tons of such materials, and ILs should be designed for these new technologies.

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