

Ionic Liquids

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Ionic liquids (ILs) are salts that exist in the liquid state below 100 °C or at room temperature. They are also referred to as molten salts, ionic fluids, liquid organic salts, neoteric solvents, and designer solvents. These salts are usually a combination of an organic cation {i.e., ammonium (1), sulfonium (2), phosphonium (3), pyridinium (4) or imidazolium (5)} and organic/inorganic anions (i.e., PF_6^- , BF_4^- , Cl^- or Br^-).

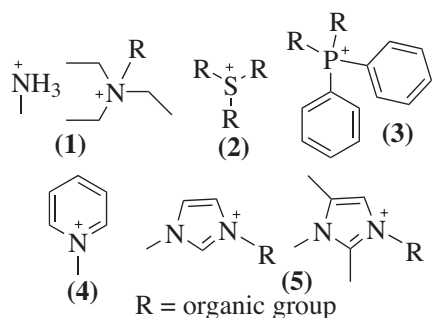


Figure 1. Common cations used in ILs

The cation is preferably asymmetrical, i.e., the alkyl groups should be different, for ILs to be in its liquid state at room temperature. By choosing the suitable cation/anion combination, one can adjust the polarity and hydrophilicity/hydrophobicity of ILs. This property of ionic liquids has made them known as "designer solvents".

Apart from these properties, ILs also exhibit other interesting properties such as negligible vapor pressure, non-flammability, high thermal and chemical stability, and high conductivity.

Synthesis of ILs

Simple salts and binary ionic liquids are the two main categories of ionic liquids. Simple salts consist of a single anion and cation, while binary ionic liquids involve an equilibrium between different ions. The first room temperature ionic liquid, $[\text{EtNH}_3][\text{NO}_3]$ (MP 12 °C), was discovered as early as in 1914. However, the

interest in these substances did not surge until the discovery of binary ionic liquids.

The synthesis of ionic liquids typically consists of two primary steps. (Figure 2)

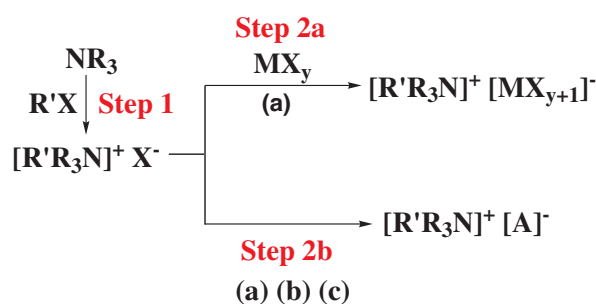


Figure 2. Synthesis routes to ILs. (a) Lewis acid (b) Bronsted acid (c) Ion exchange resin

The first step is the fabrication of the desired cation. This can be achieved by either protonating an amine using an acid or by a quaternation reaction between an amine and a halo alkane, followed by heating the mixture. The second step involves an anion exchange. This process can be carried out by treating halide salts with Lewis acids to produce Lewis acid-based ionic liquids. AlCl_3 based salts are the Lewis acid-based ionic liquids that have been extensively studied for various applications. Anion exchange reactions can also be utilized to synthesize Bronsted acidic and ion exchange resin based ILs.

In addition to traditional techniques, novel and improved approaches have emerged to synthesize ionic liquids. Microwave (MW) irradiation and power ultrasound (US) are such nonconventional methods, used either separately or in combination, which have drastically reduced reaction times and increased yields. Various other techniques such as sonication, ring opening processes, acid-base neutralizations, and the utilization of macrocyclic crown ethers have also been employed for synthesis of ILs.

Classes of ILs

Ionic liquids can be categorized into different classes based on their chemical structures and properties. Some of these classes include protic and aprotic ionic liquids, task-specific ionic liquids, chiral ionic liquids, polymeric ionic liquids, chelating ionic liquids, dicationic ionic liquids, bio-ionic liquids, and neutral ionic liquids.

Protic and Aprotic ILs

The transfer of a proton between equimolar Bronsted acid and base pairs allows for an easy and cost-effective production of protic ILs with a high degree of purity. These ILs are characterized as pure mixtures with exceptional ionic behavior and distinctive hydrogen bonding properties. Protic ILs have remarkable conductivity, stability, catalytic activity, and thermal efficiency. As a result they show exceptional bonding properties. Protic or Bronsted acidic ILs, *i.e.*, ethylimidazolium trifluoromethanesulfonate (6), can be simply produced *via* two steps; this includes the preparation of zwitterions and subsequent neutralization or IL synthesis.

On the other hand, aprotic ILs, *i.e.*, N,N-dimethylethanolammonium propionate (7), lack proton transfer but have a wide range of cations and anions. Their multistep synthesis produces stronger covalent bonds, which enhance the electrochemical and thermal properties.

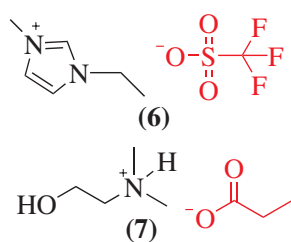


Figure 3. Protic and aprotic ILs

Task specific Ionic Liquids

Task specific ionic liquids (TS-ILs) also known as functionalized ILs, have drawn significant attention over the past few decades because of their customizable properties which are achieved by altering the combination of cations and anions. These ILs have shown potential in various organic synthesis reactions, catalytic reactions, as well as in chiral compound

synthesis and nanoparticle synthesis. The synthesis process for TS-ILs could be time-consuming due to the presence of various active functional groups that are highly reactive towards a wide range of reactants.

Chiral Ionic Liquids

Chiral ionic liquids (CILs) are compounds with a chiral cation or anion or both. *{i.e., pyridinium CIL (8) imidazolium CIL (9), (10), (12) and guanidinium CIL (11)}* (See Figure 4). These are used in various applications like asymmetric synthesis, spectroscopy, and chromatography. CILs with amino acids as building blocks have gained attention for their multiple interaction sites. They are derived from environmentally sustainable raw materials like sugars, amino acids, alkaloids. CILs have opened new possibilities in chiral chemistry and diverse fields.

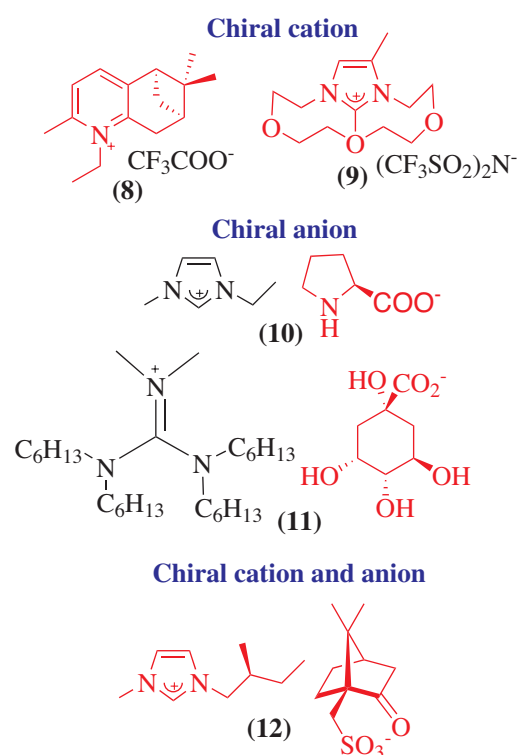


Figure 4. Chiral ILs

Polymeric Ionic Liquids

Polymeric ionic liquids (PILs) are formed by polymerizing ionic liquid monomers, resulting in a polymer backbone with repeating motifs of the respective monomeric units, *i.e.*, Imidazolium vinyl (13), imidazolium norbornene (14), and imidazolium diacrylate (15) monomers (Figure 5). PILs possess

properties of both ILs and typical polymers, making them attractive as well-defined polyelectrolytes. They show promising applications such as polymer self-assembly, dispersion, and reinforcement. By combining the advantages of ILs and polymers, polymeric ILs offer new designing opportunities using advanced materials with tailored properties having potential in various fields.

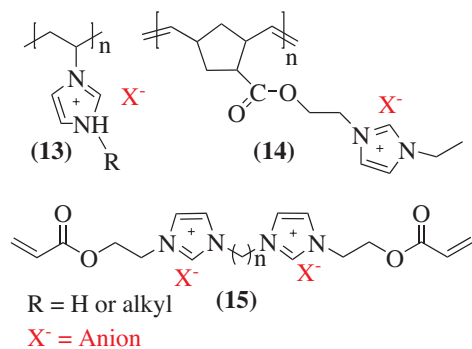


Figure 5. Polymeric ionic liquids

Chelating Ionic Liquids

Chelating ionic liquids (ChIL) are a specific type of ionic liquid where the constituent ions possess ligands that enable them to act as coordinating species, e.g., Cu^{II} -based ChIL (16) (Figure 6), while traditional ionic liquids are non-coordinating, ChILs can facilitate electron transfer between the anion and cation through coordination interactions. This unique property has led to the development of coordinating complexes based on mercury and ferrocenium cations. These complexes have been investigated for various applications and depict potential in the fields of catalysis, electrochemistry, and material science.

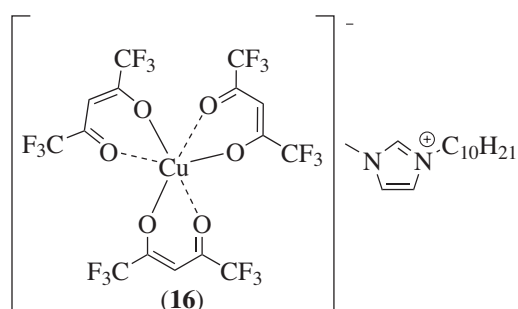
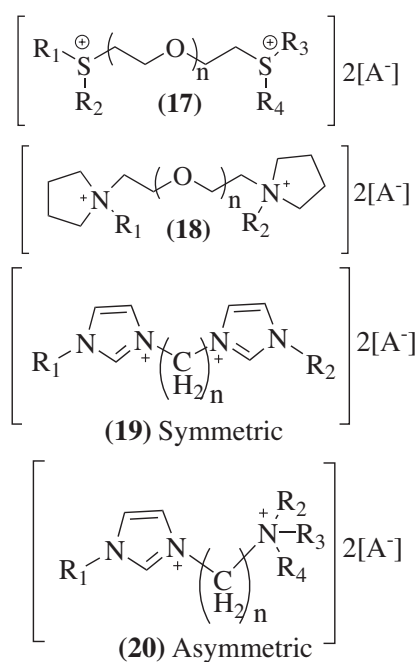


Figure 6. Cu^{II} -based ChIL

Dicationic Ionic Liquids

Dicationic ionic liquids (DILs) form a new category of ILs composed of a dication and an anion. They can be classified as homo-anionic or hetero-anionic

DILs. These are further categorized as symmetrical and asymmetrical DILs. Symmetrical DILs consist of two identical cations connected by a spacer, while asymmetrical DILs have two different cation head groups. The Figure 7 shows the structures of sulfonium (17), pyrrolidinium (18) and imidazolium (19) and (20) based DILs. DILs offer advantages over mono cationic ILs in terms of thermal stability, volatility, and tunable properties. They are used as lubricants and solvents and have the potential to be applied in gas chromatography and catalysis. DILs are a promising area of research for designing advanced materials with unique properties.



$\text{R} = \text{Alkyl group}, \text{A} = \text{Anion}$

Figure 7. Structures of DIL

Bio-ionic Liquids

Bio-ionic liquids (B-ILs) have been developed as an alternative to traditional alkyl imidazolium and alkyl benzimidazolium based ILs, which are known to be potentially toxic and poorly biodegradable. B-ILs are synthesized using recyclable and sustainable bio-precursors that are non-toxic (or minimally toxic), environmentally friendly, and biodegradable.

Choline (21), a precursor of phospholipids that is found in the cell membranes of animals and plants, is commonly used as a cation for the synthesis of bio-ILs. H-succinate (22), H-malate (23), ascorbate (24), coumarine-3-carboxylate (25) are some anions

employed to prepare BILs (Figure 8).

By utilizing bio-based materials, B-ILs address the concerns associated with traditional ILs and offer a more environmentally conscious alternative for various applications.

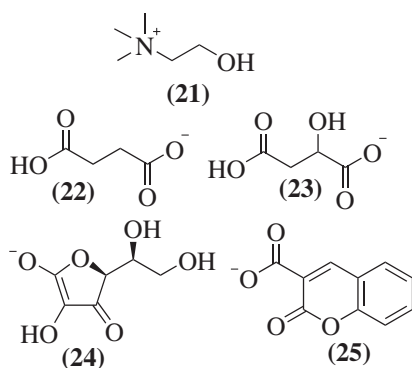


Figure 8. Structures of ions used in B-ILs

Neutral Ionic Liquids

Neutral ionic liquids (N-ILs) are a class of ILs where the counter anions form weak electrostatic interactions with the cations, resulting in low melting points and viscosity. Anions PF_6^- , BF_4^- , NO_3^- and cations ammonium (1), sulfonium (2) are examples of the neutral ions that are used to synthesize neutral ionic liquids. Despite their low interaction strength, N-ILs demonstrate excellent electrochemical and thermal stability. This combination of properties makes N-ILs ideal to be used as inert solvents in a wide range of applications.

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