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Task-Specific Ionic Liquids

*Ralf Giernoth**

catalysis · gas absorption · ionic liquids · luminescence · magnetic properties

Dedicated to Professor Joachim Bargon

In recent years, ionic liquids have attracted the attention of many chemists as a result of their unique properties as solvents for chemical transformations. The focus of this Minireview is on applications of so-called "task-specific" ionic liquids, whereby the role of the ionic liquid goes beyond that of a solvent. Such ionic liquids find application in a wide range of areas, including catalysis, synthesis, gas absorption, and analysis.

Introduction

Ionic liquids (ILs) have become omnipresent in the recent chemical literature, for they can be used as highly customizable solvents for almost any synthetic purpose.[1] Nonetheless, the majority of modern applications, especially in industry, lie beyond their use as solvents. The "unique" properties of these materials (which are, in fact, not unique but very diverse) give rise to a surprising number of applications. This Minireview gives a short and certainly incomplete introduction to the various fields of application in which the focus is *not* on solvents. In particular, functionalized (so-called "task-specific"[2]) ionic liquids that have been synthesized with a particular application in mind are discussed. Nonsolvent applications of ionic liquids in biotransformations and organocatalysis have been covered previously[3] and are therefore also beyond the scope of this Minireview.

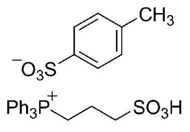
1. Catalysis

Catalysis is most certainly the major use of ionic solvents with regard to synthetic applications,[1] and there are many examples of ionic solvents that also play the part of an active catalyst in a chemical transformation. Nonetheless, if such an ionic catalyst exceeds a certain complexity, its use as a solvent soon becomes unfavorable for simple economic reasons. In these cases, the "ionic liquid" may be used like a classical catalyst. In many reports on catalysis of this type, the term "ionic liquid" is used to describe the catalyst, although the fact that the catalyst is a liquid might be totally unimportant in this context.

1.1. Ionic Liquids as Catalysts

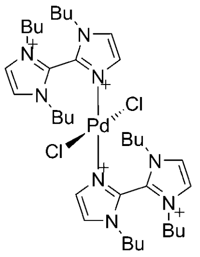
The catalytic effect of certain ionic liquids in various applications was noticed early in IL history and has sometimes been termed the "ionic-liquid effect",[4] mainly as a result of a fundamental lack of understanding. Today, it is well-known that common impurities in ILs (like traces of halides or acid) are—unsurprisingly—able to catalyze specific reactions. Of course, it is also possible to incorporate functional groups into either the anion or the cation of the IL and to exploit their specific interactions for catalytic applications. Thus, the term "task-specific ionic liquid" was born.[2]

Among the first examples of task-specific ionic liquids was the phosphonium sulfonate depicted in Scheme 1.[5] This salt was shown to mediate all kinds of acid-catalyzed reactions, such as esterification and dehydration reactions, and pinacol rearrangements.



Scheme 1. One of the first ionic-liquid catalysts.[5]

More often, the active catalyst is generated from an ionic liquid and a transition-metal salt. A typical example—a palladium complex that catalyzes Heck reactions—is shown in Scheme 2.[6]



Scheme 2. Example of a catalytically active transition-metal–IL complex.[6]

1.2. Metal-Containing Ionic Liquids

Many examples of ILs that contain metals have been reported.[7] Of course, these metals can often also act as transition-metal catalysts. In

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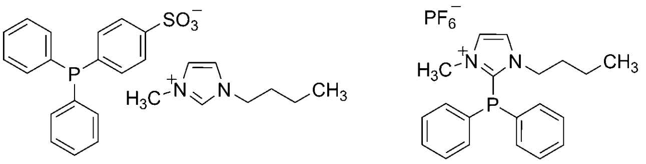
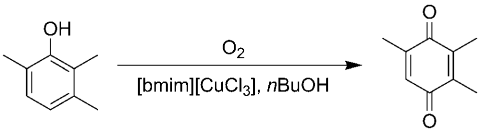
[*] Priv.-Doz. Dr. R. Giernoth
Department für Chemie, Universität zu Köln
Greinstrasse 4, 50939 Köln (Germany)
Fax: (+49) 221-470-5102
E-mail: ralf.giernoth@uni-koeln.de
Homepage: http://www.ralfgiernoth.de

the vast majority of catalytic experiments with metal-containing ILs, the ionic liquid is also utilized as the solvent. In the most straightforward examples, ILs simply act as the ligands for the transition-metal catalysts (Scheme 3).[8]



Scheme 3. Ionic-liquid ligands for transition-metal catalysis.[8]

A very interesting example in which the metal-containing anion also acts as a catalyst was reported by Sundermeyer and co-workers.[9] In this case, a mixture of copper chloride with [bmim]Cl generated an oxotetracuprate, which was used for the aerobic oxidation of 2,3,6-trimethylphenol to trimethyl-1,4-benzoquinone (Scheme 4).



Scheme 4. Aerobic oxidation with a copper-containing ionic liquid.[9] $[bmim]^+ =$ 1-butyl-3-methylimidazolium.

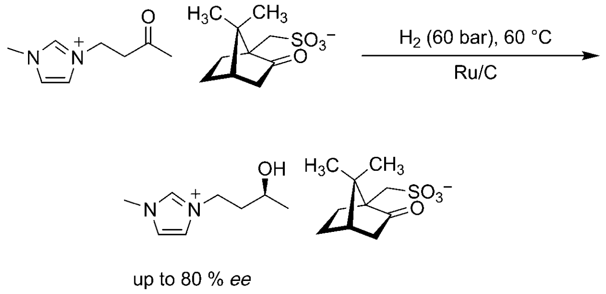
Palladium-containing ILs, such as $[bmim]_2[PdCl_4]$, have also been used for typical palladium-catalyzed reactions.[10] Many more examples can be found in a review by Lin and Vasam.[7]

1.3. Chiral Ionic Liquids

A lot of effort has gone into the development of chiral ionic liquids, and probably even more into finding suitable applications for them. However, successful applications of chiral solvents in enantioselective synthesis are very rare.[11] Still, two applications stand out: Wasserscheid et al.,[12] and more recently Warner and co-workers,[13] showed that chiral ILs can show enantiomeric recognition as shift reagents in solution NMR spectroscopy. In both cases, the center of chirality was located within the IL cation.

Ralf Giernoth completed his PhD in 1999 under the guidance Prof. Joachim Bargon at the University of Bonn as a physical chemist, and then switched to organic chemistry. After postdoctoral research with Dr. John Brown at the University of Oxford (UK), he started his own independent research in 2001 at the University of Cologne, where he finished his "habilitation" in 2006. In 2009, he was an acting professor of organic chemistry at the University of Karlsruhe (TH). His main research interests include ionic liquids, catalysis, and in situ spectroscopy.

The second application is based on anion-directed chirality transfer.[14] In this case, the hydrogenation of an IL composed of a prochiral cation and a chiral, enantiomerically pure anion gave the hydrogenated cation with up to 80% *ee* (Scheme 5). The result can be explained by strong ion-pairing effects. This enantioselective transformation has great potential, as the method is fundamentally different from established processes.



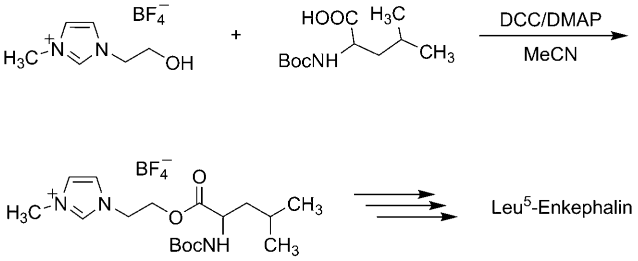
Scheme 5. Use of a strong ion-pairing effect for the enantioselective hydrogenation of an IL cation.[14]

2. Ionic Liquids as Supports for Synthesis

A concept known from combinatorial and peptide synthesis for quite some time has also been transferred to IL chemistry: the Merrifield synthesis, in which the molecule of interest (often an oligomer) is bound to a solid phase (often a resin) throughout the synthesis and is only cleaved after the last synthetic step.[15] This technique simplifies purification of the intermediates dramatically.

An ionic liquid can also do this job, with the fundamental difference that the synthesis is now carried out on a *liquid* support, frequently in a biphasic system.[16] This idea was first described by Bazureau and co-workers (who named the technique ionic-liquid-phase organic synthesis, "IoLiPOS")[17] and by Vaultier and co-workers,[18] who described many possible applications in two patents. In principle, a functionalized ("task-specific") ionic liquid is required as a linker to the liquid phase, just as the classical Merrifield resin links the substrate to a solid bead. A general approach was reported by Miao and Chan for the synthesis of oligopeptides (Scheme 6).[19] In this way, a pentapeptide was synthesized in good yield without the need for chromatography.

This approach was used by de Kort et al. for the multistep synthesis of an antithrombotic drug.[20] After cleavage from the IL, the product was obtained in 11% overall yield following a seven-step one-pot synthesis. An application in combinatorial chemistry was reported by Fraga-Dubreuil and Bazureau.[17a] They demonstrated the potential of this method through the synthesis of a small library of 4-thiazolidinones under microwave irradiation.



Scheme 6. Synthesis of an oligopeptide on an ionic-liquid support.[19] Boc = *tert*-butoxycarbonyl, DCC = *N*,*N*′-dicyclohexylcarbodiimide, DMAP = 4-dimethylaminopyridine.

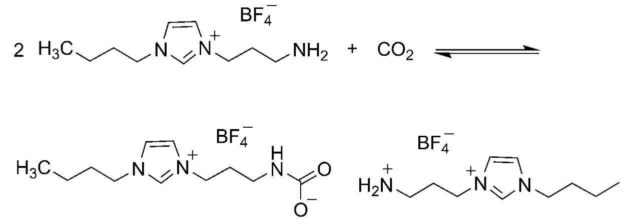
3. New Materials: Magnetism and Luminescence

As mentioned in Section 1.2, many ILs containing transition metals are known. Therefore, it is not surprising that liquids with pronounced magnetic properties have been described. Among the first examples were those reported by Okuno et al.,[21] who described the ionic liquid [bmim][$FeCl_4$] as a material with a very large magnetic susceptibility and demonstrated that nonmagnetic materials can be transported and separated readily in this IL with the help of magnetic-field gradients.

Del Sesto et al. described a larger variety of magnetic ILs with iron-, cobalt-, manganese-, and gadolinium-containing anions.[22] The ILs all showed simple paramagnetic behavior over a temperature range of 300 K but still responded strongly to a magnetic field. Mudring and co-workers focused on a dysprosium-based system,[23] as the magnetic moment of Dy^{3+} is twice the size of that of Fe^{3+}. Interestingly, the dysprosium-containing IL also displayed luminescence, a behavior already known for lanthanide ions dissolved in water-free ionic liquids.[24] This discovery might open the way to completely new materials for advanced computer and television display technologies.

4. Gas Absorption

The interplay between ionic liquids and gases has always been a challenging field of research. A striking feature of "common" ILs is that only very low concentrations of simple gases, such as H_2 and O_2, dissolve in them, whereas very large amounts of CO_2 or SO_2 can be dissolved in them easily.[25] The high solubility of CO_2 and SO_2 can be exploited for the capture and absorption of these gases.[26] Davis and co-workers put some effort into the design of a special task-specific IL that can capture CO_2 specifically by chemisorption.[27] The imidazolium cation in this IL contains an amine functionality, which forms a carbamate upon the addition of CO_2. In this way, a maximum CO_2 uptake of 0.5 mol per mole of the IL was reached within 3 h. The process can be reversed by heating to 80–100 °C under vacuum (Scheme 7).



Scheme 7. Chemisorption of CO_2 by a task-specific ionic liquid.[27]

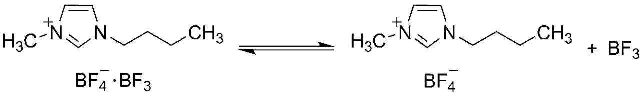
The same research group went on to produce a collection of 63 salts through combinatorial click chemistry.[28] These salts were based on a bifunctional anion containing an amine and a sulfonate group in combination with an ammonium cation. The salts were predominantly ILs; a few products were more like a resin, plastic, or gel. All were capable of reversible CO_2 capture.

An equivalent structural motif based on doubly amino functionalized phosphonium ILs was also shown by Zhang et al.[29] to be very effective for this purpose. In this case, the IL anions consisted predominantly of amino acids. This motif had been described earlier by Ohno and Fukumoto;[30] however, their systems have never been used for the dissolution and capture of gases.

In 2008, Noble and co-workers demonstrated that the synthesis of a task-specific IL for the single purpose of CO_2 capture is often not necessary, since a mixture of a suitable amine with an IL functions just as well.[31] They used this understanding to develop polymeric composite materials that could potentially be used as technical materials for gas absorption.[32]

The physisorption of SO_2 in various BF_4- and Tf_2N-based ILs was reported by Riisager and co-workers (Tf = trifluoromethanesulfonyl).[33] At room temperature and under atmospheric pressure, 1–2 mol SO_2 could be absorbed per mole of the IL. Riisager and co-workers also showed that the gas could readily be desorbed again under vacuum or upon heating, and that no chemical transformation in the IL took place during this process. Several cycles of absorption/desorption were demonstrated without any loss of capacity.

On the basis of these findings, the company Air Products and Chemicals developed a commercial product for the storage of toxic gases.[34] PH_3 and BF_3 are absorbed in suitable ILs through chemical complexation (Scheme 8) and stored in standard gas cylinders. Since no high-pressure gas cylinders are needed, safety is greatly improved.



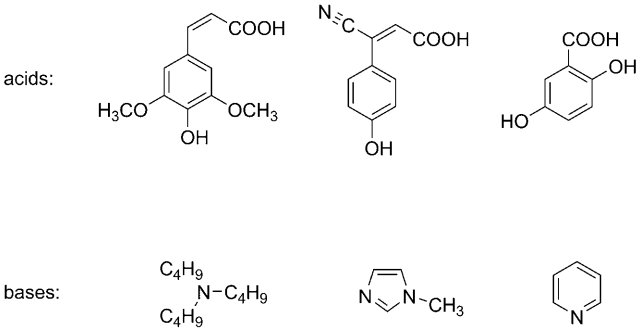
Scheme 8. Storage of BF_3 in [bmim]BF_4.[34]

5. Analysis

Quite early in IL history, ionic liquids were applied as stationary phases in gas chromatography by Armstrong et al.[35] These experiments led to the remarkable finding that ILs can potentially interact strongly with polar as well as nonpolar substrates simultaneously. These results were used to develop a system for the characterization of ILs on the basis of their multiple solvation interactions.[36]

These days, ILs are frequently used in liquid chromatography,[37] especially for challenging separation problems, as they enable surface modification of the stationary phase through interaction with the hydroxy groups of the silica. Owing to their low vapor pressure, these modifiers are considered "greener" than many other alternatives.

ILs have also found their way into mass spectrometry. Suitable ionic solvents have themselves been used as matrices to trap reactive intermediates in MALDI MS studies;[38] however, examples of the use of equimolar mixtures of a conventional MALDI matrix compound with an organic base (Scheme 9) as ionic-liquid matrices for MALDI MS are more frequent.[39] The advantages of this approach are a much improved sample homogeneity and thus the prevention of unwanted "hot spots" during the MALDI experiments.



Scheme 9. Typical acids and bases that combine to form ionic-liquid matrices for MALDI mass spectrometry.[39]

6. Industrial Applications

The most famous industrial application of ionic liquids is most certainly the BASIL process of BASF.[40] In this process, the IL is not used as a solvent but as an acid-scavenging agent (Scheme 10). The technology can be applied to all kinds of chemical processes in which acid scavenging is of importance. Interestingly, this new reaction design enabled the development of a completely new, very small, and extremely effective stream reactor.

The company IoLiTec together with Wandres Micro-Cleaning developed an ionic-liquid-based technology for cleaning sensitive surfaces.[1] The IL is sprayed onto a rotating brush system, where it acts as an antistatic agent. In this way, the efficiency of the cleaning process is enhanced substantially as compared to wetting with conventional aqueous solutions.

The company Linde developed an ionic compressor for the compression of gases.[41] The system is much more efficient than standard compressors, because the number of moving parts could be decreased dramatically.

There are certainly many more current applications of ionic liquids that are unknown outside the companies concerned, and certainly many more applications to come. A comprehensive overview of the state-of-the-art in industry can be found in a recent review by Plechkova and Seddon.[41]

7. Unusual Applications

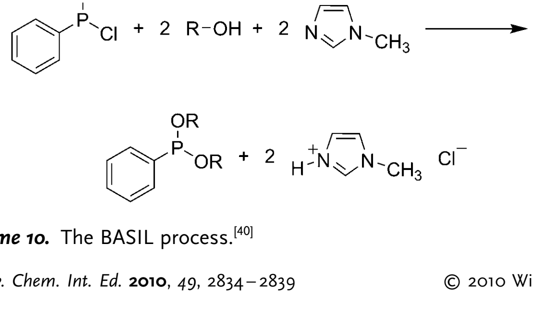
The lubricating properties of ionic liquids were also described quite early in modern IL history.[42] Recently, it was demonstrated that ILs show improved lubrication and anti-wear properties relative to those of conventional lubricants.[43] It was also pointed out that the development costs associated with ILs are relatively low. On the downside, there are still severe problems with oxidation as well as thermal corrosion. This problem was tackled recently by the MacFarlane research group.[44] They found that homogeneous films formed by phosphonium–NTf_2 ILs on metal surfaces were quite protective against corrosion.

As ionic liquids are salts and therefore electrolytes, they are also among the usual suspects for potential new battery technologies.[45] Lithium-battery technology in particular, although it delivers batteries with high capacities and lifetimes, suffers from severe safety issues (e.g. because of small crystals that precipitate from the electrolyte). In this field, the application of ionic-liquid electrolytes is expected to result in enhanced safety, higher capacities, and higher energy densities (and thus smaller batteries). ILs are also exploited in energy production as part of the redox couple in certain dye-sensitized solar cells.[46]

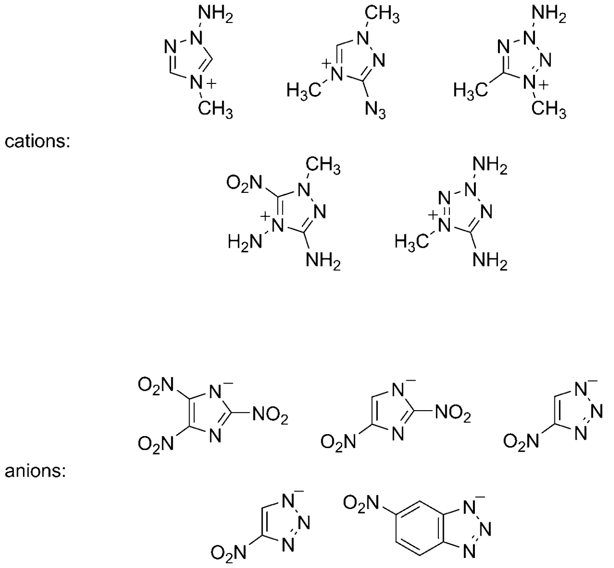
Recently, Lütz and co-workers described ionic liquids as "performance additives" in electroenzymatic reactions.[47] In oxidoreductase-catalyzed reactions, the addition of small amounts of an IL (up to 10 vol%) led to enhanced conductivity of the reaction medium and to the higher stability of biocatalysts and cofactors.

Task-specific ILs are currently also finding their way into pharmaceutical products.[48] The fundamental idea is to incorporate a known active pharmaceutical component into the anion or the cation of the IL, or even into both. Thus, a multitude of active-agent combinations is imaginable. For example, an IL derived from didecyldimethylammonium bromide and sodium ibuprofen ("didecyldimethylammonium ibuprofen"), would show both antibacterial and anti-inflammatory activity.

Finally, ionic liquids have also been described as "energetic materials".[49] The use of ILs with a high nitrogen content as explosives (for civil as well as military purposes) can improve safety in the handling of such materials (Scheme 11). Additionally, their high nitrogen content renders these materials quite "green", as the main products of the thermal reaction are nitrogen, carbon dioxide, and water



Scheme 10. The BASIL process.[40]



Scheme 11. IL cations and anions for energetic materials.[49]

(although clearly all explosives with a high nitrogen content share this property, regardless of whether they are ionic or not).

8. Conclusion

Ionic liquids have arrived in everyday chemistry. These days, nearly every chemist knows of the wide variety of possibilities offered by ionic solvents. A “parallel world” has also evolved in which the solvent properties of ILs are less important. In this domain, ILs must be considered as task-specific molecules or, more generally speaking, as new and modern materials that are ready to solve new problems.

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