Ionic liquids: green organic transformation with dual solvent-catalyst strategy and its multidisciplinary applications

Líquidos iônicos: transformação orgânica verde com estratégia de duplo catalisador solvente e suas aplicações multidisciplinares

Líquidos iónicos: transformación orgánica verde con estrategia dual solvente-catalizador y sus aplicaciones multidisciplinarias

DOI:10.34117/bjdv10n6-012

Submitted: May 03rd, 2024
Approved: May 24th, 2024

Nandkishor Bhagwan Shirsath
PhD in Chemistry
Institution: Department of Chemistry, M.S.G. College Malegaon
Address: Malegaon, Maharashtra, Índia
E-mail: shirsathnandkishor91@gmail.com

Milind C. Nagare
Master in Chemistry, NET
Institution: Department of Chemistry, ACS College Manmad
Address: Malegaon, Maharashtra, Índia
E-mail: milind7nagare@gmail.com

Kuldeep T. Padhyar
Master’s in Chemistry, NET
Institution: Department of Chemistry, M.S.G. College Malegaon
Address: Malegaon, Maharashtra, Índia
E-mail: kpadhyar@gmail.com

Avinash U. Nerkar
Master in Chemistry, NET
Institution: Department of Chemistry, M.S.G. College Malegaon
Address: Malegaon, Maharashtra, Índia
E-mail: aunerkar@gmail.com

Gokul V. Suryawanshi
Master in Chemistry, NET
Institution: Department of Chemistry, M.S.G. College Malegaon
Address: Malegaon, Maharashtra, Índia
E-mail: gklsuryawanshi24@gmail.com

Tulsidas S. Savale
PhD in Chemistry
Institution: Department of Chemistry, M.S.G. College Malegaon
Address: Malegaon, Maharashtra, Índia
E-mail: anilsavale23@gmail.com
ABSTRACT
Ionic liquids (ILs) are liquid organic salts owning a lot of interesting properties that rapid increase various research to study their utilization in numerous fields. The enormous utilization and scope of ILs in a diversity of fields have been presented based upon available literature. ILs were firstly addressed as a green alternative to traditional solvents because of their almost non-existent vapor pressure as environmental replacement of most common volatile solvents in industrial processes for their damaging effects on the environment. Systematic and brief investigation of the several IL applications has been done highlighting some recent significant advances in every zone. This review will contribute to helpful the significant knowledge of all branch of research based on ILs. Apart from this, the tasks associated with the industrial use of ILs have been discussed, which require further investigation.

Keywords: ionic liquids, volatile solvents, synthesis, applications.

RESUMO
Os líquidos iônicos (LIs) são sais orgânicos líquidos que possuem muitas propriedades interessantes, o que faz com que várias pesquisas aumentem rapidamente para estudar sua utilização em diversos campos. A enorme utilização e o escopo dos ILs em uma diversidade de campos foram apresentados com base na literatura disponível. Os ILs foram primeiramente abordados como uma alternativa verde aos solventes tradicionais, devido à sua pressão de vapor quase inexistente, como substituto ambiental dos solventes voláteis mais comuns em processos industriais por seus efeitos prejudiciais ao meio ambiente. Foi feita uma investigação sistemática e breve das diversas aplicações de IL, destacando alguns avanços significativos recentes em cada área. Essa revisão contribuirá para auxiliar o conhecimento significativo de todos os ramos de pesquisa baseados em ILs. Além disso, foram discutidas as tarefas associadas ao uso industrial de ILs, que requerem mais investigação.

Palavras-chave: líquidos iônicos, solventes voláteis, síntese, aplicações.

RESUMEN
Los líquidos iónicos (LIs) son sales orgánicas líquidas que poseen una gran cantidad de propiedades interesantes que hacen que aumente rápidamente la investigación para estudiar su utilización en numerosos campos. A partir de la bibliografía disponible, se han presentado la enorme utilización y el alcance de los LI en diversos campos. En primer lugar, los IL se consideraron una alternativa ecológica a los disolventes tradicionales, debido a su presión de vapor casi inexistente, para sustituir a los disolventes volátiles más comunes en los procesos industriales por sus efectos nocivos para el medio ambiente. Se ha realizado una investigación sistemática y breve de las diversas aplicaciones de los IL, destacando algunos avances significativos recientes en cada zona. Esta revisión contribuirá a ayudar al conocimiento significativo de todas las ramas de investigación basadas en los LIs. Aparte de esto, se han discutido las tareas asociadas con el uso industrial de las LIs, que requieren una mayor investigación.

Palabras clave: líquidos iónicos, disolventes volátiles, síntesis, aplicaciones.
1 INTRODUCTION

Ionic liquids have been generating increasing interest over the last decade [1]. Most chemical reactions have been carried out in molecular solvents. For two millennia, most of our understanding of chemistry has been based upon the behaviour of molecules in the solution phase in molecular solvents. Recently, a new class of solvent has emerged i.e. ionic liquids [2]. Ionic liquid is a liquid that consist of organic cations and organic, inorganic anions, but it is different from molten salts [3]. Recently, molten salts and ionic liquids has been distinguished on the basis of melting point [4]. Molten salts are usually defined as a high melting, highly viscous and highly corrosive liquid, while ionic liquids are defined as pure compounds, consisting only of cations and anions (i.e. Salts), which melt at or below 100°C.

Ionic liquids are known by several different names like neoteric solvents, designer solvents, ionic fluids, and molten salts [5]. Ionic liquids (ILs) are a new generation of chemicals that have a great potential for contributing to the greenness of chemical processes and developing new applications. ILs have also gained popularity as ‘green’ alternatives to volatile organic solvents (VOCs) to be applied in electrochemical,
synthetic and separation processes [6,7]. Moreover, reaction products may be separated more easily from an ionic liquid than from conventional solvents. These benefits make ionic liquids an attractive choice of solvent in many important chemical processes, with examples reported in the areas of catalysis, biocatalysis, [8] synthetic chemistry [9] and electrochemistry [10]. They also have various useful properties, such as non-flammable, noncorrosive, and non-volatile under atmospheric condition [11]. They also non-toxic, highly polar, Easy recyclable.

Table 1 shows a comparison of the physical properties of ionic liquids, molten salts and volatile organic solvents.

<table>
<thead>
<tr>
<th>Physical Property</th>
<th>Ionic Liquids</th>
<th>Volatile Organic Solvents</th>
<th>Molten salts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basic components</td>
<td>Ion pairs</td>
<td>Molecules</td>
<td>Ion pairs</td>
</tr>
<tr>
<td>Viscosity</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Conductivity</td>
<td>High</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Corrosive</td>
<td>Low</td>
<td>Medium</td>
<td>High</td>
</tr>
<tr>
<td>Flammability</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Melting points</td>
<td>-20 – 150 °C</td>
<td>&lt; -20 °C</td>
<td>&gt; 200 °C</td>
</tr>
<tr>
<td>Boiling points</td>
<td>&lt; 400 °C</td>
<td>30-100 °C</td>
<td>&gt; 400 °C</td>
</tr>
</tbody>
</table>

Sources: Drawn by Authors

1.1 PROPERTIES OF IONIC LIQUIDS THAT MAKE THEM MORE ATTRACTIVE INCLUDE

As a solvent ionic liquid posse several advantages over conventional organic solvents, which make them environmentally compatible Ionic liquids exhibit many properties which make them potentially attractive media for many organic transformations due to easy handling, recyclability and thus leading to cheap and environmentally benign reaction conditions.

- Negligible vapour pressure [12]
- Non-flammable [13]
- Large liquid range (span of temperatures between melting and boiling point of a liquid) [13]
- High thermal/chemical/electrochemical stability [14]
• Solvating ability [15]
• Tunable miscibility with water or organic solvents [16]
• Generally, do not coordinate with metals, enzymes [17]
• Chiral ionic liquids may control stereoselectivity [18]
• Easy recyclability [19]

2 SYNTHESES OF IONIC LIQUIDS

Synthesis of ionic liquids includes 1 or 2 steps [20]. Initial step is quaternization reaction (like SN₂ reaction), desired cation has to be generated, (most common cations in ionic liquids are nitrogen or phosphorous containing organic ions) Some examples of cations present in ionic liquids are as follows: N, N-dialkylimidazolium, Alkylammonium, N-alkylpyridinium, Alkylphosphonium, Pyrazolium, Oxazolium,[21] Triazolium, Thiazolium and Sulphur containing ionic liquids are known. In second step, means in metathesis reaction or Anion Exchange reaction. Anion exchange reactions can be carried out by treatment of halide salts with Lewis acids, strong acid or ion-exchange resin to form Lewis acid-based ionic liquids.

2.1 COMMON CATIONS AND ANIONS OF ILS. [22-24]

![Figure 1 Common Cations and Anions of ILs](Sources: Drawn by Authors)

By replacing one organic cations or anions, we can obtain versatility in ionic liquids. This is one of the strong characteristics of ionic liquids [25].
Figure 2 General used synthesis routes for ILs (abbr. Py:pyridine, Pyr:N-alkylpyrrolidine, Im:N-alkylimidazol, TfO:triflate.

Figure 3 Common cations and anions of ILs

Sources: Drawn by Authors
3 TASK SPECIFIC IONIC LIQUIDS [TSILs]

In 1999, Davis Jr. and Forrester introduced the concept of “task-specific ionic liquids” in the field of ionic liquids [26]. Task-specific ionic liquid may be defined as ionic liquids in which a functional group is incorporated enabling the liquid to behave not only as a reaction medium but also as a reagent or catalyst in some chemical reactions or processes [27] (i.e. ionic liquid containing functional groups) (Figure 3).

3.1 SYNTHESIS OF TSILS

Synthesis of TSILs involves the displacement of halide from an organic by a parent imidazole, phosphine, and so forth where by the organic halide already incorporates a desired functional group. The displacement reaction is followed by anion exchange.

![Synthesis paths for the preparation task-specific ionic liquids](image)

Sources: Drawn by Authors
Recently, various types of “task-specific ionic liquids” (TSILs) have been designed and synthesized for specific purposes such as catalysis, organic synthesis, separation of specific materials as well as for the construction of nanostructure materials and ion conductive materials etc [28,29].

4 SYNTHETIC APPLICATION OF IONIC LIQUID AND TASK-SPECIFIC IONIC LIQUID

Depending upon the functional group attached to the cation and anion, the ionic liquid may behave as an acidic, basic and organo-catalyst.

4.1 ASYMMETRIC HYDROGENATION

Rh-Catalyzed asymmetric hydrogenation of N-acetylphenylethenamine using in [bmim][SbF6]–iPrOH two-phase solvents systems [30].

![Scheme 1 Asymmetric hydrogenation](image)

Sources: Drawn by Authors

4.2 HYDRO FORMULATION REACTION

Platinum-catalyse dhydroformylation of oct-1-ene in bmimSnCl₃ [31].
4.3 KNOEVENAGEL CONDENSATION

Knoevenagel condensation reaction between 2-hydroxybenzaldehyde derivatives and dialkylmalonates or chlorodialkylmalonate in IL [32].

4.4 HECK REACTION

Heck reaction is palladium catalyzed reaction in which, aryl iodides and aryl tosulate are normally used as substrates, polar solvents such as DMF and acetonitrile are employed, in case of aryl bromides or chlorides are employed, it is necessary to use more active catalysts or add phosphine ligands in order to retain the catalytic activity. By utilizing 1-butyl-3-methylimidazolium bromide (bmimBr) as solvent, aryl bromides react with styrene to afford stilbenes in high yields without adding a phosphine ligand [33].
4.5 SYNTHESIS OF ETHYL-2-AMINO-4-ARGIO-3-CYANO-6-METHYL-3,4-DIHYDRO-2H-PYRAN-5-CARBOXYLATE

4H-Pyrane is synthesized from a reaction of aromatic aldehydes with malononitrile and ethyl acetoacetate in presence of water and [2-aemim][PF₆] was reported to Y. Peng and G. Song [34].

4.6 SYNTHESIS OF 5-ARGIO-2,3,4,4A,5,5A,12,12A-OCTAHYDROTETRACENE-1,6,11(11AH)-TRIONE

J. M. Khurana and coworkers reported the Facile and convenient one-pot tandem approaches for the synthesis of privileged medicinal scaffolds, 12-aryl-2,3,4,12-tetrahydrobenzo[b]xanthene-1,6,11-trionederivatives, by reaction between various aromatic aldehyde, 2-hydroxy-1,4-naphthoquinone and cyclic 1,3 diketone under
extremely mild reaction conditions using a catalytic amount of \( \text{H}_2\text{SO}_4 \) in water or in the presence of the acidic ionic liquid bmim[HSO\(_4\)], which could be recycled [35].

**Scheme 6** 5-argio-2,3,4,4a,5,5a,12,12a-octahydrotetracene-1,6,11(11aH)-trione


### 4.7 BIGINELLI REACTION

Ganapathi P. et. al prepare pyrimidone derivatives from one pot multi component reaction using ethyl acetoacetate, diamide and simple/substituted aryl aldehyde with the assistance of Lewis acid. The literature shows that, the Biginelli reaction required longer reaction time, expensive catalyst and gives very low percentage of yield [43-46].

**Scheme 7:** Biginelli reaction
4.8 CARBONYLATION OF ETHYLENE

The ILs utilize with bronsted acid SO₃H functionalized with palladium catalyst for enhance the stability of ILs. This stopping it from precipitating as palladium black, but also gives in biphasic reaction mixture, which helped the product separation and permitted the reuse of precious metal catalyst [47,48].

![Scheme: 8 Carbyonylation of ethylene](image)

Sources: Drawn by Authors

4.9 WITTIG REACTION

The Wittig reaction is a convenient method for C-C double bond formation. However, the separation of the product and the byproduct, triphenylphosphine oxide, is a major problem. When an ionic liquid is used as solvent, the product and phosphine oxide can be easily separated by combining an ether extraction and a toluene extraction after the reaction is complete [49,50].

![Scheme: 9 Wittig reaction](image)

Sources: Drawn by Authors

4.10 STILL REACTION

The Stille reaction is a valuable reaction, where an organotin compound and an electrophilic reagent are reacted to form a C-C bond under mild conditions in the presence of palladium catalyst. In the reaction of vinyltributyltin and iodocyclo-hexenone in an
ionic liquid, the product can be extracted with ether, and the catalyst is retained in the ionic liquid [51,52].

![Scheme: 10 Still reaction](image)

**Sources:** Drawn by Authors

### 4.11 FRIEDEL-CRAFTS REACTION

The best example for C-C formation is Friedel-Crafts reaction. In the benzylation of anisoles catalyzed by copper triflate in bmimBF₄, methoxybenzophenone is quantitatively obtained within 1h, with a p-/o-product ratio of 96/4.

![Scheme: 11 Friedel-Craft reaction](image)

**Sources:** Drawn by Authors

### 4.12 REDUCTION

Kabalka and research group have described this reduction usingtrialkylborane in which bmimBF₄, emimBF₄, and 1-ethyl-3-methylimidazolium hexafluoro-phosphate (emimPF₆) are used as solvents. Such as when benzaldehyde was reduced by tributylborane in emimPF₆, the reaction proceeded rapidly at 100 °C to give the product in high yield [54,55].
4.13 ENZYMATIC REACTION

Enzymatic reactions consuming ionic liquids have also been described. Transesterifications in organic solvents are well recognized as a valuable synthetic method for the preparation of optically-active compounds. In the asymmetric transesterification of allylic alcohols using ionic liquids, the chosen products are afforded in similar yields to those of organic solvent systems [56, 57, 58].

5 MULTIDISCIPLINARY APPLICATIONS OF ILS

ILs are liquid organic salts owning a lot of interesting properties that prompt various researchers to explore their utilization in various fields [59, 60]. They are regarded as “designer solvents”, and “solvents of the future” [61-63]. They have been found applicable in a diversity of fields in advance research such as electrochemistry [64], nanotechnology [65], analytical chemistry [66], extraction processes, and many more, thus, branded as “solvents of the future” [67-70].

Nowadays, scientists are engaged searching Multidisciplinary uses of single material, which are alternative to traditional material. From last few years, water has emerged as a useful reaction medium for a number of chemical reactions [71]. But it has
certain limitations notable is the low miscibility of organic substrates in water, which has restricted its applications in a number of chemical reactions [72]. IL is an advanced class of compounds that have received wide attention as green solvent alternatives [73]. Ils have number of versatile applications in different fields such as in multicomponent reactions [74], as solvent, as catalyst [75], electrochemical devices [76] energy storage devices, separation, lubricants and additives etc. [77,78].

Figure 5 Multidisciplinary applications of ILs [79,80]

6 CONCLUSION

Ionic liquids (ILs), as the new materials of multi-functionality and widely used in various fields of research. Environmentally friendly reaction processes have been vigorously being studied from the standpoint of green chemistry and based on the properties of easy separation, low toxicity, selective miscibility, negligible vapor pressure and Non-flammable. ILs plays an important role in organic synthesis as the green alternative solvent. The ILs is new field of research and development will be opened the new pathways for achieving non-polluting “green chemistry”. 
ACKNOWLEDGMENT

An author acknowledges DST-FIRST for financial support. We are sincere, thanks to Dr. A. P. Hire and also Principal M. S. G. College Malegaon Camp, Head Department of Chemistry, M. S. G. College Malegaon Camp for providing infrastructure and laboratory facilities.
REFERENCES


[34] Y. Peng, G. Song, Catalysis Communications, 2007, 8, 111.


[58] Ionic liquids, www.tcichemicals.com


[61] Li H., et. al. *J. Colloid Interface Sci.* **2024**, 6, 1204-1215.


