Use of Ionic Liquids as Metal Ions Extractant: A Review

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Abstract: *Ionic liquids (ILs) have become potent agents of organic transformation in a matter of years. At room temperature, IL is a fluid that is made up only of ionic species. Because of their many intriguing characteristics and the fact that reactions conducted in ILs differ from those conducted in traditional molecular solvents in terms of both thermodynamics and kinetics, these are of fundamental interest to all chemists. Uses of ILs as alternatives in extractions of metal ions in both of academic and industrial research are other areas of keen interest to the researchers. These are environmentally friendly substitutes for common workplace and laboratory risks like volatile organic compounds (VOCs).*

Key Words: *Ionic liquids (ILs), ionic species, volatile organic compounds (VOCs), solvents, extractants and catalysts.*

1. INTRODUCTION :

Ionic liquids (ILs) have become potent agents of organic transformation in a matter of years. At room temperature, IL is a fluid that is made up only of ionic species. Because of their many intriguing characteristics and the fact that reactions conducted in ILs differ from those conducted in traditional molecular solvents in terms of both thermodynamics and kinetics, these are of fundamental interest to all chemists. These are environmentally friendly substitutes for common workplace and laboratory risks like volatile organic compounds (VOCs), which are employed in conventional solvent extraction. ILs are liquids at near or below 100°C. The ILs those remain liquids even at the room temperature are known as room temperature ionic liquids (RTILs). The first RTIL [EtNH$_3$] [NO$_3$] was reported[1] in 1914. It melts at 12°C. Hurley and Wier[2] in 1951 developed low melting salts with chloroaluminate ions for low-temperature electroplating of aluminium. During the 1970s and 1980s, these liquids were studied mainly in electrochemical applications. Interest of the scientists in the field of ILs did not develop until the discovery of binary ILs made from mixtures of aluminium (III) chloride and *N*-alkylpyridinium[3] or 1,3-dialkylimidazolium chloride.[4] In the mid 1980s, low melting point ILs were proposed as solvents for organic synthesis by Fry and Pienta[5] and Boon et al.[6] ILs are broadly classified in two main categories: (i) simple salts (made of a single anion and cation) and (ii) binary ILs (salts where equilibrium is involved). [EtNH$_3$][NO$_3$] is a simple salt, whereas mixtures of aluminium (III) chloride and 1, 3-dialkylimidazolium chlorides (a binary IL system) contain ionic species of different nature. In the example cited above, the properties of the binary ILs depend on the mole fractions of aluminium (III) chloride and 1,3-dialkylimidazolium chloride.[7]

The characteristics of ILs are determined by the particular structure of the cation and anion. By switching out the anion, one can alter the characteristics of ILs. When one organic cation is in the presence of various inorganic anions, it forms distinct ILs. Quaternary ammonium, dialkylimidazolium ions, and N-alkylpyridinium derivatives are the most frequently reported organic cations. There are a number of anions such as Cl$^-$, Br$^-$, OH$^-$, SH$^-$, NO$_3^-$, ClO$_4^-$, BF$_4^-$, AlCl$_4^-$, CF$_3$COO$^-$, CH$_3$COO$^-$, CF$_3$SO$_3^-$ and PF$_6^-$, which are used as their counter anions. [8,9] Most widely studied ILs cations include 1-alkyl-3-methylimidazolium (C$_n$mim) and N-alkylpyridinium (C$_n$py), where the alkyl group is derived from an alkane. The structure of C$_n$mim and C$_n$py cations is shown ahead:
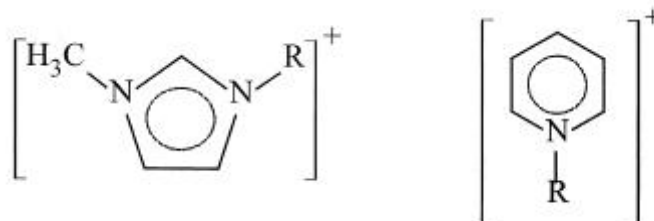
Generally, two strategies are developed in order to synthesize ILs. First the free acid can be simply protonated to create the desired cation or to use a haloalkane to carry out the quaternization of a phosphine or suitable amine, such as pyridine[10], imidazole, isoquinoline[11], piperadine, 1-methylpyrrolidine,[12] or trialkylamines,[13] the counter ion of the IL naturally comes from the reagent. Second strategy involves incorporation of the desired anion on a cation by different anion exchange methods. These two strategies are demonstrated below.[14]
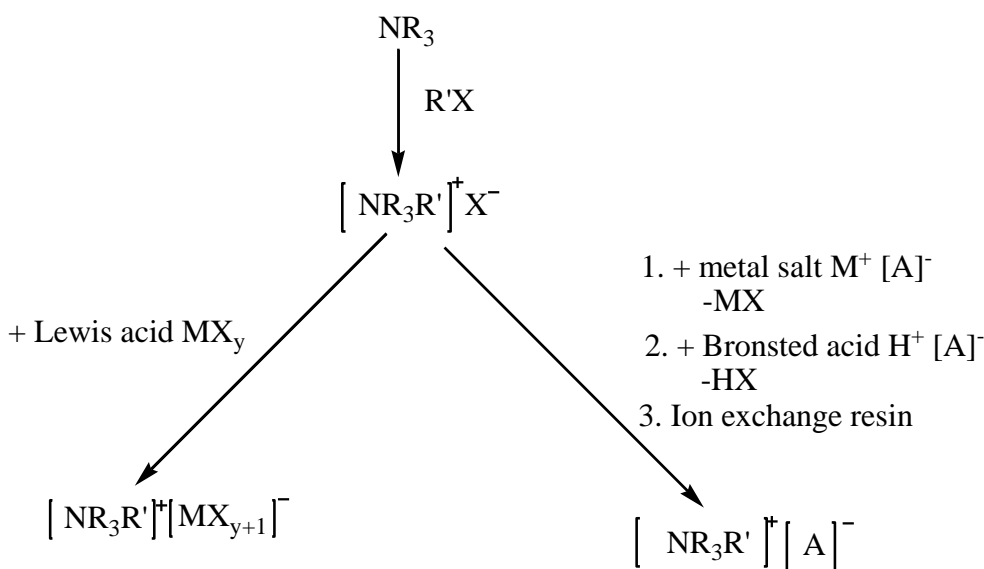
There are three primary benefits to the alkylation process. One is that a large variety of haloalkanes are reasonably priced. Two, at relatively low temperatures, the substitution reactions on the haloalkanes typically proceed without any problems. Three, the metathesis[15] reactions readily exchange the halides anions to produce a range of ILs.
 Scientists have been very interested in using ILs as solvents and catalysts due to their unique qualities as liquids.[16] In organic synthesis, these have been extensively reported as catalysts [17] and solvents [18]. ILs are highly polar, non-coordinating solvents due to the presence of poorly coordinating ions.[19] These are immiscible with a number of organic liquids and provide a non-aqueous, polar alternative for two phase systems. The hydrophobic ILs has also been used as immiscible polar phases with water. ILs have also been reported in liquid chromatography as stationary phase.[20] A wide range of inorganic and organic materials[9] can be solubilized in ILs, hence, an unusual combination of reagents can be brought into the same phase. These are also good solvents for enzyme, e.g., lipase and the activity of the dissolved lipase is retained after dissolution.[21]

ILs has extremely low volatility, hence have low vapour pressures[8] and can be used in high vacuum systems. These have good thermal stability[22], high conductivity[23], and a large electrochemical window.[24] As ILs are made of ions, therefore, are being considered as alternatives to the conventional electrolytes materials[25] and used in electrochemical applications.[26]

In general, ILs consists of a salt where one or both the ions are large, and have a low degree of symmetry. These factors tend to reduce the lattice energy of the crystalline form that results in lower melting point of the salt.[27] The temperature range of ILs can be up to 300^0C [8,11]. Thus, these allow wide reaction kinetic control, which coupled with their good solvent properties, allows small reactor volumes to be utilized. These properties make ILs safer to work with,

easier to recycle, and less likely to pollute the atmosphere than the traditional solvents. These scientific and operational properties make ILs as green catalysts and solvents.[28,29] For these reasons, ILs are taking the place of traditional catalysts and volatile organic compounds (VOCs) in extractants and solvents.

Since the anion and cation, which make up ILs, are modifiable, the solvents can be design to have specific characteristics.[4, 30] Thus; it is possible to define the specific end use of an IL. The phrase "designer solvents" has gained widespread usage[31], according to the term; their characteristics can be changed to meet the needs of a specific procedure. The change of the length of alkane chain or branching affects hydrophobicity[32], melting point[33] or viscosity[34] of ILs. The right choice of anion and alkyl chain length of the cation can regulate the water miscibility of the ILs. A series of fluorinated anions have been used to produce hydrophobic RTIL.[32] In1-alkyl-3-methylimidazoliumtetrafluoroborate ($[C_nmim][BF_4]$) based ILs, where the alkyl chain length is less than 6 carbon atoms, the ILs are miscible with water at 25°C. However, when carbon chain is longer (> 6 carbon atoms), these form a separate phase on mixing with water.[7] The melting points of $[C_nmim][BF_4]$[35] and 1-alkyl-3-methylimidazolium hexafluorophosphates ($[C_nmim][PF_6]$)[36] are also the function of the length of the 1-alkyl group.

Further, it is well known that the compounds having quaternary N-atom have the antimicrobial activity. The quaternized pyridine moieties do not only have potential to act as catalyst, but are also known as biocides.[37] Compounds containing quaternized nitrogen are reported as strong anti microbiological agents.[38] The quaternary ammonium and pyridinium compounds have significant toxic effects on a variety of bacteria and fungi.[39] Therefore, the ILs behave as antimicrobial agents.[40] Variation of the cationic and anionic components of the ILs alter their antimicrobial activity. Alkyl chain length of the substituent in pyridinium, imidazolium, and quaternary ammonium salts largely affects the antibacterial activity.[41] Substitution of the anion has minimal effects on the antibacterial activity of the pyridinium and imidazolium compounds. Hence the antibacterial activity of ILs is largely driven by the alkyl chain branching and hydrophobicity of the cation.[42]

2. Designing Ionic Liquids as Extractant

There is a common ground in many separation processes: in order to separate a particular product from the mixture, separation must occur and an efficient separation process has its adjustable conditions. Physical characteristics like viscosity can change as a result of interactions between immiscible phases, and this can have an impact on how well a reactor or separation device performs. The Carda-Broch study[43] demonstrated that water saturation has a major impact on the physicochemical characteristics of ILs, resulting in an order-of-magnitude decrease in viscosity when water molecules dissolve in the ionic-liquid phase. Even the structural isomers of ILs have quite different physical properties.[43]

Uses of ILs as alternatives in liquid/liquid extractions in both of academic and industrial research are other areas of keen interest to the researchers. ILs are becoming important tool for environmentally sustainable processing, along with certain aqueous processes, supercritical fluids[44] or perfluorinated solvents.[45] The separation processes in ILs depends upon its immiscibility with water and the dissolution of the ILs into an aqueous phase is measurable even for hydrophobic ILs. The use of ILs in processing is also based on their reactivity patterns, and the formation of separate phases that allow the easy separation of products.[46] Further, ILs are good candidate for separation and extraction processes and analytical techniques[46] due to their good reusability.[8] An IL can be designed to have a property like miscibility with a targeted mixture for use in the desired extractions processes. The relative solubility of the ionic and the extraction phases can also be adjusted to make the separation processes more facile. The need to develop new technologies to reduce the polluting nature of the traditional separations has resulted in seeking new solvent alternatives that intend to maintain the mechanics of liquid/liquid separations while imparting more environmentally-friendly characteristics to the components involved. The liquid/liquid two-phase systems continue to be favorable for the development of many separation processes. A challenge in chemical manufacturing is to develop effective processes that minimize detrimental environmental consequences, such as treatment of aqueous waste by separating hazardous materials through liquid-liquid extraction.[47]

The negligible solubility of hydrophobic ILs in aqueous systems affects interfacial properties, and hence, use of these compounds in liquid/liquid extraction is full of potential, are possible candidate as extractants[48] and also useful in separation techniques in organic synthesis.[49]   Therefore, RTILs have been used as direct replacements for the conventional organic solvents in multiphase bioprocess operations, e.g., the liquid-liquid extraction of the antibiotic and two-phase biotransformation processes.[50] Industrial scale up for the use of ILs as extractants, however, requires

consideration of the fluid properties of the ILs. It is important to know how low concentrations of other chemicals affect their physical properties.

3. Extraction of Metals Ions by Ionic Liquids

The hydrated nature of most of the metal ions lowers their affinity in the hydrophobic phase. It is, thus, necessary to change the hydration environment of the metal ions by either using organic ligands which provide a more hydrophobic region around the metal or with inorganic anions that forms softer and more extractable anionic complexes with the metal ions.[135-137] Ideally, in a biphasic system, the extractant would remain in the hydrophobic phase to ensure the complete removal of the metal ions from the aqueous phase. Thus, for any extractants to find use as alternative to the traditional separation processes, it should be able to quantitatively partition metal ions to the solvent phase.

Most metal ions are hydrated, which reduces their affinity in the hydrophobic phase. The hydration environment of the metal ions must therefore be altered, either by using inorganic anions that form softer and more extractable anionic complexes with the metal ions or by using organic ligands that provide a more hydrophobic region around the metal.[51] For the maximum extraction of the metal ions from the aqueous phase in a biphasic system, the extractant should ideally stay in the hydrophobic phase. Additionally, it ought to be able to successfully form a complex with the intended metal ions at the same time. For the purpose of appropriately designing ILs, it is easy to understand such conditions, under which particular metal ion species can be extracted selectively from the aqueous streams containing inorganic complexing ions.

It has been reported that aqueous metal ions are poorly soluble in ILs[52], with the exception of situations in which they are coordinated with or solvated by hydrophobic molecules that are added to the IL phase[53], or by hydrophilic complexing anions, which promote the transport of metal ions into the IL phase. In order to serve as both an extracting agent and a hydrophobic solvent, the designer of an alternative to conventional organic solvents should incorporate a metal ion ligating functional group into one of the ions of the IL in their separating agent.[54] Due to the metal cations propensity to stay hydrated in the aqueous phase, the partitioning of the metal ions into an IL extracting phase in liquid/liquid systems is minimal. Therefore, it's essential to look for an extractant that combines with the metal ions directly to make them more hydrophobic.[55]

By altering the hydration environment of the metal ions with either organic ligands or inorganic anions, the extraction of metal ions by the IL phase can be enhanced.[52] Compared to the complexes known to exist in molecular solvents, the complexes formed in ILs differ significantly. The dissociation, disproportionation, and degradation reactions of anionic metal complexes in aqueous solutions are restricted by the function of ILs as ionic solvents and increased their stability.[56]

Compared to traditional solvents, the partitioning of the metal ions from the aqueous solution into ILs containing extractants (such as calixarenes, crown ethers, or 1-(pyridylazo)-2-napthol) is significantly higher. When employed in the extraction of metal ions,[57] ILs with complexing ligands provide extremely high distribution coefficient values (D_M).[58] The D_M for the extraction of M^{n+} is defined as follows[59].

$$D_M = \left\{ \frac{(C_i - C_f)}{(C_f)} \right\} \frac{\{\text{volume of aqueous solution}\}}{\{\text{volume of IL}\}}$$

where C_i and C_f represent the initial and final concentrations of M^{n+} in the aqueous phase.

Organic solvent[59] containing dicyclohexano-18-crown-6 (DCH18C6) when used in the extraction of Sr^{2+}, afford D_M values those are less than 1. However, in ILs, D_M values are of the order of 10^4. Due to the large D_M values, ILs has unique solvation properties for ionic species. In IL-crown ethers based extraction processes due to the large D_M values; it is very difficult to strip the extracted metal ions. Such stripping of ions is required for the recyclability of the ILs or crown ethers. Due to these limitations with crown ethers and ILs based extraction processes for metal ions, some recent advances have been made in research activities leading to the use of some macrocycle ligands those have strippable binding sites.[59] These macrocycle extractants are synthesized by replacing one of the oxygen atoms of crown ethers by

an aza group.[60] In these macrocycle extractants, aza groups are the strippable sites. These sites are pH sensitive and the metal cations are removed via protonation of the aza group as is shown in the following figure.[59,61]
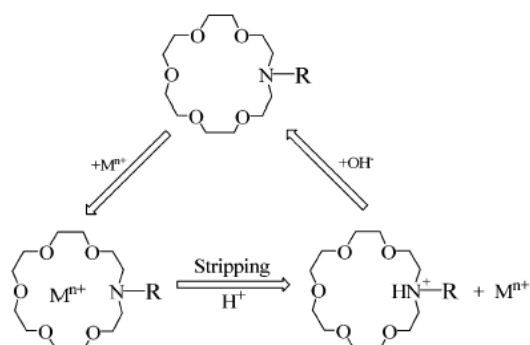
Due to the longer alkyl chain the solubility of the aza-substituted crown ethers in water decreases. The aza-substituted crown ethers in ILs are used in the extraction of Sr^{2+} and Cs^+ from the aqueous solutions.[59] The complexes[62] of Sr^{2+} and Cs^+ with crown ether ligands transfer easily into the IL phase than these can transfer into a molecular solvents. In some ILs the extraction of Sr^{2+} phase transfer reaction changes from ion-pairing/solvation in 1-octanol to cation exchange, hence there is a change in the coordination environment of the Sr^{2+}-crown ether complex.[63] For this change in phase transfer mechanism, the high ionic character of the ILs are not only the responsible factor, but the low charge density of Cs^+ and Sr^{2+} may be the important factors.[59] Wei et al.[64] have reported, that there is high distribution ratio for metal–dithizone complexes in IL phases. Therefore, dithizone was used as metal chelator to extract different metals such as Cu, Zn, Pb, Ag and Cd from the aqueous phase. Some heavy metal ions are extracted by using $C_n$mim derived ILs.[65] Although ILs have properties that suggest they would be attractive replacements for organic solvents in chemical industries, yet the understanding and prediction of physical properties of ILs is of key import.

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