INTRODUCTION

From simple detergents to life saving drugs to plastics, many of life's essential commodities would be impossible without the chemical industry. Few people choose to live without the benefits of modern chemistry, but often the benefits are associated with other fields, such as medicine, materials, or engineering. Of late, the chemical industry has been increasingly regulated by stringent and compelling demands for greener processes, and the development of cost-effective and environmentally benign catalytic systems in order to reduce harmful emissions and effluents and ensure worker safety. However, many chemical industry processes have been or still are highly polluting. In the past 15 years, ionic liquids have provided solution to problems accompanying increased production with sustainable green approaches. It is mainly attributed to their unique physical properties that are mainly in accordance to a green chemistry point of view and a synthetic chemistry point of view. Such properties include polar, non-coordinating nature, generally low flammability due primarily to low volatility, and their ability to dissolve a range of organic and inorganic compounds. Exploitation of these properties has resulted in an increased use of ionic liquids in both separations and in catalysis.

Even though the term ionic liquid was introduced only recently, the history of ionic liquids dates back to 1914 when Walden reported the physical properties of molten salt [EtNH$_3$][NO$_3$]. Earlier developments in the field of ionic liquids were critically reviewed by Gorden in 1969. It was the pioneering study of Wilkes and co-workers, that resulted in increasing popularity of ionic liquids as reaction and extraction media in research and development, and later widely been promoted as “green solvents.” The first successful use of an ionic liquid, dialkylimidazolium chloroaluminate, as a catalyst in Friedel-Crafts acylations was reported in 1986.
However, moisture sensitivity and decomposition of this chloroaluminate salt under normal atmospheric conditions were two major drawbacks that precluded their practical use. After this report, a resurgence of the rich chemistry of ionic liquids began. The pioneering work of Seddon and his associates then engraved the ionic liquids to its well-known versatility.\textsuperscript{6}

Today ionic liquids are regarded as eco-friendly alternatives to volatile organic solvents in chemical processes, due to their negligible vapor pressure and non-flammable nature. They have intrinsic ability to dissolve a wide range of organic, inorganic and organometallic compounds. The solubility of gases \textit{e.g.} H\textsubscript{2}, CO and O\textsubscript{2}, is generally good which makes them attractive solvents for catalytic hydrogenations, carbonylations, hydroformylations and aerobic oxidations. Moreover, their physical and chemical properties such as hydrophobicity, hydrophilicity or solvent miscibility can be tuned by selecting the appropriate cation and anion. Thus, depending on their structure, they can be designed to be immiscible with water or some organic solvent (\textit{e.g.}, alkanes, ether, \textit{i}-PrOH, \textit{etc.}), which renders them more useful for facilitating catalyst recovery from the reaction mixture. Moreover, switching from an organic solvent to an ionic liquid often results in marked improvements in catalytic performance.

Several general methods by which the ionic liquids can be synthesized are depicted in \textbf{Scheme 3.1}
Chapter 3: Recent Developments of Task Specific Ionic Liquids in Organic Synthesis

Scheme 3.1

Composition depends on the proportion of Lewis acid

Combination with the Lewis acids

Ion exchange reaction leading to interchange of anions

Metathesis with the protic acid or metal salts
3.2 Task Specific Ionic Liquids

Davis and co-workers\textsuperscript{7} first demonstrated the concept of designing IL to interact with a solute in a specific fashion, showing that a thiazolium IL could function as solvent-catalyst for the benzoin condensation. They outlined the concept in a brief review\textsuperscript{8} by introducing the term “task-specific ionic liquids” (TSILs) to describe IL which incorporate functional groups designed to impart to them particular properties or reactivities\textsuperscript{9}. The Task Specific Ionic Liquids (TSILs) may be defined as ionic liquids in which functional group is covalently tethered to the cation or anion (or both) of the IL. These can be considered as liquid version of solid supported catalyst with added advantage of kinetic mobility and large operational surface area. Today TSILs form an important class of ionic liquids that has received increasing attention over the last few years because it is possible to form any specific IL composition depending upon user’s needs of desired physical, chemical and biological properties. Apart from this, there are several rationale for the incorporation of a functional group into an IL. First, the inclusion of the functional group will doubtless alter the solvent parameters of an IL. The parameters like polarity, H-bond acidity and basicity, polarizability, etc. are the attributes that make any chemical a good or poor solvent for a given solute. A second rationale for the inclusion of a functional group in an IL is to imbue the salt with a capacity to covalently bind to or catalytically activate a dissolved substrate. For example, a primary amine functionalized imidazolium salt can separate CO\textsubscript{2} from gas streams\textsuperscript{10}, while ionic liquids bearing appended sulphonic acid groups were used as solvent-catalyst for esterification\textsuperscript{11}. Till date, various types of TSILs have been designed to accomplish the specific tasks like catalysis, organic synthesis, chiral induction, synthesis and stabilization of nano-materials, electrochemical applications, catalyst surface modifiers etc., and they have been comprehensively reviewed by various authors. The first in depth review in the field...
of TSIL appeared in the year 2004 by Davis\textsuperscript{8} which dealt with synthesis of TSIL and their applications in organic synthesis, catalysis, separation, and electrochemistry. Later on developments in the field of functionalized imidazolium TSILs has been reviewed by Sang-gi Lee\textsuperscript{12}. Winkel et al.\textsuperscript{13} gave an account of applications of Task Specific Chiral ionic liquids in asymmetric synthesis. In a recent minireview of TSILs, Ralf Giernoth\textsuperscript{14} have taken account of TSILs as catalyst and support for synthesis, as new magnetic materials, as gas reservoir, in chromatography and in industrial applications.

Present overview of ionic liquids give an update of recent developments in the field of TSILs with particular emphasis on their applications in organic synthesis, catalysis and nanoparticle synthesis.

3.2.1 Acidic and basic TSILs

The chemical property that imparts a variety of physical characteristics to the ionic liquids which has been little investigated is the relative acidity or basicity of the component ions. The commonplace starting point that many of the ions are inert is not always correct, as one looks further a field for task specific ions. Here, we survey recent work with a range of anions and cations having distinct Lewis acidity or basicity and functionalization of anion or cation depending upon the task. The ionic liquids containing Lewis base anions can exhibit a base catalysis phenomenon, which can be utilized, for example, in a variety of acetylation reactions. The majority of ions used in the formulation of ionic liquids can be considered in terms of the Lewis definition of acids and bases i.e. whether they are capable of accepting or donating an electron pair. However, there are also a number of ions that must be considered according to the Brønsted definition viz. those that are able to donate or accept a proton. For example, a number of ionic liquids containing protonated cations and anions like dihydrogen phosphate and hydrogen sulfate fall into this category.
Salunkhe et al.\textsuperscript{16} investigated the Knoevenagel condensation of Meldrum’s acid with aldehyde in various ionic liquids. The enhancement in rate of reaction was observed in Brønsted acidic ionic liquid [Hmim]Tfa. Knoevenagel condensation of Meldrum’s acid with aromatic and heteroaromatic aldehydes resulted in corresponding ylidene derivatives\textsuperscript{15} (Scheme 3.2) whereas that with ortho-hydroxy aldehydes gave corresponding coumarin-3-carboxylic acid derivatives (Scheme 3.3).

\begin{equation}
\begin{align*}
\text{苯甲醛} + \text{Meldrum’s acid} &\rightarrow \text{yridene derivative} \\
\text{正羟基醛} + \text{Meldrum’s acid} &\rightarrow \text{coumarin-3-carboxylic acid derivative}
\end{align*}
\end{equation}

\textbf{Scheme 3.2}

Dabiri et al.\textsuperscript{17} reported a novel one-pot tandem synthesis of 2-styryl-4(3H)-quinazolinones in same acidic ionic liquid [Hmim]Tfa. Isatoic anhydride, aniline or ammonium acetate, and triethylorthoacetate were reacted in the presence of imidazolium trifluoroacetate [Hmim]Tfa. Subsequently, an aromatic aldehyde was added to the mixture to afford corresponding quinazolinone product in high to excellent yields (Scheme 3.4).

\begin{equation}
\begin{align*}
\text{Isatoic anhydride} + \text{aniline} + \text{ArCHO} &\rightarrow \text{quinazolinone}
\end{align*}
\end{equation}

\textbf{Scheme 3.4}
Wang et al.\textsuperscript{18} developed some Brønsted acidic benzimidazolium based ionic liquids and explored their use as environmentally benign catalysts for acetalization of aldehydes. They found the ionic liquid $[\text{PSebim}]\text{HSO}_4$ (Figure 3.1) more acidic among the studied ILs and was efficient for acetalization. The advantages of this IL over previous reports are good solubility of aromatic aldehydes, high activity and selectivity, no need of excess diols (quantitative use).

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure3.1.png}
\caption{Figure 3.1}
\end{figure}

Both the homogeneous and heterogeneous catalysts have counter (interlocking) advantages and disadvantages. So the catalyst having properties of both can be a “dream catalyst”. Leng and co-workers\textsuperscript{19} developed a non-conventional propane sulphonate functionalized heteropoly acid based ionic liquid for esterification (Scheme 3.5). These ionic liquids contain three organic cations and an inorganic heteropolyanion. Their melting points (above 100°C) make them non-conventional ionic liquids. These ionic liquids being soluble in starting materials i.e. carboxylic acids and alcohols works as homogeneous catalyst and being insoluble in product i.e. esters at the end of reaction IL comes out of reaction mixture as if it is a heterogeneous catalyst.
In a very recent report of TSIL, Das and others\textsuperscript{20} have reported a sulfonic acid functionalized ionic liquid for efficient synthesis of indole derivatives (Scheme 3.6). The lucrative advantage of this IL is that it could be reused up to ten cycles without any substantial loss of catalytic activity. The catalyst is versatile as it is also applicable to both aliphatic and aromatic amines and in synthesis of bis (indolyl) methane.
Ranu et al.\textsuperscript{21} described unusual results in which the task specific ionic liquid [bmim]OH provided chemo selectivity in Michael addition of active methylene compounds on conjugated ketones, esters and nitriles. The vinyl ketones and chalcones gave mono addition products while unsaturated esters and nitriles gave bis-addition products (Scheme 3.7). The method is operationally simple and giving 82-96% yields for a wide range of substrates. Additionally, the IL can be reused up to six cycles without any substantial loss of catalytic activity.

\[ R \quad + \quad \begin{array}{c} \text{[bmim]OH} \\ \text{X= CN, CO}_2\text{R} \end{array} \quad \xrightarrow{X= \text{COR}} \quad \begin{array}{c} \text{X} \\ \text{R}_1 \quad \text{R}_2 \end{array} \]

Scheme 3.7

A basic functionalized ionic liquid, 1-butyl-3-methylimidazolium hydroxide ([bmim]OH), catalyzed the three-component condensation reaction of acid chlorides, amino acids, and dialkyl acetylenedicarboxylates in water to afford functionalized pyrroles in high yields. Yavari and co-workers\textsuperscript{22} studied the reaction in ten different ionic liquids out of which [bmim]OH was found to be effective at 80°C. The reaction was found to be faster for aromatic acid chlorides containing electron-withdrawing substituents (Scheme 3.8).
Zhang et al.\textsuperscript{23} synthesized and used the basic TSIL [mammim]TfO (Scheme 3.9) in promotion of hydrogenation of CO\textsubscript{2} to formic acid with ruthenium supported on silica as heterogeneous catalyst. Satisfactory catalytic activity and high selectivity are the advantages of this method. The unique features of recovery of formic acid and reuse of catalyst makes this approach compatible to industrial application.
Pavlinac\textsuperscript{24} and others in their recently published review have taken an account of halogenation of organic compounds in ionic liquids. The review involves brief discussions on ionic liquid mediated fluorofunctionalization, chlorofunctionalization, bromofunctionalization and iodofunctionalization of organic compounds. Wang et al.\textsuperscript{25} described application of a meticulously designed and synthesized ethanolamine functionalized task specific ionic liquid for the palladium catalyzed Heck reaction (Scheme 3.10). This IL performs a multifunctional role of base, ligand and reaction media with added advantage of recyclability of the system. The catalyst system is very effective for a wide spectrum of substrates giving excellent yields.

\[
\text{R}_1^X \text{R} \quad + \quad \text{CH} = \text{CH}_2 \quad \overset{\text{TSIL}}{\xrightarrow{\text{Pd(OAc)}_2, 100^\circ C}} \quad \text{R}_1^\text{R}
\]

Scheme 3.10

3.2.2 Task Specific Ionic Liquids-Solid Catalysts-Metal nanoparticles

Green and cost-effective catalysts with high efficiency and selectivity are the cornerstones of contemporary synthetic chemistry. Even though easily separable heterogeneous catalysts are preferred in the industry, these have some shortcomings like heat or mass transfer and lower chemo- and stereo-selectivities. This can be circumvented by surface modification of solid catalysts. Recently, the concepts of
Solid catalysts with ionic liquids (SCILs) and Supported ionic liquid phase catalysts (SILPCs) have drawn much attention because their combination is looked upon as a future option to integrate heterogeneous and homogeneous catalysts. In their first of its kind report Menhert\textsuperscript{26-27} and Riisger \textsuperscript{28-29} demonstrated the use of ionic liquids in Supported liquid phase catalysts (SLPC). Gu\textsuperscript{30} and others used hydrophobic ionic liquid for coating the solid surface of silica supported sulphonic acid catalyst to enhance the selectivity. They successfully demonstrated (Scheme 3.11) the significant impact on activity of silica-supported sodium catalyst by coating it with the IL [DBIm]SbF\textsubscript{6} (1-butyl-3-decylimidazolium) leading to enhanced activity towards the Michael reaction of indoles and α-β-unsaturated ketones in water.

![Scheme 3.11](image_url)
Chapter 3: Recent Developments of Task Specific Ionic Liquids in Organic Synthesis

The enhanced activity provides scope to perform the reaction under neutral conditions making it possible to carry out the reaction with acid labile substrates. Interestingly this reaction did not proceed without IL highlighting the significance of IL.

Apart from enhanced activity, selectivity is another significance of coating the supported catalysts with ILs. The IL showed catalytic selectivities when a set of organic reactions in water were catalyzed by catalyst coated with IL. Etherification of 1-tolyl-1-ethanol catalyzed by SiO$_2$-SO$_3$H led to 30% of 4-methylstyrene as side product reducing the yield of the desired ether to 61%. However, coating of SiO$_2$-SO$_3$H with 25 wt % of [C$_8$MIm] NTf$_2$ (1-methyl-3-octylimidazolium) led to a significant selectivity improvement$^{31}$ and the ether was obtained with 96% yield (Scheme 3.12).

![Scheme 3.12](image)

Metals and Nanomaterials in Ionic Liquids

The search for more efficient catalytic systems that might combine the advantages of both homogeneous (catalyst modulation) and heterogeneous (catalyst recycling) catalysis is an essential requirement of modern chemistry. With the
advances of nanochemistry, it has been possible to prepare “soluble” analogues of heterogeneous catalysts. However one of the difficulties of using nanoparticles as catalyst is providing stability to small nanoparticles while retaining the activity. Ionic liquids have been shown to provide “electrostatic” stabilization for metal nanoparticles and more surface area for the reaction to take place. So ionic liquids in turn control the stability and activity of nanoparticles. Multiphase systems of Ionic liquid-nanoparticles facilitate easy recovery of nanoparticles. There have been several reviews covering the preparation and application of nanoparticles in ionic liquids, with the most recent having been published in the 2009. The present account of ionic liquids is intended to update the reader about the recent work in the field of combination of two cutting edge topics- nanoparticles and ionic liquids.

Recently, Redel and co-workers have synthesized stable cobalt, rhodium and iridium nanoparticles by thermal decomposition under argon from \( \text{Co}_2(\text{CO})_8 \), \( \text{Rh}_6(\text{CO})_{16} \) and \( \text{Ir}_4(\text{CO})_{12} \) dissolved in the ionic liquids \([\text{bmim}]\text{BF}_4\), \([\text{bmim}]\text{OTf}\) and \([\text{btmA}]\text{NTf}_2\) \([\text{bmim} = \text{n-butyl-methyl-imidazolium}, \text{btmA} = \text{n-butyl-tri-methyl-ammonium}, \text{OTf} = \text{O}_3\text{SCF}_3, \text{NTf}_2 = \text{N}[\text{O}_2\text{SCF}_3]_2\). They prepared uniformly distributed nanoparticles of about 1–3 nm in \([\text{bmim}]\text{BF}_4\). Increase in size was observed with increase in molecular volume of the ionic liquid anion from \([\text{bmim}]\text{OTf}\) to \([\text{btmA}]\text{NTf}_2\). Importantly, among these nanoparticles the rhodium or iridium nanoparticle/IL systems function as highly effective and recyclable catalysts in the biphasic liquid–liquid hydrogenation of cyclohexene to cyclohexane (Scheme 3.13) with activities of up to 1900 mol\(_{\text{product}}/\text{(mol metal h)}\) and quantitative conversion.

![Scheme 3.13](attachment:image.png)
Cal et al.\textsuperscript{36} reported the use of palladium nanoparticle for Ullmann reactions in tetrabutyl ammonium salt ionic liquids as a reservoir of catalyst with aldehydes as the reductant (\textbf{Scheme 3.14}). This type of “ligand-free” catalysis is gaining considerable importance because it avoids the use of toxic or expensive phosphane ligands and allows catalyst recycling. The role of TBAA (tetra butyl ammonium acetate) is crucial for this process, as this ionic liquid behaves simultaneously as a base, ligand and reaction medium and has effect on the chemoselectivity of the catalysis which cannot be obtained by replacing this ionic liquid with a generic source of acetate anions.

\[
\begin{array}{c}
\text{Hal} + \text{aldehyde} \xrightarrow{\text{Pd}_{\text{colloids}} (3\%) \quad \text{TBAA (1g)}} \text{products of aldehyde}
\end{array}
\]

\textbf{Scheme 3.14}

Taher and co worker\textsuperscript{37} reported Pd-NHC–ionic liquid matrix immobilized into ionic liquid layers coated on the surface of Fe\textsubscript{3}O\textsubscript{4} (\textbf{Scheme 3.15}) by a simple process. These immobilized Pd-NHC exhibited both high catalytic activity and stability for the coupling between aryl bromide and arylboronic acid in water. Importantly, this catalyst was simply recovered by an external permanent magnet and recycled without a significant loss in the catalytic activity.

\[
\begin{array}{c}
\text{R}^- \text{X} \quad \text{R} \quad \text{B(OH)}_2 \xrightarrow{\text{Pd-NHC@Fe}_3\text{O}_4-\text{IL}} \text{K}_3\text{PO}_4, \text{TBAB, H}_2\text{O} \quad \text{R}^- \text{X} \quad \text{R} \quad \text{R}
\end{array}
\]

\textbf{Scheme 3.15}
In one of recently published article, Salunkhe et al.\textsuperscript{38} have demonstrated the dramatic effect of ionic liquids on shape of copper nanoparticles (Figure 3.2) and their application in 1,3-dipolar cycloaddition reactions of azides and aryl and sugar based terminal alkynes. The change in anion led to change in shape of the nanoparticles. It was observed that both the ILs used alone could not stabilize the nanoparticles and polyvinyl pyridine (PVP) needed to be use as capping agent for these nanoparticles. Spherical nanoparticles were obtained in [bmim]BF\textsubscript{4} while cubical nanoparticles were obtained in [bmim]PF\textsubscript{6}. Both types of nanoparticles have shown profound effect on the cycloaddition reaction between azides and terminal alkynes.

(A) BMIM.BF\textsubscript{4}/water with PVP

(B) BMIM.PF\textsubscript{6}/DCM with PVP

Figure 3.2
Very recently, Wang and others\textsuperscript{39} demonstrated effective depolymerization of poly (ethylene terephthalate), PET (Scheme 3.17), using iron containing imidazolium based ionic liquid 1-butyl-3-methylimidazolium tetrachloroferrate \([\text{bmim}]\text{FeCl}_4\). The advantages of use of this IL are relatively low reaction temperature, good conversion with enhanced selectivity in comparison with \(\text{FeCl}_3\) and \([\text{bmim}]\text{Cl}\).

\[\text{Oligomers} \quad \xrightarrow{\text{[bmim]}\text{FeCl}_4} \quad \text{Oligomers}\]

\textbf{Scheme 3.17}

\textbf{3.2.3 TSIL as reaction media}

Nucleoside chemistry is an important area of research, but one in which solvent choice is severely compromised by poor solubility. Most organic solvents are not suitable; the exceptions are undesirable from an environmental point of view. In one of earlier investigations\textsuperscript{40}, it was shown that the ionic liquids were suitable, since the solubility of nucleosides was very good, especially in a series of methanesulfonate salts. The acylation of 2’-deoxyribonuclosides was studied in this ionic liquid. This investigation illustrated the benefits of solubility and recoverability, as well as efficient reaction conditions, which ionic liquids can provide for nucleosides (Scheme 3.18).
Recently, TSILs based on 1,2,3-triazolium salts have been prepared by well known copper catalyzed click reaction with the intention of simultaneous multifunctionalization of the cation (Scheme 3.19).\textsuperscript{41} This has an added advantage of controlling both chemical (introduction of functional moiety) and physical (introduction of alkyl chain) properties at a time. This has brought forward the new concept of Multi Task Specific Ionic Liquids.

Shinde et al.\textsuperscript{42} demonstrated the synergistic effect of tertiary alcohol functionalized ionic liquid in nucleophilic fluorination. The dual advantage of
combination of ionic liquid and tertiary alcohol was acceleration of reaction with minimization of side reactions (Table 3.1) The weak H-F hydrogen bonding maintained the inherent nucleophilicity and reduced the basicity of fluoride anion which in turn reduced the side reactions.

![Chemical reaction](image)

**Table 3.1**: Effect of IL on nucleophilic fluorination

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Equivalent</th>
<th>Isolated yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-BuOH</td>
<td>0.5</td>
<td>22</td>
</tr>
<tr>
<td>[bmim]OMs</td>
<td>0.5</td>
<td>30</td>
</tr>
<tr>
<td>[bmim]OMs/ t-BuOH</td>
<td>0.5 / 0.5</td>
<td>37</td>
</tr>
<tr>
<td>ROMs CsF CH$_3$CN 100°C</td>
<td>0.5</td>
<td>97</td>
</tr>
</tbody>
</table>

Bellina et al.$^{43}$ synthesized a series of glycerylimidazolium (Figure 3.3) based ionic liquids aiming at their applications to palladium catalyzed coupling reactions. They extensively studied the physical and physico-chemical parameters such as thermal stability, hydrogen bonding, conductivity and application of these series of TSIL for Heck reaction.

![Figure 3.3](image)
Park and co-workers\textsuperscript{44} studied the cyanoisilylation of carbonyl compounds (Scheme 3.21) using scandium triflate as catalyst and found a dramatic increase of catalytic activity in ionic liquid [bmim]SbF\textsubscript{6}. This enhanced catalytic activity is attributed to enhancement of the Lewis acidity of the catalyst by anion exchange between ionic liquid and scandium triflate.

\[
\begin{array}{c}
\text{R}_1 \text{R}_2 \text{C}=\text{O} + \text{TMSCN} \xrightarrow{\text{Sc(OTf)}_3 \quad \text{[bmim]SbF}_6} \text{TMSO} \text{CN} \quad \text{R}_1 \text{R}_2 \\
\text{r.t.}
\end{array}
\]

**Scheme 3.21**

In their first of its kind report of highly selective anodic fluorination of aromatic compounds, Sawamura et al.\textsuperscript{45} used an iodoarene appended TSIL (Figure 3.4) as mediator in a HF based IL. Compared with conventional mediatory systems, TSIL as mediator has reduced mobility due to viscosity of IL further leading to easy fluorination.

\[
\begin{array}{c}
\text{I} \quad \text{O} \quad \text{N}^+ \quad \text{N}^- \\
\end{array}
\]

**Figure 3.4**

In a recent report, Kundu et al.\textsuperscript{46} put forth a new class of zwitterionic catalyst for stereoselective aza-Henry reaction (Scheme 3.22). The catalyst demonstrated high stereoselectivity predominantly forming syn product. Based on
effective scaled up reactions and reusability, catalyst was found to be commercially useful.

\[
R_1\text{--NH}_2 + R_2\text{--CHO} + \begin{array}{c}
\text{NO}_2 \\
\text{R}_3 \\
\end{array} \xrightarrow{\text{IBS, neat, r.t.}} \begin{array}{c}
\text{NH} \\
\text{R}_1 \\
\text{NO}_2 \\
\end{array} \begin{array}{c}
\text{R}_2 \\
\text{R}_3 \\
\end{array}
\]

4-(1-imidazolium) butane sulfonate 4-(3-Methylimidazolium) butane sulfonate

Scheme 3.22

In their attempt towards understanding the role of IL in catalysis at molecular level, Chakraborti and co-workers\textsuperscript{47} have studied role of IL in O-t-Boc formation and deprotection (Scheme 3.23), with the aid of NMR and MALI-TOF-TOF-MS techniques. In their study they found that apart from imidazolium based electrophilic activation of substrate through hydrogen bonding, the hydrogen bonding interaction of counter anion of IL plays crucial role in nucleophilic activation of other reactants. So there is synergetic effect of both the ions of an ionic liquid in catalyzing any reaction.
3.2.4 Chiral Ionic Liquids

Chiral Ionic liquids (CILs) are receiving increasing attention due to their ease of synthesis and properties. These new chiral solvents could play a central role in enantioselective organic chemistry and hopefully expand the scope of chiral solvents. A significant transfer of chirality in these solvents can be expected due to their high degree of organization. It has been reported that most of the ILs possess a polymeric behavior and are highly ordered H-bonded liquids (three-dimensional networks of anions and cations linked together by hydrogen bonds). These specific properties suggest that CILs could outperform the classical chiral solvents for asymmetric induction.\textsuperscript{48-50}

Many chiral ionic liquids have been synthesized which incorporate one or more functional groups, and thus they belong to the class of functionalized chiral ionic liquids. Since the functional group is intended to perform a desired task, these functionalized ionic liquids are also referred to as task specific ionic liquids. Chiral ionic liquids and functionalized chiral ionic liquids are discussed in this section.\textsuperscript{51}

There are several published reviews covering the preparation and application of chiral ionic liquids, with the most recent two have been published in 2005.\textsuperscript{52-53}
The present account is intended to update the reader about the recent work in the field of chiral ionic liquids and functionalized chiral ionic liquids.

The more efficient, economic, and simple way to prepare enantiomerically pure ILs is to use precursors derived from the chiral pool either for the generation of the CILs anion or cation or for both. Therefore, chiral ionic liquids are mainly compounds having a central chirality. However, some new CILs having an axial or a planar chirality have also been developed. The first example dealing with the preparation of such a chiral ionic liquid was reported by Earley in 1999 (Scheme 3.24)\(^ {54}\). The chirality was brought by the lactate anion. The [bmim] lactate ionic liquid was simply prepared by anion exchange between [bmim]Cl and commercially available sodium (S)-2-hydroxypropionate in acetone.

![Scheme 3.24](image)

Later on many novel chiral ionic liquids have been synthesized. Recently Bonanni et al.\(^ {55}\) reported a straightforward strategy for the synthesis of series of novel pyrrolidinium ionic liquids based on tartaric acid (Figure 3.5).
Siyutkin et al.\textsuperscript{56} designed and synthesized (S)-proline modified task specific ionic liquid for the direct asymmetric aldol reaction between cycloalkanones and aromatic aldehydes in the presence of water (Figure 3.6).

Li and co-workers\textsuperscript{57} synthesized novel sulfur-functionalized ionic liquids. Epoxidation of aromatic aldehydes with benzyl bromides was investigated using these organocatalyst CIL. \textit{trans}-Epoxides were obtained with excellent diastereoselectivity and enantioselectivity up to 72\% ee. The organocatalyst could be easily reused for five times without remarkable decrease in yields and enantioselectivities (Scheme 3.25).
A library of novel CIL-modified silanes was synthesized using combinatorial approach by Li and co-workers. The chiral discrimination abilities of these chiral ionic liquids were screened using $^{19}$F-NMR spectroscopy (Scheme 3.26).
The chiral ionic liquids prepared from TBAB and natural amino acids were used as cocatalysts in the asymmetric cycloaddition of carbon dioxide to propylene oxide (PO) at room temperature in the presence of chiral silane catalyst. The synergistic effect between catalyst and IL was studied. The system was found to exhibit good activity for the asymmetric cycloaddition of carbon dioxide to epoxide under very mild conditions (Scheme 3.27).\(^5^9\)

A polymeric ionic liquid (IL)-functionalized chiral salen ligand (PICL) was synthesized by covalent polymerization between amino (–NH\(_2\)) group of 1,3-dipropylamineimidazolium bromide with chloromethyl (–CH\(_2\)Cl) group at two sides of 5,5’ positions in the typical chiral salen ligand (Figure 3.7). Treatment of the synthesized PICL with Mn(OAc)\(_2\)·4H\(_2\)O and LiCl under aerobic oxidation yielded the corresponding polymeric IL-functionalized chiral salen Mn(III) complex (PICC). Comparable catalytic activity and enantioselectivity relative to the
monomeric chiral salen Mn(III) complex were observed. Furthermore, recovery of the polymeric catalyst was readily accomplished by simple precipitation in n-hexane, and subsequently reused (10 times) without significant loss of reactivity and enantioselectivity.  

\[
\begin{align*}
\text{N} & \text{N} \\
\text{Mn} & \text{O} \\
\text{N} & \text{tBu} \quad \text{Cl} \\
\text{N} & \text{H} \\
\text{N} & \text{H} \\
\end{align*}
\]

\((n=\sim 17)\)

**Figure 3.7**

Highly enantioselective Michael addition of cyclohexanone to aryl nitroolefins in the presence of an ionic liquid anchored pyrrolidine (10 mol%) and TFA (5 mol%) generated the corresponding adducts in high yields (up to 95%) with excellent diastereoselectivities (up to >99:1 dr) and enantioselectivities (up to >99% ee) (Scheme 3.28). Furthermore, the catalyst could be recycled and reused at least eight times without loss of its catalytic activity.  

\[
\begin{align*}
\text{O} & \quad + \quad \text{Ar} \quad \text{NO}_2 \\
\text{Scheme 3.28} \\
\end{align*}
\]
A novel family of chiral imidazolium-based ionic liquids containing a chiral moiety and a free hydroxyl function were designed and synthesized using isosorbide as a biorenewable substrate (Scheme 3.29). These chiral ionic liquids were found to catalyze the aza Diels–Alder reaction to give good yields and moderate diastereoselectivities. Chiral ionic liquids were recycled without much loss in efficiency.\(^6^2\)

![Scheme 3.29](image)

Various chiral ionic liquids based on simple chiral natural products such as carbohydrates\(^6^3\) (Figure 3.8), terpenes\(^6^4\) (Figure 3.9) and abietane\(^6^5\) (Figure 3.10) have been synthesized recently. These ionic liquids could find applications as new chiral solvents or catalyst for a range of asymmetric reactions in future.
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Figure 3.8

Figure 3.9

a: $X = \text{I}, R = \text{Me}$
b: $X = \text{I}, R = \text{Et}$
c: $X = \text{Br}, R = \text{n-Pr}$
d: $X = \text{Br}, R = \text{i-Pr}$
e: $X = \text{Br}, R = \text{n-Bu}$
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3.3 Conclusion:

Even though, ionic liquids have been explored for the past 15 years, the domain of task specific ionic liquids is still in infant stage. The ionic liquids in conglomeration of their basic properties with desired properties for the reaction under study could become the next arsenals available in the armory of green chemistry. Present industrial applications of ionic liquids involve acid scavenging agent, antistatic agent, in gas compressors, chromatography, batteries, and many more. Even ILs in their next generation can play an important role as tunable active pharmaceutical ingredients (APIs)\textsuperscript{65} in pharma industry. However, there are some limitations with the use of ILs. The exact role of ionic liquids in carrying out reactions is still under-explored. Apart from this, the other issues such as toxicity, purification, development of improved product isolations and high cost are needed to be addressed in future research for full commercialization of ILs.

However, taking into account the wide window of properties and applications of ILs, research in the field of task specific ionic liquids have great potential to grow in near future.
3.4 References:

   


