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History and Development of Ionic Liquids

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1.1 Introduction

For the past two decades, the term ionic liquid (IL) has been familiar to a very small number of research groups. However, ILs have attracted significant attention as innovative fluids in a wide range of research fields during this period [8, 60]. Generally, ILs are liquids that exist only in ionic form [79]. ILs can be defined as liquids consisting of ions with a melting point ≤ 100 °C. In another way, ILs, which exist as liquids at or near room temperature, are frequently termed room temperature ionic liquids (RTILs) [54]. In 1914, Paul Walden reported ethylammonium nitrate as the first IL [13]. According to Walden, the liquid, i.e. ethylammonium nitrate, composed of cations and anions and a minimal amount of molecular species, is an IL. Since the nineteenth century, several synonyms and abbreviations have been given to ILs by different research groups. Among the scientific community, the most frequent synonyms of ILs are molten salt, molten organic salt, low-melting salt, fused organic salt, ambient temperature ILs, neoteric solvent, and many more [40].

ILs are associated with unique features such as high ionic conductivity, high viscosity, low volatility, nonflammability, negligible vapor pressure, tunable solubility, and a wide electrochemical potential window [82]. All the mentioned IL properties can be altered by tuning the combination of the cations and anions of the ILs. Hence, ILs can also be termed “designer solvents” [55]. Due to their unique properties, ILs are used in various research applications. A multidisciplinary research on ILs is developing, including materials science, biotechnology, chemical engineering, chemistry, energy field, and atmospheric chemistry. Due to the low-volatile, non-flammable nature of ILs, they are highly preferred over any conventional organic volatile solvents or catalysts in various physical and chemical processes [73].

Furthermore, recently, green technology has been the greatest challenge for researchers concerning environmental hazards. The linkage between ILs and green chemistry is associated with the solvent properties of ILs [17]. ILs are also entitled to green solvents as they possess negligible vapor pressure and high thermal stability, resulting in advantages such as product recovery, desulfurization of liquid fuel, ease

of containment, and recycling capability [42, 51]. ILs never possess the explorer risk compared with volatile organic solvents. In terms of volatility, molecular solvents could not (except molten polymers) reach even near the ILs.

ILs can exhibit high polarity. Based on the normalized polarity scale, the polarities of tetramethylsilane and water are 0.0 and 1.0, respectively, whereas the polarity of ILs is usually in the range of 0.6–0.7 [85]. Due to their high polarity, ILs are used as catalysts in various chemical and biochemical reactions. ILs easily dissolve in different solvents, including organic, inorganic, polar and nonpolar, and polymeric compounds. From the chemical engineering perspective, the most critical disadvantage, i.e. gas/liquid–solid mass transfer limitations during catalytic reactions, is resolved using efficient IL catalysts, as reported in detail by Tan et al. [75].

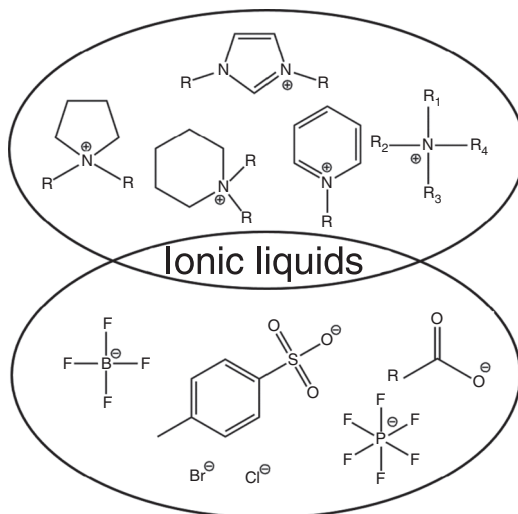
In view of the growing field of renewable energy, it is necessary to replace the conventional volatile electrolytes with green electrolytes in energy storage devices such as batteries, supercapacitors, fuel cells, and dye-sensitized solar cells. [44, 84]. ILs are appropriate in energy storage devices because of their high conductivity, low volatility, nonflammability, and high electrochemical and thermal stability. Imidazole- and pyrrolidinium-based electrolytes have exhibited promising outcomes as electrolytes in lithium-ion batteries and capacitors [14]. However, the investigation and deep learning of ILs as electrolytes for new devices such as hybrid batteries and Al oxygen/ion batteries and for CO₂ reduction are in the early stages [53].

Millions of ILs can be synthesized by tuning the combination of cations and anions with desired properties and applications. Based on their properties and applications, ILs can be classified as task-specific ILs, energetic ILs, magnetic ILs, polyionic liquids, and supported ILs. [52]. For a specific process, screening for appropriate ILs is a prerequisite. To identify the structure–performance relationships, it is required to determine the nature of the interactions between cations–cations, anions–anions, and cations–anions of IL species [12]. Therefore, experimental, theoretical, and computational methods are needed to summarize the proper nature of ILs. More profound knowledge of IL nature at the microscopic scale will support the interpretation of macroscopic fluid phenomena and therefore endorse the application of ILs in industry. The multiscale features of ILs extending from the molecular level to the industrial level have been described by Dong and his coworkers [38]. Because of a wide range of applications and prospects of the ILs in the industry, ILs were exclusively named as "solvents of the future" in industrial processes [65]. However, the toxicity of ILs is identified as an emerging limitation for practical applications of ILs. ILs containing high alkyl chain lengths or fluorine anions are more toxic [97]. The toxicity can be affected by changing the structure of ILs. Hence, a detailed toxicity analysis is recommended before real-life applications of ILs. The brief history, development, and future scope are further summarized in the next section.

1.2 Constituents of ILs

ILs are usually made up of organic cations and inorganic anions. Generally, nitrogen- (imidazolium, pyrrolidinium, pyridinium, ammonium, choline, etc.) or

Figure 1.1 Widely studied cations and anions of ionic liquids.



phosphorus-containing cation moieties with linear or branched alkyl chains are used to prepare ILs.

The most commonly used anions are halides (Cl^- , Br^- , I^-), nitrate [NO_3^-], chloroaluminates [AlCl_4^- , Al_2Cl_7^-], hexafluorophosphates [PF_6^-], tetrafluoroborate [BF_4^-], alkyl carboxylate [RCOO^-], acetate [CH_3COO^-], trifluoromethylsulfonate [CF_3SO_3^-], triflate [OTf^-], and bistriflamide [NTf_2^-]. Recently, amino acids are also used as anions. The most studied cations and anions are shown in Figure 1.1.

1.3 The Brief History

There are numerous inceptions to the story of ILs in which they were recognized independently. The reporter's opinion will essentially influence the history of ILs [88]. The background of the ILs started with the finding of molten liquid salt. In the early 1990s, Paul Walden was searching for liquid molten salt at a particular temperature at which he could have accomplished his experiment. In 1914, Walden discovered ethyl ammonium nitrate [$\text{EtNH}_3^+[\text{NO}_3^-]$] with a melting point of 12°C and termed it the first protic ionic liquid (PIL) [47]. Further, Walden and his coworkers formulated the "Walden rule", which correlates the equivalent conductivity (λ) as well as viscosity (η) of the liquid (aqueous solution).

$$\lambda\eta = \text{Const}$$

Later on, the Walden rule could not interpret the properties of low-melting silver salt. Further, the Walden rule was modified to the fractional Walden rule by a group of molten salt chemists from a German school [5]. The fractional Walden rule is as follows:

$$\lambda\eta^\gamma = \text{Const}$$

where γ is a constant $0 < \gamma < 1$. But after that, there was no potential progress for molten salt studies for a prolonged time. According to the partial Walden rule, the Arrhenius activation energy for conductivity was lower than that for viscosity in the case of a low-melting silver iodide salt. Therefore, the silver iodide salt is a good conductor even in its crystalline state near its melting point temperature. The Walden rule was unable to predict the “superionic” behavior of molten salt, which made Walden rule very useful for the classification of ILs.

Furthermore, in the mid-nineteenth century, chemists observed the so-called “red oil” during Friedel–Crafts reactions. The “red oil” was the first documented observation of ILs [88]. Using nuclear magnetic resonance (NMR) technique, chemists were able to identify the structure of “red oil,” which was the stable intermediate in Friedel–Crafts reactions termed sigma complex, which was basically heptachlorodialuminate salt (Figure 1.2). Prof. Jerry Atwood from the University of Missouri termed the structure early IL. Afterwards, ILs started to be used as either catalysts or solvent systems for organic reactions. Their effects on the reaction rates and their antimicrobial activity and toxicity were further premediated.

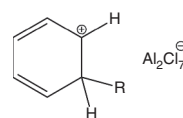


Figure 1.2
Structure of heptachlorodialuminate salt.

Numerous literature surveys suggested that chloroaluminate molten salts attracted significant attention in the mid-nineteenth century. The research based on chloroaluminate molten salts was mainly conducted by the US Air Force Academy in Colorado Springs. Since the early 1960s, the Air Force Academy has endorsed their research in molten salts/IL systems. The chloroaluminate molten salts were used in various research fields, especially electrochemistry. Hurley and Weir were the first to study the potential benefits of molten salts [40]. They mixed aryl and N-substituted alkyl pyridinium halides with several metal halides and nitrates to achieve low liquids for electrochemical extractions. At room temperature, they discovered the formation of liquid 1-ethylpyridinium bromide-aluminum chloride ($[\text{C}_2\text{py}]\text{BrAlCl}_3$). First, they presented a phase diagram for the system, including two eutectics at 1 : 2 at 45 °C and 2 : 1 at –40 °C molar ratios. Bromochloroaluminate was developed at the 1 : 1 M ratio (88 °C). In 1975, Bob Osteryoung and his group further studied $[\text{C}_2\text{py}]\text{BrAlCl}_3$ (2 : 1 M ratio mixture) species for the electrochemical study of ferrocene, ferrous(II) diimine complexes, and hexamethyl benzene [98]. The first paper based on the $[\text{C}_2\text{py}]\text{BrAlCl}_3$ system was published by the Osteryoung group, and the patent was granted by the Air Force Academy. In 1979, Robinson and Osteryoung used 1-butylpyridinium chloride-aluminum chloride ($[\text{C}_4\text{py}]\text{-AlCl}_3$) for electrochemistry and Raman spectroscopy [64]. George Parshall and his group synthesized $[\text{Et}_4\text{N}][\text{GeCl}_3]$ (melting point of 68 °C) and $[\text{Et}_4\text{N}][\text{SnCl}_3]$ (melting point of 78 °C) and used them as solvents for hydrogenation reactions [21]. Further, he also worked on $[\text{Et}_3\text{NH}][\text{CuCl}_2]$ to explore different ammonium and phosphonium chlorocuprate systems. Warren Ford worked on alkyl ammonium alkyl borides and found that triethylhexylammonium triethylhexylboride IL is less viscous among all. In 1983, Chuck Hussey and his groups published a review

article on “Room Temperature Molten Salt Systems”. This review includes the development, properties, and application of chloroaluminate systems [16].

Moreover, in the 1980s, research on ILs was carried out by new researchers like Ken Seddon and Tom Welton. In 1981, Evans et al. [26] started the study on $[\text{EtNH}_3][\text{NO}_3]$. They investigated the thermodynamic properties of its solutions of krypton, ethane, methane, and *n*-butane. They mainly studied the “hydrophobic bonding” present in the system [11]. They illustrated that $[\text{EtNH}_3][\text{NO}_3]$ as a non-aqueous solvent could be used in biochemical systems. Colin Poole and his coworkers used $[\text{EtNH}_3][\text{NO}_3]$ as a stationary phase in gas–liquid chromatography [61].

Early in the 1980s, John Wilkes and his coworkers discovered the 1-alkyl-3-methylimidazolium chloride-aluminum chloride ($[\text{C}_n\text{C}_1\text{im}]\text{Cl}-\text{AlCl}_3$) IL system and examined the transport properties of the systems. Later on, the introduction of 1-alkyl-3-methylimidazolium cations promoted an argument on the role of hydrogen bonding in the structure of ILs. However, all the controversies were fixed by identifying the imidazolium ring protons, which can act as hydrogen bond donors in the presence of hydrogen bond acceptors. Afterwards, researchers focused on removing chloroaluminate species from IL-chloroaluminate systems. Abdul-Sada and his group worked on that [3].

In the 1990s, extensive research was performed on ILs by many groups worldwide. In 1992, Wilkes et al. first synthesized water- and air-stable 1-ethyl-3-methylimidazolium-based ILs [89]. Over the period, several moisture-stable ILs have been synthesized. In 1996, Bonhote et al. synthesized a new class of ILs by introducing $[\text{NTf}_2]^-$ anions [9]. This class of ILs is significantly less viscous and highly conductive. Fraser and MacFarlane’s group also introduced a new subclass of ILs based on phosphonium cation [27]. In 1998, ILs became very popular in the scientific community when the journalist Michael Freemantle wrote the first report in *Chemical & Engineering News* [91]. Based on the application in different research areas, millions of ILs were synthesized by tuning the combination of cations and anions. Therefore, ILs are termed as “designer solvent.” Ken Seddon had carried forward the extensive research on ILs in the Queen’s University Ionic Liquids Laboratory (QUILL). Later, he initiated the collaboration between the academy and industry to explore the industrial applications of ILs.

Further, ILs are used as a green solvent in green technologies. In 2000, Robin Rogers led a NATO Advanced Research Workshop on “Green Industrial Applications of Ionic Liquids” in Heraklion [81]. During this time, Jim Davis termed ILs as task-specific ILs. In 1999, Joan Brennecke discovered the first biphasic system combining ILs with supercritical CO_2 . Numerous studies were published on CO_2 and other gas solubilities in different ILs. Due to negligible vapor pressure and the nonvolatile nature of ILs, researchers have focused on using ILs as lubricants. In 2001, Ye et al. reported the promising performance of ILs as a lubricant for the first time [92]. In 2004, Phillips and Zabinski used ILs as additives for conventional lubricants [59].

The most significant breakthrough in the application of ILs was the utilization of ILs in energy storage devices. ILs can exhibit a wide electrochemical potential window and high conductivity. Therefore, to maximize the energy density of the

devices such as lithium-ion batteries, supercapacitors, fuel cells, and dye-sensitized solar cells, ILs are used as electrolytes. Furthermore, ILs are used in separations in analytical chemistry and nuclear chemistry. The first application of ILs at the commercial level was BASF's BASIL (biphasic acid scavenging utilizing ionic liquids) process. ILs are also a promising candidate for pharmaceutical applications. In 1998, Davis discovered the first IL derivative from the pharmaceutical constituent (API).

1.4 Ionic Liquid-Like Systems

During the last century, there was a massive argument on the properties and the characteristic features of molten salt vs. ILs. There was a bit of confusion over which materials should be counted in the IL family and which should be left out. The term IL solely defines a liquid comprised of ions. The restriction is that ILs should be liquid below 100 °C temperature. Tom Welton said, *“Room-temperature ionic liquid, non-aqueous ionic liquid, molten salt, liquid organic salt, and fused salt have all been used to describe salts in the liquid phase. With the increase in electronic databases, the use of keywords as search tools is becoming ever more important. While authors are free to choose any name that they wish for their systems, I would suggest that they at least include the term ionic liquid in keyword lists”* [86]. However, the system consisting of molecular constituents can also often be termed an IL system. For example, the deep eutectic solvents (DESs) are IL-like systems. The first DESs were discovered by Abbott et al., where choline chloride was mixed with urea (1 : 2 M ratio). Here the formation of ions occurs due to the strong H- bond between the donor molecules and the chloride ion. Therefore, the cation–anion interactions are suppressed, resulting in a low melting point and the system performing like the IL system.

Later, based on deep learning, it was found that different types of H-bonds were present in the system. The urea was responsible for creating a H-bonded complexed cation [urea(choline)]⁺ additional to [Cl(urea)₂]⁻ ion. In the first paper of Andy Abbott, he termed the system as the DES but not the IL system. Later, another group of materials was included in the IL family, i.e. lithium-glyme-solvated IL system [2]. Here, glyme was added to Li salt to make complex cations [Li(glyme)]⁺. Due to the large size of the complex cations, the interactions between the cations and anions are lowered, causing the low melting point of the system. Watanabe et al. first discovered the system and used it in the application of lithium-ion batteries. When 5 M lithium perchlorate-diethyl ether was utilized for organic reaction, it was designated as “fused salt” comprising both [Li(ether)]⁺ and [Li(ether)₂]⁺ ions.

1.5 The Generation of ILs

To achieve green technology, it is necessary to replace volatile organic solvents. Hence, instead of volatile organic solvents, researchers have focused on the

production of IL media for various applications, especially in biocatalytic processes. ILs can resolve the disadvantages of organic solvents, such as high volatility, high flammability, and low thermal and chemical stability. Therefore, ILs have recently been used as solvents in various applications, from biology to electrochemistry. But still, ILs are associated with certain drawbacks in terms of their toxicity and biodegradability [77]. Several recent reports stated that the ILs, including alkylmethylimidazolium cations, primarily used in biocatalysis, are ecotoxic, and the ecotoxicity escalates with the alkyl chain length of the cations. Hence, those ILs cannot be termed “green solvents.” Concerning environmental hazards and health and safety issues, it is essential to synthesize less toxic, biodegradable ILs. Presently, three different generations of ILs can be classified, as illustrated below and represented in Figure 1.3. ILs can be categorized into three distinct generations based on their toxicity [99].

1.5.1 First-Generation ILs

As stated before, the first known IL was ethylammonium nitrate, as reported by Walden. Afterwards, several ILs were synthesized with different combinations of cations and anions. In the 1980s, Wilkes et al. started the vast research on first-generation ILs [100]. These ILs are associated with cations such as alkylpyridinium, alkylimidazolium, and dialkylimidazolium. In the case of anions, chloroaluminate and metal halides are mainly used. But those anions are highly reactive with water and air. Those ILs are not appropriate for biotransformations. Due to their high hygroscopic nature, the first-generation ILs are always carefully handled under an inert atmosphere. Due to this drawback, the application of the first-generation ILs is very inadequate. Therefore, researchers have further focused on the synthesis of moisture-insensitive ILs.

1.5.2 Second-Generation ILs

The second-generation ILs appeared after a decade. In this category, the chloroaluminate anions are replaced by the anions that are less reactive with air and water, such as Cl^- , Br^- , I^- , PF_6^- , BF_4^- , and $\text{C}_6\text{H}_5\text{COO}^-$. In the case of the selection of cations, ammonium- and phosphonium-based cations are included along with alkylpyridinium, alkylimidazolium, and dialkylimidazolium. The second-generation ILs possess certain properties such as a low melting point, low viscosity, and high solubility. Hence, they hugely succeeded in attracting research interest in several applications in the early 1990s [77]. The maximum number of literature published is in biocatalysis applications. In the early 2000s, the first literature on biocatalysis with ILs media was published. However, second-generation ILs are also toxic, similar to first-generation ILs.

Further, the second-generation ILs are very costly. Gorke et al. stated that the high costs were associated with starting materials and final product purification [32]. Therefore, researchers have further focused on synthesizing less toxic, low-cost ILs.

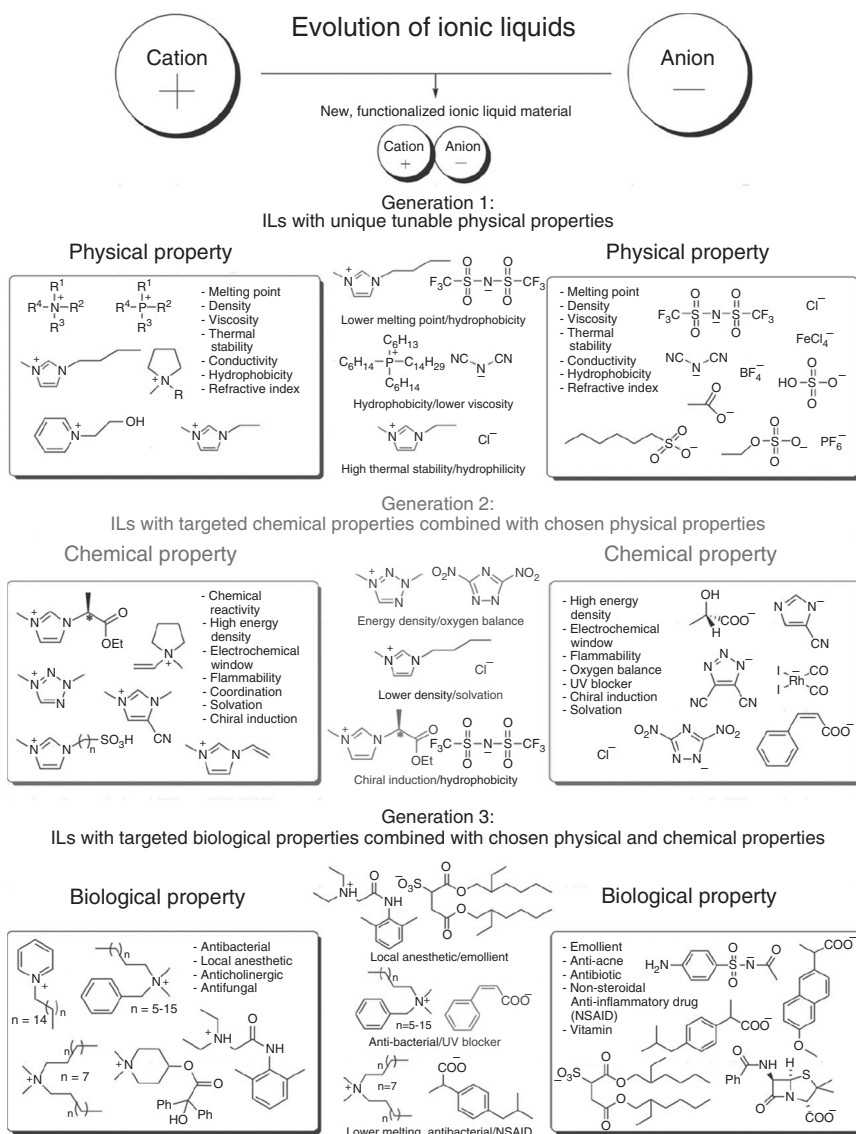


Figure 1.3 The evolution of the scientific focus on ILs from unique physical through unique chemical and now biological property sets. Source: Hough et al. [99]/Royal Society of Chemistry.

1.5.3 Third-Generation ILs

The third-generation ILs is mainly associated with cations such as choline. Generally, amino acids, alkylphosphates, alkylsulfates, bis(trifluoromethanesulfonyl) amide (TFSI) $[(CF_3SO_2)_2N^-]$, and sugars are used as hydrophobic anions [99]. The choice of cations and anions is based on their being less biodegradable, less toxic, and low cost. The third-generation ILs is also termed as advanced ILs. These ILs

are mainly characterized by their biological activity, such as being bacteriostatic, fungicidal, and herbicidal. Their biological activity is generally related to the anion, where the cations are premeditated to enhance their potentiality in various applications.

This generation also includes a new class of solvent systems, termed “deep eutectic solvents” [80]. DES are highly water-soluble and more hydrophilic than the second-generation ILs. DESs are not liquids at room temperature. They are basically mixtures of salts such as choline chloride, alcohols, amides, amines, urea, and carboxylic acids. As this generation is new to the research field, very few reports have been published. But due to their low toxicity and low cost, the third-generation ILs will reach the commercial level soon [39].

1.6 Structural Development of ILs

Based on the applications, altering the properties of ILs is a prerequisite. The properties of the ILs can be changed by tuning their structures with different combinations of cations and anions. On the basis of cation and anion combinations and their properties, ILs are classified into several categories.

1.6.1 Task-Specific ILs (TSILs)

Theoretically, millions of ILs can be synthesized by switching the combinations of different cations and anions. Davis et al. first established the perception of designing IL, which can interact with a solute in a specific fashion [19]. For the benzoin condensation reaction, Davis et al. showed that thiazolium-based IL could perform as both solvent and catalyst. Further, he introduced the term “task-specific ionic liquids” (TSILs) and described the concept of TSIL in a brief review [18]. He explained how the properties and reactivity of the ILs could be changed by incorporating functional groups into the IL moieties. The TSILs can be defined as ILs with functional groups incorporated covalently into the cations or anions of the ILs. TSILs are also coined as functionalized ILs. Over the last few decades, TSILs have received remarkable consideration owing to their precise properties that can be altered according to the user’s needs by tuning the combination of cations and anions [15]. In the last 15 years, several types of TSILs have been intended to perform specific tasks such as organic synthesis (Michael addition, Heck reaction, Knoevenagel condensation, etc.), nanoparticle synthesis, simulation of chirality, CO₂ adsorption, and electrochemical applications. [30, 67]. The first synthesized TSIL is 3-sulfopropyl triphenyl phosphonium *p*-toluene sulfonate, as shown in Figure 1.4.

Lee and his coworkers have reviewed the developments in functionalized imidazolium TSILs [46]. Further, Giernoth et al. have shown the potential of TSILs as a gas reservoir, new magnetic materials in chromatography, and other industrial applications. For example, the imidazolium-cation-based IL, including amine functionality, can form carbamate upon the addition of CO₂ [30]. In this chemisorption approach, the maximum uptake of CO₂ is 0.5 mol per mole of IL (Scheme 1.1).

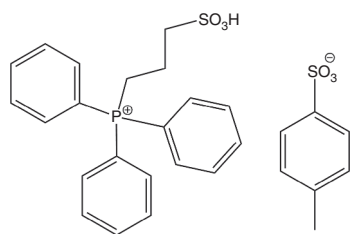
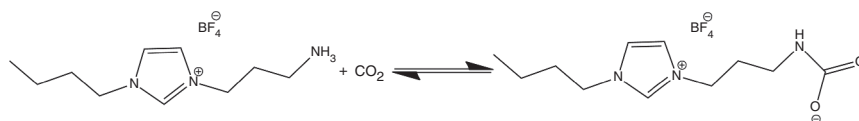


Figure 1.4 Structures of 3-sulfopropyl triphenyl phosphonium *p*-toluene sulfonate.



Scheme 1.1 Chemisorption of CO_2 by a task-specific IL.

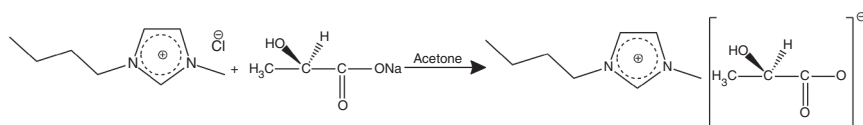
However, the synthesis of TSILs is a bit difficult and time-consuming process. The active functional groups present in TSILs are highly reactive toward the wide range of reactants.

1.6.2 Chiral ILs

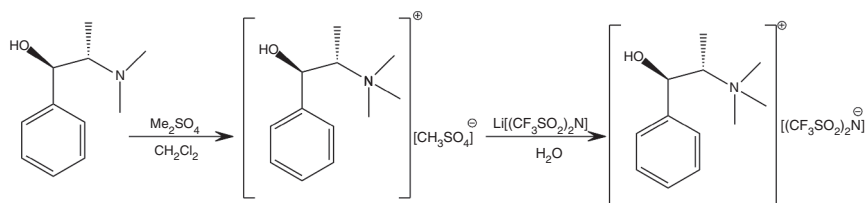
So far, the RTILs have been used as an alternative to conventional organic solvents for several organic reactions due to their low volatility. The enormous majority of studies associated with RTILs include achiral syntheses [22]. However, there is a rapid growth in literature indicating that chiral ILs have wide applications in the areas of synthesis of chiral compounds, liquid chiral chromatography, liquid crystals, stereoselective polymerization, and NMR chiral discrimination. [71]. In 1996, Herrmann et al. described the synthesis of *N*-heterocyclic carbenes of the corresponding imidazole moieties and validated their utilization in an asymmetric homogeneous catalysis reaction [7]. However, there was no consequent attention in the case of the solid precursor (the chiral imidazolium chloride salt).

In 1997, Howard and his coworkers synthesized homochiral dialkylimidazolium bromide salt as a Lewis acid catalyst for the Diels–Alder reaction. In 1997, Seddon and his coworkers studied 1-butyl-3-methylimidazolium ([BMIM]) lactate as the first chiral IL [25]. This chiral IL was synthesized from [BMIM][Cl] and sodium (*S*)-2-hydroxypropionate via anion exchange (Scheme 1.2) [7].

The chiral ILs are associated with a chiral center either at the cations or the anions or both within the ILs. These ILs are promoted as catalysts or solvents for the asymmetric synthesis of chiral compounds. The additional benefit of this synthetic



Scheme 1.2 Synthesis of [BMIM][lactate].



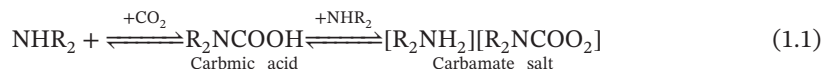
Scheme 1.3 Chiral ILs derived from the “chiral pool.”

approach is the high yield. The synthesis of chiral ILs is challenging because of their chiral nature. In 2002, Wasserscheid and group described the development of numerous new chiral ILs synthesized directly from the “chiralpool” [83]. For example, chiral hydroxyl ammonium salts were prepared by Scheme 1.3.

In 2002, Saigo et al. reported the synthesis method and structure of a novel imidazolium-based IL with planar chirality [43]. In 2003, Bao et al. defined the synthesis of chiral imidazolium ILs from chiral amines (*D*- α -phenylethylamine) and amino acids (*L*-alanine, *L*-valine, and *L*-leucine) with 30–33% yields [6]. In 2004, Vo Thanh et al. premeditated an effectual procedure for preparing chiral ephedrinium ILs using solvent-free conditions and microwave irradiation [78]. The chiral ILs are used in many organic reactions, such as asymmetric Michael addition, enantioselective hydrogenation reactions, enantioselective photodimerization, Heck reaction, and asymmetric dihydroxylation.

1.6.3 Switchable Polarity Solvent ILs

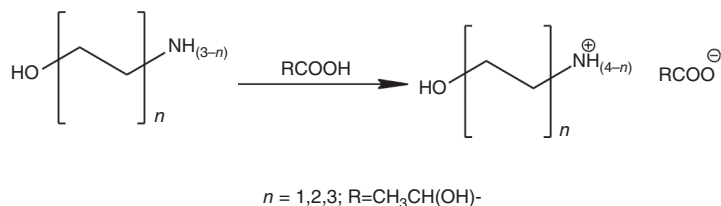
Switchable ILs are generally derived from alcohols and organic bases [62]. However, their precise solvent structure is still under investigation. They are used in various applications such as gas capture, separations, and nanomaterial synthesis. Predominantly, switchable ILs are green, nonaqueous absorbents for CO_2 capture [50]. The improvement of viscosity and regeneration efficiency of switchable ILs is still required. An activator is applied during the synthesis of switchable ILs, which promotes them to equilibrate between very low polarities and high polarities for both anions and cations. Secondary amines are typically used to get switchable ILs by applying CO_2 as an activating agent to form the carbamate salt reaction in Eq. (1.1) [57].



The switchable ILs with high polarity were obtained with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and alcohol which switched from lower to higher polarity while activated with CO_2 .

1.6.4 Bio-ILs

Imidazolium- and benzimidazolium-based ILs with long alkyl chain lengths are generally toxic, less biodegradable, and also related to other disadvantages.



Scheme 1.4 Synthesis of (2-hydroxyethyl)-ammonium lactate-based ILs.

Researchers have started to discover a new class of ILs derived from sustainable bioprecursors to overcome those limitations. Bio-ILs are comparatively less toxic, biodegradable, and biocompatible [31]. As choline is a precursor of the phospholipids that include biological cell membranes, choline is used as a cation to synthesize ILs. The choline-containing ILs are more promising and biocompatible than the other bio-ILs. Apart from choline, 2-hydroxyalkyl-ammonium cation is also used to synthesize bio-ILs (Scheme 1.4). Usually, amino acids and acetic acid are used as counteranions. Scheme 1.4 represents the synthesis.

The European Standards methods are used to scrutinize the toxicity and biodegradability of ILs. For example, according to the European Standards, (2-hydroxyethyl)-ammonium lactate was noted to have the highest biodegradable (95%) levels. Choline-based bio-ILs are used for drug delivery, solvents for biopolymers, sensors, and actuators [69].

1.6.5 Poly-ILs

When ILs are incorporated into the polymer chains, they introduce a new class of polymeric materials. Polymerized ILs, termed poly-ILs, are formed by repeating units of each monomer and associated through a polymeric backbone to develop a macromolecular structure [63]. Poly-ILs can be dimers, trimers, or oligomers. Based on the application of poly-ILs, several numbers of poly-ILs can be synthesized by tuning the monomeric unit of ILs with some unique properties [94]. Poly-ILs are usually synthesized by the direct radical polymerization of IL monomers. In the 1970s, Salamone et al. first synthesized poly-ILs with vinyl imidazolium-based ILs [66]. However, the synthesized poly-ILs were not able to attract significant attention at the time. In the late 1990s, Ohno et al. discovered several poly-ILs for the application of solid ion conductor materials [56]. Recently, numerous task-specific poly-ILs have been developed based on their applications. The foremost design efforts toward synthesizing novel poly-ILs are based on vinylimidazolium. Further, poly-ILs with phosphorous-containing cations (PILs) have attracted attention in catalysis and gene delivery applications. Döbbelin and his group discovered new poly(diallyldimethylammonium TFESI) poly-ILs with high ionic conductivities [23]. Apart from the linear poly-ILs, researchers have focused on nonlinear or branched poly-ILs due to their high thermal stability. Poly-ILs are also used as photoresists, corrosion inhibitors, dispersants, and stabilizers. These branched or hyperbranched poly-ILs are used in phase transfer systems. Tang et al. have reported several new

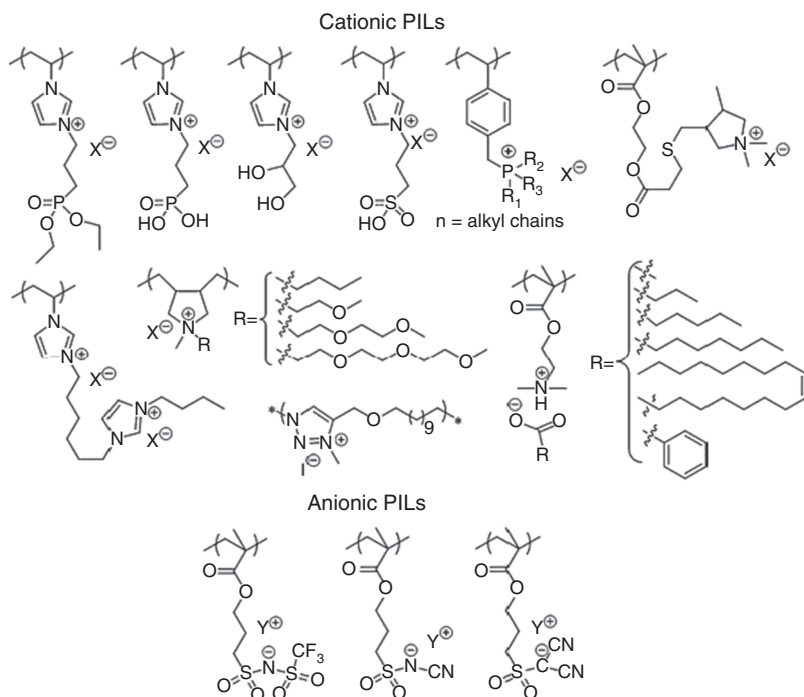


Figure 1.5 Recently reported poly-IL chemical structures. Source: Yuan et al. [95] / Elsevier.

imidazolium- and tetraalkylammonium-based poly-ILs with unique dielectric properties, mainly used as microwave-absorbing materials [76].

Poly-ILs exhibit unique properties such as wide electrochemical potential windows, low glass transition temperatures, and high thermal stability. Hence, poly-ILs have attracted significant attention due to their wide range of applications in various research fields such as electrochemistry, materials science, catalysis, separation studies, and analytical chemistry. In electrochemistry, poly-ILs are used as polyelectrolytes or polyelectrolyte membranes in fuel cells, supercapacitors, lithium-ion batteries, dye-sensitized solar cells, polyelectrolyte membranes, and organic transistor devices. [68]. However, the major drawback of poly-ILs is that the ionic conductivity of poly-ILs is lowered by at least two magnitudes compared to the corresponding IL monomer unit. Figure 1.5 shows the structure of recently reported poly-ILs.

1.6.6 Energetic ILs

In the arena of materials science, energetic ILs are one of the most useful materials. Commonly, energetic materials are compounds that can store large amounts of chemical energy and are able to release the energy under certain conditions such as shock, heat, and friction. Due to global concerns and safety issues, researchers have focused on synthesizing environmentally friendly, green energetic ILs. Hence, a new class of nitrogen-enriched ILs has received significant attention [96]. Energetic

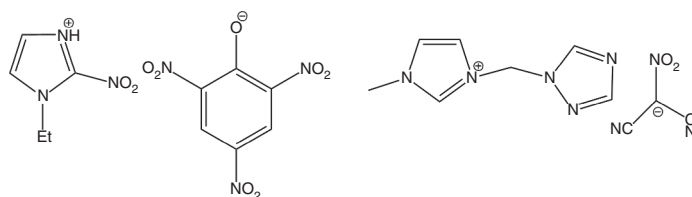
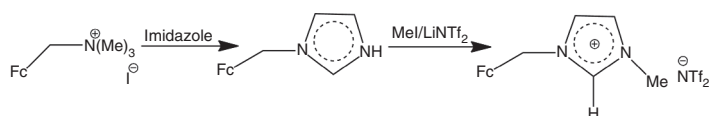


Figure 1.6 Structures of energetic ILs.

ILs, including nitrogen-rich heterocycles such as pyrazole-, triazole-, tetrazole-, and guanidinium-based materials, possess high density, high thermal stability, low vapor pressure, and high heat of formation [58]. In general, bulky anions containing energetic groups ($-\text{NO}_2$, $-\text{N}_3$, $-\text{CN}$, etc.) are used to synthesize energetic ILs. In the earlier 1890s, quaternary ammonium nitrate salts, i.e. hydroxyethylammonium nitrate and ethylammonium nitrate, had been synthesized and defined as energetic ILs. However, for almost 80 years, no further development for energetic ILs was reported. In 1996, Klapötke and his coworkers analyzed the physical and structural properties of hydrazinium azides [45]. In 2001, Drake and his co-workers reported “energetic hydrazinium salts” in a US patent. They have also discovered the potential applications of hydrazinium salts as propellant fuels [24]. Drake and his co-workers further defined some heterocyclic-based salts with NO_3 , ClO_4 , and $\text{N}(\text{NO}_2)$ anions in 2003. The first approach of using dicyanamide-based ILs in propellant formulations was recommended in 2008. Afterwards, a wide range of lanthanide-based energetic ILs such as 4-amino-1-ethyltriazolium, 1,5-diamino-4-methyl tetrazolium, 4-aminotriazolium, guanidinium, and 4-amino-1-butyltriazolium have been synthesized with lanthanide (La, Ce) nitrate ($[\text{Ln}(\text{NO}_3)_6]_3$) anion [96]. Lanthanide-containing energetic ILs can exhibit good photochemical stability and luminescence properties. The structures of energetic ILs are shown in Figure 1.6.

1.6.7 Metallic ILs

In 1948, Hurley et al. synthesized the first metal-containing IL, or metallic IL, from $[\text{EMIM}]\text{Cl}-\text{AlCl}_3$ system for the application of Al electroplating [41]. Further, in 1972, Parshall et al. used the tetraalkylammonium chlorostannate IL/ PtCl_2 system as a catalyst in catalytic olefins reactions [101]. In 1986, an acidic $[\text{EMIM}]\text{Cl}-\text{AlCl}_3$ system was used as a catalyst for the Friedel–Crafts reaction [10]. Later, in 1990s, Seddon, Welton, Dupont, and their groups gave significant attention to the ILs and their derivatives, comprising main group metals as well as transition metals. Hence, researchers have focused on synthesizing metal-containing ILs with ammonium, pyrrolidinium, imidazolium, choline, and pyridinium moieties and simple inorganic or halometallate anions for several applications [48]. Shreeve et al. have reported the preparation of ferrocene (Fc)-containing RTIL (Scheme 1.5) [29].



Scheme 1.5 Formation of metal-containing ILs containing ferrocenium.

1.6.8 PILs

PILs are a subclass of ILs, in which proton transfer takes place between acids and bases, resulting in the formation of the H-bond between proton donors and an acceptor site. The PILs are closely related to Brønsted acidic ILs. Hence, PILs are used as either solvents/catalysts or both for various organic reactions such as hydrolysis and dehydration. Further, PILs are significantly less viscous and highly conductive, due to which they can also be used as electrolytes in energy storage devices [74]. The ionic conductivities of the PILs increase with decreasing molecular mass. The synthesis of PILs occurs via two steps: the first step includes the formation of zwitterions, and the second step includes the neutralization or synthesis of ILs. PILs are also used in various drug delivery applications.

1.6.9 Acidic ILs

RTILs are also categorized into acidic, basic, and neutral ILs. The acidic ILs are composed of the protic ammonium, pyrrolidinium, and imidazolium cations. The acidic ILs are mainly of two types, i.e. Lewis acidic ILs and Brønsted acidic ILs. The Lewis acidic ILs are synthesized by using ZnCl_2 , AlCl_3 , pyrrolidinium, pyridinium, and imidazolium salts [4]. Lewis acidic ILs exhibited higher melting points than the analogous chloroaluminate salts; however, they still remain fluids at room temperature. The structures of Lewis acidic ILs are shown in Figure 1.7.

The first Brønsted IL (ethanolammonium nitrate) was discovered by Gabriel in 1888 [28]. This Brønsted IL is synthesized by the reaction of equimolar Brønsted acids and Brønsted bases (Scheme 1.6). These Brønsted acidic ILs are used as solvents or catalysts for various organic reactions such as Knoevenagel condensation, alcohol dehydrodimerization, and pinacol rearrangement. [35].

1.6.10 Basic ILs

Basic ILs can be formed using basic anions, mainly inorganic bases. For example, acetate, lactate, formate, cyanide, and dicyanamide anion are commonly used basic anions. Subsequently, these basic anions are able to deliver some advantages, such

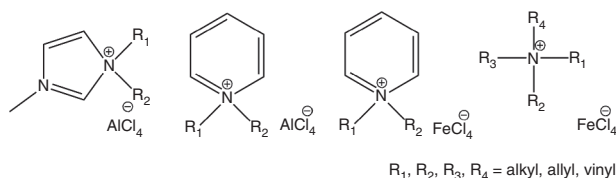
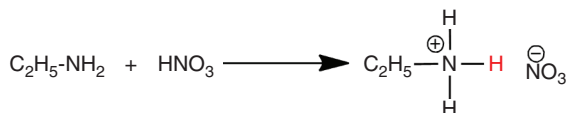


Figure 1.7 Structures of Lewis acidic ILs.



Scheme 1.6 Synthesis of Brønsted acidic ILs with acidic hydrogens on cations by proton transfer from Brønsted acids to Brønsted bases.

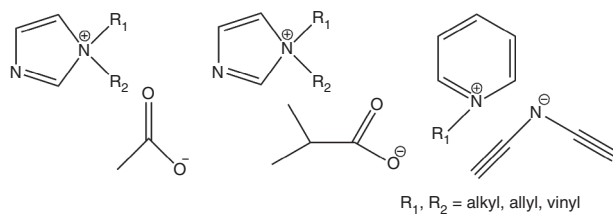


Figure 1.8 Structures of basic ILs.

as low viscosity, catalytic properties, and different solubilizing properties [34]. The structures of basic ILs are shown in Figure 1.8. The basic ILs can replace the usual inorganic bases as they are noncorrosive, nonvolatile, and highly soluble with many organic solvents. For instance, basic ILs are used in organic reactions such as aldol condensation, Markovnikov addition, and aza-Michael reactions [90].

Instead of using basic anions, an alternative way to design basic ILs is to incorporate a basic site into the cations. Those ILs are generally more thermally stable ILs than those with basic anions.

1.6.11 Neutral ILs

Neutral ILs exhibit weak electrostatic interactions between the cations and anions. Therefore, these ILs are less viscous, possess low melting points, and have high thermal stability. Hence, these neutral ILs are used as inert solvents in a wide range of thermal windows [36]. Generally, the anions such as hexafluorophosphate (PF_6^-), TFSI, tetrafluoroborate (BF_4^-), methanesulfonate (mesylate), thiocyanate (SCN^-), and *p*-toluenesulfonate (tosylate) are used to synthesize neutral ILs.

1.6.12 Supported ILs

Supported ILs signify a class of materials with typical characteristics and considerable potential concerning their promising applications in various research fields. Supported IL systems are mainly used in catalytic reactions such as hydrogenation, Friedel–Crafts reactions, Heck reactions, and hydroformylations (Rh-catalyzed). The first supported Lewis acidic IL catalysts were discovered in the 1990s.

1.6.13 Magnetic ILs

Nowadays, magnetic ILs have attracted extensive attention due to their several applications. The RTILs, which can exhibit paramagnetic properties by themselves without adding any magnetic particles, are defined as magnetic ILs [102]. The paramagnetic properties of magnetic ILs are induced by either cations, anions, or both. Figure 1.9 represents the common cations used to prepare the magnetic ILs. The cations generally used to synthesize magnetic ILs are 1-ethyl-3-methylimidazolium and 1-butyl-3-methylimidazolium. Apart from these imidazole cations with longer alkyl chain lengths, trihexyl(tetradecyl)phosphonium cations are also used to

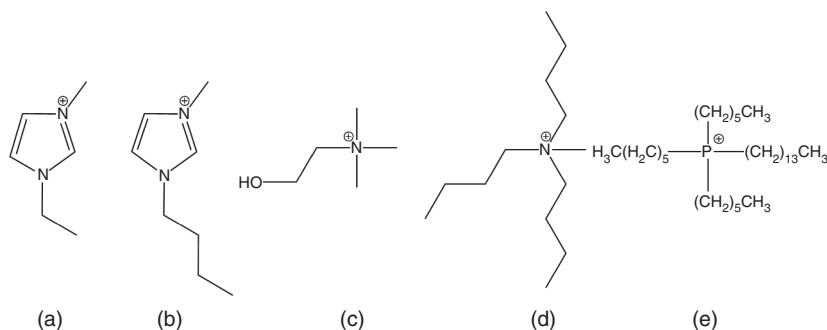


Figure 1.9 Common cations in magnetic ILs: (a) [Emim], (b) [Bmim], (c) [P_{6,6,6,14}], (d) [choline], and (e) [Aliquat 336].

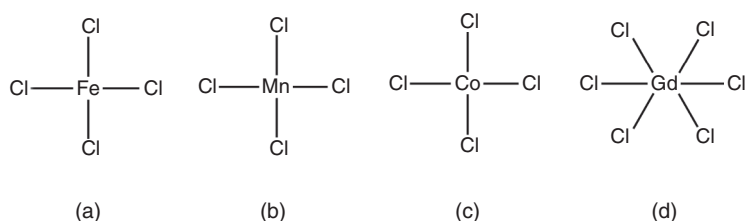


Figure 1.10 Common anions in magnetic ILs: (a) [FeCl₄], (b) [MnCl₄], (c) [CoCl₄], and (d) [GdCl₆].

prepare magnetic ILs [103]. Transition metals or lanthanide complexes are usually utilized as anions to synthesize magnetic ILs. Del Sesto and his coworkers have studied the magnetic ILs with Fe(III), Co(II), Mn(II), and Gd(III) comprising anions [20]. In 2004, 1-butyl-3-methylimidazolium tetrachloroferrate, [Bmim][FeCl₄], was known as the first magnetic IL, which was synthesized by Hayashi and Hamaguchi [72]. Further, Yoshida and coworkers described the magnetic properties of FeCl₄ and FeBr₄, anion-based magnetic ILs [93] (Figure 1.10).

The metal-containing magnetic ILs can exhibit the common properties of RTILs, including photophysical properties and potential responses to the external magnetic field. The emissions of magnetic ILs are toxic with respect to human health and environmental hazards. However, their negligible vapor pressure and low flammability decrease air emissions risk. According to literature reviews, the anions containing [FeCl₄] and [GdCl₆] are less toxic, whereas [CoCl₄] and [MnCl₄] are highly toxic. Magnetic ILs are used in different research areas such as fluid–fluid separations, polymer chemistry, electrochemical and medical devices, and magnetic fluids.

1.7 Scope of ILs

Since the last century, the extensive and continuous research on ILs has accelerated the improvement of green and sustainable chemistry. ILs are considered green solvents due to their specific and unique properties. Especially “air- and

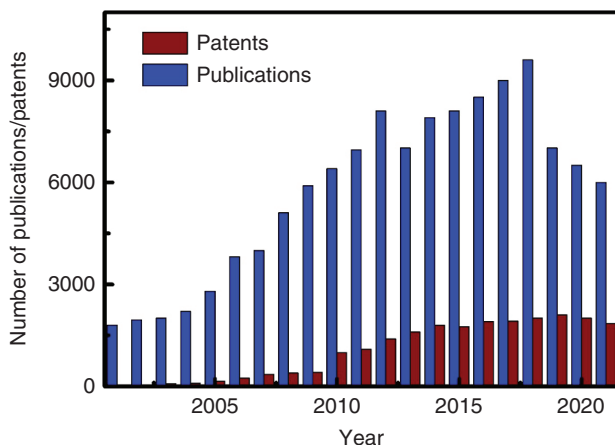


Figure 1.11 The number of publications and patents each year from 2001 to 2021. Source: SciFinder - Chemical Abstracts Service (CAS), a division of the American Chemical Society (ACS), Columbus, Ohio, USA; <https://scifinder.cas.org> (accessed 22 April 2022).

moisture-stable” ILs can replace conventional volatile organic solvents. Furthermore, ILs demonstrate numerous promising approaches in various research fields such as synthesis, biological science, materials science, physical chemistry, nuclear physics, sustainable energy science, heredity, and medicinal chemistry. The application of ILs is enhanced both at the academy and industry levels. According to Welton, the 1990s marked the birth of a new field of ILs [86]. Afterwards, the fundamental and applied research on ILs was exponentially enhanced by the birth of the new area of ILs. More than 90 000 publications have been reported by the scientific community since 1990 [33]. The total number of publications in each year from 2001 to 2021 is presented in Figure 1.11. The interest in industrial applications of ILs further expands the number of patents shown in Figure 1.11. Morton and Hamer from the intellectual property firm Mathys & Squire LLP have reported a remarkable article on the application of ILs. They acknowledged that imidazolium or pyridinium ILs are primarily used in recent patents with different applications. Hence, there is a vast scope to explore the synthesis and properties of new ILs to apply in various research fields.

1.8 Commercialization of ILs

The thought that ILs could replace conventional solvents generated a lot of curiosity in academic as well as industrial societies. This replacement is initiated by the EU REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) regulations intended to minimize the environmental hazards and ensure safety. They have listed the hazardous chemicals and started to substitute them with green substances. ILs have been used as alternative solvents, catalysts, or electrolytes in various applications, as shown in Figure 1.12. In the past few years, numerous

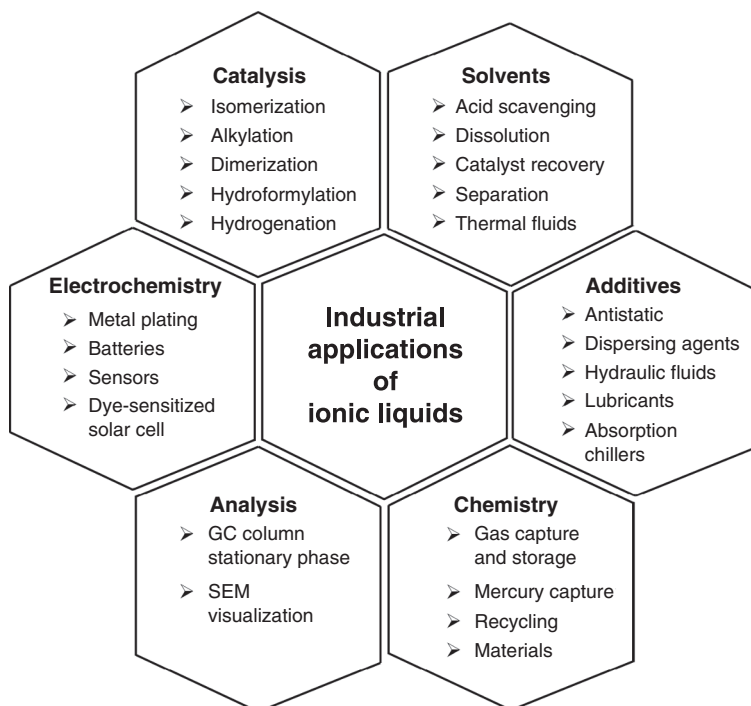


Figure 1.12 Design of some well-known applications of ILs.

IL products have been industrialized. In 2008, Plechkova and Seddon published the first review article on the commercial visions of ILs [60]. The latest published book, *Commercial Applications of Ionic Liquids*, including 57 applications of ILs, has provided a comprehensive perception of various industrial processes [70].

The first reported commercial IL technology was developed by the Texas Eastman Division of Eastman Chemical Company in 1996. A Lewis base IL (tetraalkylphosphonium iodide) was used for the isomerization of 3,4-epoxybut-1-ene to 2,5-dihydrofuran. They manufactured 1400 tonnes of product per year until 2004 and further continued the process in association with Cytec Industries, a major IL manufacturer [33]. Professor Daniel Armstrong, University of Texas at Arlington, has developed moisture dicationic and polycationic ILs for gas chromatography (GC) columns. A range of capillary GC columns is currently available with IL technology. The technique is also utilized to detect water using a thermal conductivity detector (TCD). The columns are now commercially available from Sigma Aldrich.

The IL technology is further utilized in several metal processing applications for electrochemical applications, such as Scionix's chromium electroplating process. DES system with choline chloride and chromium(III) chloride is used for this electroplating process. The use of ILs helped to enhance the current efficiencies (>90%) and minimize corrosion [33]. Further, NOHMs Technologies used ILs as an alternative electrolyte (NanoLyte) in lithium-ion batteries, resulting in 400% additional

cycle lifetime [33]. NantEnergy has used ILs in Zn-air batteries. ILs are also commercially used in dye-sensitized solar cells (DSSCs) [33].

For large-scale utilization of ILs, QUILL has collaborated with a Malaysian oil and gas company. They have developed a novel technique to remove mercury from natural gas [1]. For this process, a chlorocuprate(II) IL impregnated on a high surface area support or SILP (supported IL phase) has been used [87]. Furthermore, in 1999, QUILL collaborated with Chevron and started using ILs as alkylation catalysts and established a demonstration unit with ISOALKYTM technology (2010–2015) to optimize reaction conditions. In 2016, Chevron developed a new chloroaluminate IL alkylation catalyst. The China University of Petroleum-Beijing has also commercialized an IL-based alkylation process [37, 49].

The US Department of Defense has started using IL in the “natural fiber welding” process. The method includes ILs, such as $[\text{C}_2\text{mim}][\text{AcO}]$, for processing natural fibers (cellulose, hemicellulose, silk, etc.) to develop a gelatinous network that preserves the inherent polymer structure.

The ILs are also used in operating fluids in which ILs act as heat transfer materials or lubricants. Mettop GmbH, in collaboration with Proionic, established a new cooling technology (ILTEC) to permit direct water substitution with an equivalent viscosity IL (IL-B2001), which could offer a higher operating temperature.

Further, ILs are also used as additives in a broad range of applications. IoLiTec, a renowned manufacturing company, carried forward their research and further found out the IL performance as additives in different applications such as dispersing agents (commercial), cleaning additives (commercial), and alcohol synthesis (pilot). Furthermore, Institut Français du Pétrole (IFP) developed a homogeneous IL-based catalyst for the dimerization of light alkenes. Therefore, there has been a start-up in utilizing ILs at the commercial level since the last century due to their unique properties. However, ILs have not been commercialized solely because they possess limitations such as high cost, recyclability, and toxicity. ILs are still not “inherently green,” but they can expand the green metrics by constructing more sustainable processes, both economically and environmentally.

1.9 Conclusions

This chapter includes a brief history of ILs starting from the first discovery of the IL reported. Over the past 30 years, enormous research has been conducted in this field. To date, plenty of ILs have been synthesized, characterized, and analyzed, and their properties are acknowledged in an acceptable way. The development of ILs on their structure and applications are discussed in this chapter. Further, the growing challenge of the commercialization of ILs is also briefly illustrated. However, many limitations still persist that need to be overcome. ILs should not only be appreciated as a new class of materials, but they should also be elucidated as a perception to consider diversity in chemistry. There is a lot of hope that ILs will become a promising green material for different research fields by resolving certain limitations in their properties.

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