Chapter 1

Introduction

Abstract
This Chapter covers the brief overview on the green chemistry and their needs along with its correlation with ionic liquids (ILs). As a task specific or designer solvent, various applications of ILs in different fields including synthesis, biology, for environment remedies, gel electrolytes is reviewed. At the end of the each section, aim and objectives of the proposed thesis work is described.
Chapter 1

1.1 Background

In today’s world, chemicals are used to make virtually every man-made product and play a vital role in the everyday life of people. Such products provide protection for crops and increase yields, prevent and cure disease, provide insulation to reduce energy use and also give precious other benefits that make life better for people. Due to exponential increase in the population across the globe, demands of such kind of materials are huge. Because of this, chemicals are creating a negative impact on human health and the environment, as their production and use are not managed responsibly. Although the impacts are complex and often unknown, some negative effects are very well documented, e.g. chemicals found in the environments that are persistent, bioaccumulative and/or toxic. Very recently, concern has been expressed about chemicals which interfere with the normal function of hormonal systems of humans and animals. Much effort has been spent over the years on testing, assessing and there of controlling chemicals and their impact on environment but there are still many issues and gaps which have to be overcome. As the chemicals industries are becoming more globe in nature, these challenges have to be address seriously to reduce their impact on man and the environments.

1.2 Green Chemistry

To minimize risk by minimizing hazard of chemical in environment, a concept of “Green Chemistry” was introduced in the last decade of 20th century. It’s a chemistry which deals with the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances, along with the minimization of waste production. The concept of green chemistry can be applied across the life cycle and chemical product, including its design, manufacture and uses. By a book, “Green Chemistry Theory and Practice” published in 1998, P. T. Anastas, and J. C. Warner advocated the theory behind the green chemistry, and for this reason, they are known as promoters of green chemistry model. In this book, they formulated the 12 basic principles of green chemistry and the theme underlying these principles is; use of less chemicals and energy, more secure raw materials, solvents and processes, to achieve energy deficient processes, to minimize waste production and reduced side products or secondary reactions. This ultimately promotes the use of safe, environment benign substances including solvents, the control of waste in real time and the increase of the amount of raw material present in the final product. It means that green chemistry controls risk of chemicals by intrinsic factors, such
as design or selection of chemicals with reduced toxicity and of reaction pathways that eliminate by-products or ensure that they are benign. As a consequence, academic interest in green chemistry involves worldwide research aimed at cleaner processing and it has increased significantly in the past few decades.

The question is “how one can judge that whether the alternative processes have a reduced environmental impact?” To judge, the efficiency and potential environmental impact of the chemical process, a series of green chemistry matrices of different categories were introduced. Details of these metrics along with their definitions are as follows:

- **Environmental Factor (E-factor):** It corresponds to the weight of waste per unit weight of product. It was formulated by Prof. Sheldon and has been widely used by chemists. The E-factor incorporates yield, stoichiometry and solvent utilization and can be used to access multistep reactions.

- **Atom Economy (AE):** It stands for the percentage ratio between the molecular weight of the final product and the molecular weight of the reactants. That means, it provides an idea of how much reactants remains in the final products. Moreover, it’s focused on the molecular weights, not on the mass or stoichiometry yield.

- **Carbon Efficiency (CE):** It can be calculated by the percentage of total carbon amount in the product compared to that in the reactants. Additionally, the reaction mass efficiency (RME) is also a metrics for green chemistry. RME compares the mass of the final product with the mass of the reactants in percentage. It’s almost similar to Atom Economy (AE) metrics.

- **Process Mass Intensity (PMI):** This is defined as the ratio between total mass of materials used and mass of product. It calculates, all materials used in the synthesis of 1 Kg of product including reagents, solvents, water etc. Some of the institutes and industries consider this metrics as the key mass-based green metrics to know greenness of process and used it to enhance the efficiency of process.

- **Ecoscale:** It is a tool for evaluation of the effectiveness of a synthesis reaction. It evaluates the quality of the organic synthetic process based on yield, cost, safety, conditions and ease of workup/purification. The calculation of Ecoscale
score provides a quick assessment of “greenness” of the reaction protocol. The scale of Ecoscore is from 0 to 100 with 100 representing the ideal reaction.

Among all the metrics, E-factor, atom economy, and PMI seem to be the most adequate to evaluate the “greenness” in any chemical industry because they include solvents, catalysts, reaction media and any other substance involved in the processes. Therefore, these metrics help scientists who try to fulfill one of the 12 principles of green chemistry based on “avoid waste production”. It is worth to mention that these green chemistry metrics are an oversimplification and do not allow to know some environmentally important properties, such as biodegradability, toxicity, and bioaccumulation of the chemicals used.

Section – I

1.3 Green Chemistry and Ionic Liquids

Green chemistry is concerned with the amounts of toxic organic solvents used in synthetic routes and overall chemical processes. One of the green chemistry’s principles; to reduce the use of solvent as much as possible or replacement with a less toxic/volatile. Solvents are extensively in use for synthesis separation/extraction of product, cleaning, drying, analysis and recyclic processes. Organic solvents in the chemical industry or research are one of the major problems concerning human health and safety and environmental pollution because of waste. There are many alternatives but they can be more expensive, difficult to implement, time consuming, under the well established chemical processes. In recent years, under the influence of green chemistry principles, some solvents have been replaced and methodologies changed to more benign techniques.

Ionic Lquids (ILs) are one of the new classes of solvents that offer opportunities to move away from traditional chemical processes to new, clean and green technologies. ILs are molten salt with meting point less than 100 °C. Therefore, they are variously known as liquid electrolytes, ionic melts, ionic fluids, fused salts, liquid salts, ionic glasses or charge entities. Although ILs does not completely fit to the principles of green chemistry, they are considered as good and promising candidates for future improvements that can give green credentials to their use and applications.
The discovery of ILs can be dated back to the work of Prof. Paul Walden, who was born in the Russian government of Livland on 14th July 1863 and worked on his thesis with Prof. Wilhelm Oswald in Leipzig in 1891. Among the many discoveries of Prof. Walden, the discovery of ILs was reported in the article; “About the molecular size and electrical conductivity of some molten salt”. Prof. Walden was looking for salts that are liquid at small amounts of surrounding heat in order to conduct his low-temperature studies. Since then, studies of molten salts have rarely been concerned with ILs in particular, until a renaissance of the interest in these kinds of liquids began to be registered in literature. In 1982, John Wilkes introduced, tetrachloroaluminate ILs based on N-alkyl-3-methyl imidazolium as cation and known as first generation ILs. These substances were water and air-sensitivity and therefore a second generation ILs were introduced by a group of Prof. Seddon, Hussey and Chauvin. They suggested air and water stable ILs through the replacement of moisture sensitive AlCl$_4^-$ anion by BF$_4^-$ and other anions. In 1998, Prof. Jim Davis and co-workers introduced the third generation of IL which some times is known as “designer solvents” or “task-specific ionic liquids” (TSIL). These ILs were new solvents which cannot be understood clearly, compare to kind of molten salt, Prof. Kenneth Seddon described them in facile way. Then after enormous number of reports are available in literature on synthesis, characterization and use of ILs in various applications.

1.4 Ionic Liquids: Preparation and Properties

Some of the ILs are liquid at room temperature and therefore they are known as room temperature ionic liquids (RTILs). Commonly used ILs have a large and unsymmetric cations (derivatives of imidazolium, pyridinium, pyrrolidinium, piperidinium, ammonium, phoshonoum and sulfonium) substituted with alkyl chains of different length (from C$_1$ to C$_{22}$) and inorganic anions such as halogen (Cl$^-$, Br$^-$, I$^-$), aluminochloride, (AlCl$_4^-$), tetrachloroaluminate, hexafluorophosphate (PF$_6^-$), tetrafluoroborate (BF$_4^-$) and bis (trifluoromethylsulfonyl)imide (NTf$_2^-$) and typical organic anions are alkyl sulfate, alkyl sulfonate, p-toluene sulfonate (tosylate) and trifluoroacetate (Table 1.1). The number of ions available to make an IL is obviously much wider than what is presented in Table 1.1. However, only the most relevant to the present work are shown here. Like other materials the physicochemical properties of ILs depend on the
intermolecular and intramolecular forces and consequently upon the structure of the
cation and the anion.

**Table 1.1** Possible combinations of cations and anions to form an ILs

<table>
<thead>
<tr>
<th>Cations</th>
<th>Anions</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Cation Structure" /></td>
<td><img src="image2" alt="Anion Structure" /></td>
</tr>
<tr>
<td>[\text{Cl}^-], [\text{Br}^-], [\text{I}^-], [\text{BF}_4^-], [\text{PF}_6^-], [\text{NO}_3^-].</td>
<td></td>
</tr>
<tr>
<td>[\text{CF}_3\text{SO}_3^-], [\text{AlCl}_4^-], [\text{AlBr}_4^-],</td>
<td></td>
</tr>
<tr>
<td>[\text{[(CF}_3\text{SO}_2)_2\text{N}^-], [\text{Tf}_2\text{N}^-], [\text{hfac}^-],</td>
<td></td>
</tr>
<tr>
<td>[\text{HSO}_4^-]</td>
<td></td>
</tr>
</tbody>
</table>

Enormous amount of studies have been conducted for ILs on the relationship between
their physicochemical properties and the structure of their cation and anion.\(^{20-22}\)
Moreover, ILs have a negligible vapour pressure, so they are not volatile and no
atmospheric pollution can be expected due to their use. ILs are also thermally stable so
they can be used in chemical processing and other characteristics of ILs are mentioned in
**Table 1.2.**\(^{23-25}\) All these characteristics make them useful for many applications, resulted
into the meeting up to the criteria of green chemistry.

As number of available cations and anions are large, there are literally millions of
different structures that may be formed by combining different cations and anions and the
number of possible combinations are estimated to be as high as \(1 \times 10^{18}\).\(^{26,27}\) Due to
enormous possibility for combinations of cations and anions, ILs can be synthesized as
per desire physicochemical properties and there of, their use in requird applications.
Therefore, RTILs are often known as ‘deginer solvent’ or “task specific ionic liquids
(TSILs)”. RTILs have been used for several applications and their development continues
at a considerable rate owing to their peculiar physical and chemical properties.\(^{28}\) Polarity,
hydrophilicity/hydrophobicity and other properties of ILs can be adjusted by an
appropriate combination of cations and anions.\(^{29}\)
Table 1.2 Some physico-chemical characteristics of ILs

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decomposition point</td>
<td>150-500 °C</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>Implied ≤ 30</td>
</tr>
<tr>
<td>Electrical conductivity @ 25 °C</td>
<td>&lt; 0.6 S.m(^{-1}) (max. value 11.9)</td>
</tr>
<tr>
<td>Flammability</td>
<td>Non-flammables</td>
</tr>
<tr>
<td>Melting point</td>
<td>&lt; 100 °C (max. Value 239 °C)</td>
</tr>
<tr>
<td>Temperature range liquid phase</td>
<td>From -96 to 300 °C</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.117-0.199 N/m/K</td>
</tr>
<tr>
<td>Vapour pressure</td>
<td>Negligible</td>
</tr>
<tr>
<td>Viscosity</td>
<td>usually 0.013-0.22 Pa.s (max. value 1.02)</td>
</tr>
</tbody>
</table>

The solubility of ILs is also tunable. Generally, ILs are miscible into polar solvents but not in non-polar ones. The anions usually play a vital effect on solubility than cation, but some fine tuning can be done with the alkyl chains of the cation. Solubility of ILs in water is an important property, and it also varies according to the nature of anion. Normal halides, tetrafluoroborate and triflate containing ILs are commonly miscible with water, while, hexafluorophosphate and bis(trifluormethyl sulfonyl)imide containing ILs are water immiscible. Due to the tuneable physicochemical properties and solubility in various solvents, ILs can be used in a wide range of applications, as shown in Scheme 1.1.

1.5 Ionic Liquids: Applications and Perspectives

1.5.1 Ionic Liquids in organic synthesis

Since, the invention of ILs, they were extensively used as either solvent or catalyst in various organic synthesis processes.\(^{15,30}\) They have shown great potential to replace hazardous organic solvents as reaction media while maintaining similar and sometimes enhanced chemical selectivity and reactivity. ILs have been used as solvents for nucleophilic\(^{31}\) and electrophilic\(^{32}\) reactions, including acid catalyzed reactions, and reactions catalyzed by transition metal complexes.\(^{33}\)
Scheme 1.1 Selection of applications where ILs have been used

- Electroelastic materials
- Ionic Liquids
- Lubricants & additives
- Heat storage
- Liquid crystals
- Electrolytes
- Gas separations, Extractive distillation, Extraction, Membranes, Supercritical CO$_2$/liquid extraction
- Fuel cells, Solar cells, Sensors, Batteries, Supercaps, Metal finishing,
- Analytics
- Solvents
- Artificial muscles, Robotics
- Electroelastic materials
- Lubricants fuel Additives, Templates, and Coating
- Displays
- Thermal fluids
- Separation
- SAMDI-TOF-metrics, GC-head-space solvents, Protein-crystallisation, Stationary phase for HPLC
Especially the use of ILs as solvents for transition metal complexes is at the centre of interest, because transition metal catalysts gets readily dissolved in ILs, while organic reactants and products have very low stability in ILs. This leads to the possibility of a biphasic reaction procedure.  

Many industrially important transition metal catalyzed reactions, e.g. hydrogenation, hydroformylations, oxidation, Heck coupling, Suzuki coupling, dimerization, oligomerization reactions and other well known reactions, e.g. Diels-alder, Friedel-craft reactions, Wittig reactions were carried out in ILs. Moreover, it was demonstrated that the use of ILs often leads to higher reactivities and/or selectivity. In addition to the above mentioned reactions, a new class of ILs, Bronsted Acidic Ionic Liquids (BAILs) have been widely used in various acid catalyzed reactions including esterification, Pechmann condensation, Beginelli reactions etc. In some of these reactions, BAILs played dual role; as a catalyst as well as solvent media.

Apart from these conventional organic catalyzed reactions, in recent years, a lot of attention has been focused on enzymatic reactions in ILs. Erbeldinger et al. reported the first enzymatic synthesis of Z-aspartame in [Bmim][PF\textsubscript{6}] containing 5% (v/v) water. The enzyme thermolysis exhibited excellent stability and a competitive rate in the same ILs as compared to the enzymatic reaction in organic solvents. An improved enantioselectivities were reported for transesterification of 1-phenylethanol by nine lipase enzymes in various ILs including [Bmim][(CF\textsubscript{3}SO\textsubscript{3})\textsubscript{2}M]. More systematic studies on lipase catalyzed enantio- and regioselective acylations were conducted by Park and Kazlauskas in several imidazolium- and N-alkyl pyridinium based ILs. In addition to these reports, there are many reports in which enzyme catalyst was used in ILs for better stereoselectivity of the product.

1.5.2 Ionic Liquids in cellulose processing

Cellulose or lingo-cellulose is mainly composed of cellulose, lignin, hemicellulose and extractives which are promising abundant carbon-neutral renewable resource. Increasing concerns about environmental issues and shortage of petroleum based fuel have attended much effort to use cellulose as an alternative to the petroleum products. But the efficient utilization of (ligno) cellulose has been hampered due to difficulties in the dissolution of cellulose in its natural form. This is because of three-dimentional cross-linked network
and presence of strong hydrogen bonds among the polymeric matrix. The use of IL based route has paved an environment friendly and homogeneous manner to use cellulose. In 2002, Rogers et. al.\textsuperscript{52} reported that imidazolium based ILs could dissolve ~ 25% wt cellulose with addition of non-solvents like water and ethanol. Since, this report a variety of ILs has been synthesized to provide an efficient and greener solvent system for dissolution of cellulose.\textsuperscript{53} In a recent review by Zakrzewska et. al.\textsuperscript{52d}, authors tried to correlate structure of ILs and solubility of various types of cellulose. In addition to this, two reviews by Zhu et. al. and Pinkert et. al. have presented the progresses of bio-materials derived from biopolymers with the ILs platform.\textsuperscript{54} Despite of numerous ILs capable of dissolving biomass, the mechanism of this dissolution process remains un-understood. There have been few theoretical and experimental studies based on molecular dynamic and NMR analysis. Rensing et al. investigated the interaction of chloride ion of ILs with cellulose using $^{13}\text{C}$ and $^{35/37}\text{Cl}$ NMR relaxation measurements.\textsuperscript{55} They found that anions of ILs were involved in specific interactions with the solutes and as a result the solvation process has been controlled. A molecular simulation with 1-ethyl-3-methyl imidazolium acetate, [Emim][OAc] and cellulose showed that the interaction energy between the polysaccharide chain and the ILs was 3 times stronger than that of either water or methanol.\textsuperscript{56} A thorough investigation was carried out on the use of presented pyridinium ILs for direct biomass dissolution and their characterization.\textsuperscript{57} Since, different lingocellulosic materials have different physicochemical characteristics, there are reports on the pretretment technologies based on the lignocellulosic biomass properties of each raw material.\textsuperscript{58} The purpose of pretretment of biomass was to make the cellulose structure more accessible to absorbates particularly enzymes and/or chemicals.\textsuperscript{59}

1.5.3 Ionic Liquids in Electrochemical Sensors and Biosensors

Ionic conductivity ($> 10^{-4}$ S/cm), wide electrochemical potential window ($> 1$ V), viscosity (ionic mobility $> 10^{-14}$ m$^2$/V.s), hydrophobicity, non volatility are among the most important characteristics of ILs and hence, are used as solvents in electrochemical devices like batteries, capacitor, fuel cells, photovoltaic, acuators, and electrochemical sensor.\textsuperscript{60} Recently, ILs have been used in construction of electrochemical sensors and biosensors. Due to polymer plastisizing ability and ionic nature, ILs can be a promising material for the preparation of ion selective electrodes. In 2005, Coll et al. reported use of hydrophobic ILs ([BMIM][PF$_6$]) to prepare the poly(vinyl chloride) PVC membrane and
a high selective response towards sulfate anion was observed.\textsuperscript{61} Similarly, two ILs namely 1-butyl-2,3-dimethyl imidazolium bis(trifluoro-methylsulfonyl)imide ([BDMIM][Tf$_2$N]) and dodecyl ethyl diphenyl phosphonium bis(trifluoro-methylsulfonyl)imide ([DEDPP][Tf$_2$N]) were used to plastisize the PVC and poly(methyl methacrylate) membrane respectively.\textsuperscript{62}

Since then, there are number of reports on use of various ILs for the preparation of polymeric membrane for ion selective electrodes.\textsuperscript{63} In most of these studies, hydrophobic ILs were used and they were exhibiting good and stable response to relatively hydrophobic cations and anions. Recently, in addition to ion selective membrane, ILs have been widely used in construction of carbon paste electrodes (CPEs) and are known as carbon ionic liquid electrodes.\textsuperscript{64} Compare to convention binding agent, parafine oil, ILs are good choice in preparation of CPE because of their chemical stability, low vapour pressure, low toxicity, low melting point, high ionic conductivity, good thermal and electrochemical stability. Applications of ILs in construction of all-solid-state sensor have been recently reported by Maminska et. al. and Kakuuchi et. al.\textsuperscript{65} They used 1-dodecyl-3-methyl imidazolium chloride in PVC membrane, and developed a new kind of Ag/AgCl reference electrode consisting of a Ag/AgCl electrode coated with a saturated AgCl solution in hydrophobic ILs. Because of wide electrochemical potential window, they find wide used in electrochemical biosensors as a binder and conductor. Some groups have reported increased stability of enzymes in ILs compared to organic solvents\textsuperscript{66} at ordinary temperature as well as at high temperature.\textsuperscript{67} In summing up, Table 1.3 summarizes some important hydrophobic ILs which have been widely used in construction of various electrochemical sensors and biosensors.

**1.5.4 Ionic Liquids for Environmental remediation**

In current scenario, due to industrialization, environmental pollution has (effluent from industry) become a matter of concern. The effluent contaminates soil, water and atmosphere, therefore it affects health of human as well as the aquatic life. Contamination of water due to industrial effluent is a serious matter as it contaminates sources of water including ground water, river, ponds, etc. The industrial effluent basically composed of metal as well as other organic matter including dyes, hazardous chemicals, etc. In view of this, in order to protect water pollution and to obtained pure water for day to day life, removal of these ingredients from industrial effluents received a great attention.
Table 1.3 Some common hydrophobic ILs can be used in electrochemical and biosensors.\textsuperscript{68}

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>Application</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF\textsubscript{6}])</td>
<td><img src="image1" alt="Structure" /></td>
<td>ISE\textsuperscript{(a)}</td>
<td>61</td>
</tr>
<tr>
<td>1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF\textsubscript{4}])</td>
<td><img src="image2" alt="Structure" /></td>
<td>1-CPE\textsuperscript{(b)}</td>
<td>64(b,c)</td>
</tr>
<tr>
<td>1-octyl-3-methylimidazolium hexafluorophosphate [OMIM][PF\textsubscript{6}]</td>
<td><img src="image3" alt="Structure" /></td>
<td>Voltammetric carbon paste sensor</td>
<td>144(a)</td>
</tr>
<tr>
<td>1-Methyl-3-octylimidazolium chloride [MOImCl]</td>
<td><img src="image4" alt="Structure" /></td>
<td>ISE</td>
<td>63(a)</td>
</tr>
</tbody>
</table>

(a) Ion Selective Electrode, (b) Carbon Paste Electrode

1.5.4.1 Ionic Liquids for metal ion removal

The chemical and mining industries are the main sources of metal ion pollution in aqueous streams including ground water. There are numerous conventional methods to recover and purify these metals including volatile organic solvents, non-reusable absorbents, harmful chemicals including sulphuric acid etc.\textsuperscript{68} Out of all these methods, liquid-liquid extraction is one of the most important techniques for metal ion separation as it possessess several advantage over competing techniques.\textsuperscript{69} Operation in a continuous mode, employment of relatively simple equipment and employment of only small quantities of the reagents are the only advantages. But the biggest disadvantage of classical liquid-liquid extraction is the extensive use of volatile, toxic and flammable water immiscible organic solvents. Looking to these problems, due to low vapour pressure, green solvent, non-flammable nature of ILs, they are promising candidate for the replacement of organic solvents in liquid-liquid extraction as water insoluble extractants.\textsuperscript{70} Recently, ILs are deployed as extracting agents for the recovery of valuable metal from waste water. This has been carried out by two approaches; (i) based on the
special extractants such as crown ethers, cyanex to extract the metals from the aqueous phase to immiscible IL phase.\textsuperscript{71,72} However, this system suffers from ion exchange: the extraction of the metal ion is accompanied by dissolution of the cation from the IL into the aqueous phase.\textsuperscript{73} (ii) a second and preferred option is to use (TSILs) as extractants which does not undergo for ion exchange.\textsuperscript{74} As these ILs have an ion that has a functionality, the metal extraction occurs through interaction with metal ions. There are several reports on the use of TSILs with carboxylic acid, phosphinic acid, thiourea, urea, thioether and thiol functionalities in their ions that are used for metal ion removal.

The use of hydrophilic ILs, which are miscible with water are not appropriate for metal ion extraction from water because of the recovery problem. The loss of IL can be alleviated by introducing either long alkyl chains on the cation or by using fluorinated anions such as bis(trifluoromethyl sulfonyl) imide (Tf$_2$N$^-$) or hexafluorophosphate (PF$_6^-$) which are more hydrophobic in nature.\textsuperscript{75} A 1-hexyl-3-methyl imidazolium hexafluorophosphate [HMIM][PF$_6$] was used to extract Fe$^{3+}$, Co$^{2+}$, Cd$^{2+}$ using two extractants; 1-(2-pyridylazo)-2-napthol and 1-(2-thiazoyl)-2-napthol.\textsuperscript{71c} An efficient protocol for extraction of strontium was also developed using crown ether (18C6 and their analogs) as an extractants in 1-alkyl-3-methyl imidazolium hexafluorophosphate.\textsuperscript{76} Sun et. al. reported a method in which a complexing agent EDTA showed promising results towards selectivity extract yttrium(III) from heavy lanthanides in [C$_n$MIM][PF$_6$] or [C$_n$MIM][NTf$_2$].\textsuperscript{77} In order to overcome the loss of IL, neutral complexes of mercury was extracted from a basic solution into the very hydrophobic 1-butyl-3-trimethylsilylimidazolium hexafluorophosphate [C$_4$tmsim][PF$_6$].\textsuperscript{78} The high hydrophobicity is responsible for efficient recovery of Hg ion from water. However, the use of fluorinated compounds is limited because of high prices as well as possibility of hydrolysis to produce dangerous hydrofluoric acid.\textsuperscript{79} From an economical and safety point of view, it is preferable to develope hydrophobic IL by introducing longer alkyl chains instead of using fluorinated anions.\textsuperscript{75b}

In summary, in metal ion extractions using ILs, following are the factors which are responsible for enhancement in extraction efficiency; (i) H-bonding, (ii) ion pair formation, (iii) dipolar interactions. Some strategies successfully depends on the use of an external extracting agent to provide these interactions, while other focused on modifying the structure of the IL cation and anion to provide specific interactions. The most
promising approach is the functionalization of side chains on imidazolium or pyridinium cation by a group capable to form H-bonding, electron-donating ability or chelating ability.

1.5.4.2 Ionic Liquids for dye extraction from water

Textile industries are growing almost in most part of the world and their numbers are increasing with time. These industries have the use of synthetic dyes which are used for coloring purpose. Because of high demand driven production, simultaneously, they are producing effluents containing unreacted dyes which contaminates the sources of water. As a consequence, due to environmental and health related issues, these industries are facing problems from government based pollution control agencies. Thus, treatment of effluent for the removal of dyes is a major concern for the survival of textile industries. There are various viable techniques; such as sedimentation, centrifugation, filtration, flotation, coagulation, ion exchange etc. for the removal of organic pollutants from water. Apart from these chemical methods, there are reports on the biological methods based on adsorption microbial degradation etc. Table 1.4 represents various methods for dye removal from water along with their merits and demerits.\textsuperscript{80}

The techniques depicted in Table 1.4, has one or more disadvantages and therefore, their use in industry is less viable. In recent years, ILs exhibited excellent extraction ability towards metals, as well as organic materials compare to traditional organic solvent. Since the first use of hydrophobic IL, [C\textsubscript{4}MIM][PF\textsubscript{6}] for the extraction of benzene and its derivatives, ILs were extensively used for extraction purpose.\textsuperscript{81}

Vijayaraghavan et. al.\textsuperscript{82} deployed the N-butyl-N-methyl pyrrolidinium bis(trifluoromethyl sulfonyl) imide to extract azo dyes from aqueous solution. Effect of alkyl chain length on the imidazolium cation with hexafluorophosphates on the extraction of Sudan dyes and Para red (obtained from chilli powder) and oil respectively was compared and reported by a research group of Prof. Fan.\textsuperscript{83} Very recently, Liu et. al. reported a novel hydrophobic benzothiazolium based IL for the extraction of triphenylmethyl dyes from water.\textsuperscript{80} They have shown that the hydrophobic interactions and hydrogen bondings are the driving forces for dye extractions and moreover the ILs are recoverable and reusable.
### Table 1.4 Comparison of common removal treatments for dyes/effluents

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Approach method</th>
<th>Merits</th>
<th>Demerits</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Aerobic process</td>
<td>• Partial or complete decolourization for various Dyes</td>
<td>• Cost intensive process</td>
<td>145</td>
</tr>
<tr>
<td>2.</td>
<td>Precipitation and flocculation</td>
<td>• Low disposal costs and short detection time</td>
<td>• Agglomerates separation and treatment</td>
<td>146</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Selected operating conditions</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Photo catalysis</td>
<td>• Inputs are non toxic and inexpensive., Complete mineralization at ambient conditions with shorter detection time</td>
<td>• Expensive process</td>
<td>147</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Effective only for small amount of colored compounds.</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>Ion exchange</td>
<td>• Low loss of adsorbents in regeneration</td>
<td>• Not effective for all dyes</td>
<td>148</td>
</tr>
<tr>
<td>5.</td>
<td>Enzymatic treatment</td>
<td>• Effective for specifically selected dyes</td>
<td>• Enzyme isolation and purification is tedious. Efficiency can be restricted by the presence of Interferences</td>
<td>149</td>
</tr>
<tr>
<td>6.</td>
<td>Activated carbon absorption</td>
<td>• High specific surface area and good removal efficiency for many kinds of dyes</td>
<td>• Cost intensive regeneration process</td>
<td>150</td>
</tr>
<tr>
<td>7.</td>
<td>Membrane filtration</td>
<td>• Wide variety of dyes/metals is applicable</td>
<td>• Dissolved solids cannot be removed</td>
<td>151</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Easy recovery and reuse</td>
<td>• Expensive treatment</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Concentrated sludge production</td>
<td></td>
</tr>
<tr>
<td>8.</td>
<td>Oxidation degradation</td>
<td>• Low temperature requirement</td>
<td>• High operation cost, Disposal of released aromatic amines</td>
<td>152</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Initiates and accelerates azo-bond cleavage</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.</td>
<td>Silica gels absorption</td>
<td>• Hydroxyl specific absorption for basic dyes</td>
<td>• Difficult regeneration and side reactions prevent its commercial application</td>
<td>153</td>
</tr>
<tr>
<td>10.</td>
<td>Electrokinetic coagulation</td>
<td>• Acknowledged economically feasible</td>
<td>• High sludge production and consumption of energy</td>
<td>154</td>
</tr>
</tbody>
</table>
Pei et al.\textsuperscript{84} investigated the removal of anionic dyes, such as methyl orange, eosin yellow, and orange G from water by means of a series of imidazolium based ILs. Li and Co-workers\textsuperscript{85} reported the extraction of a set of dyes from an aqueous phase using 1-butyl-3-methylimidazolium hexafluorophosphate. Looking to all reports, one can generalize that for liquid-liquid extraction of dyes or metals from aqueous solutions using ILs, hydrophobicity of IL is an essential requirement for efficient extraction as well as to prevent the loss of ILs. Therefore, as mentioned earlier in this chapter, development of fluoride free anion based hydrophobic IL is highly desirable.

1.5.5 Ionic Liquids in Biological Processes

In life science research, high purity of nucleic acids, are essential i.e. it should be free from broad range of impurities such as proteins, polysachharides, organic solvents.\textsuperscript{86} In this context, ILs provides potentials for finding applications in various bioprocessing and analytical methods used in biochemistry.\textsuperscript{87} IL offers alternatives for the separation/purification of DNAs from complex matrixes as well as their required quantifications. The isolation and purification of DNA from complex sample matrixes is a prime requirement for various biochemical processes; e.g. sequence analysis, genetic recombination, clinical hybridization and cloning. The conventional DNA extraction protocols involve hazardous organic solvents including phenol, chloroform, isoamyl acetate, which have an environmental impact. Therefore, a use of green solvent, IL in the process of DNA or protein denaturation is a matter of interest in today’s research. Very recently, ILs were used for trace amounts DNA or cytochrome C extraction.\textsuperscript{88}

In addition to this, ILs are ideal solvents or additives for immobilization and separation of enzymes,\textsuperscript{89} dissolution and regeneration of proteins,\textsuperscript{90} and electrochemical study of biomacromolecules.\textsuperscript{91} Qin, et al. depicted the electrostatic interaction between DNA and dialkyl imidazolium based ILs,\textsuperscript{92} with the help of $^{31}$P NMR and FTIR Wang’s group reported the interaction between 1-butyl-3-methyl imidazolium [Bmim$^+$] and P-O bonds of phosphate groups in the DNA strands and justify the extraction of DNA using 1-butyl-3-methyl imidazolium hexafluorophosphate [BMIM][PF$_6$].\textsuperscript{88a} An electrostatic interaction between [BMIM][BF$_4$] and DNA was investigated and Gibbs energy of surface binding ($\Delta G_b$) on a gold electrode were obtained.\textsuperscript{93} Similarly, protein–IL interaction is of great interest but, the proteins are usually insoluble in ILs and therefore very less literature is
available on Protein-IL interactions. In general, to date relatively less reports are available in (literature on interaction between ILs and DNA or protein).

For broad and multi scale application of ILs in industry or academic research, it is convenient to study their impact on humans and environment. One way to assess the cytotoxicity of IL is ‘in vitro’ testing on cell lines, which can correlate intracellular molecular or physiological mechanisms induced by ILs. In 2006, Couling et. al. first reported toxicity study of methyl imidazolium in several aquatic models; like *vibrio fischeri* (bacteria), *Daphniamagna* (the fresh water crustaceous) and the algae (*Scenedesmus quadricauda* and *chlamydomonas reinhardtii*) and found that toxicity increases with the alkyl chain length. But for the green algae; *Oocystis submarina* toxicity follow the un-usual trends i.e. [butyl-MIM] < [benzyl-MIM] < [hexyl-MIM] < [ethyl-MIM]. In contrast, the algae ‘*selenastrum capricornutum*’ shows following order of toxicity for anions of ILs, [SbF$_6$] < [PF$_6$] < [BF$_4$] < [CF$_3$SO$_3$] < [C$_8$H$_{17}$OSO$_3$] < [Br] ~ [Cl]. For cations morpholinium, pyrrolidinium, non-cyclic quaternary ammonium have lower toxicity compare to pyridinium and methyl imidazolium cations. Toxicity assays have also been performed and documented on bacteria and yeast strains. Recently, some studies were performed on cell lines. In 2004, first experiment work was done on leukenia-IPC-81 and glioma-C$_6$ rat cell lines and human cancer cell line HeLa. Later on, detailed studies on breast cancer cell line (MCF7), colon cancer cell line HT 29 and CaCo-2 were carried out. Cytotoxicities of pyrrolidium [Pyr] and Piperidinium [pip] ILs were estimated in MCF7 cells and they fall into the same toxicity scale for that of imidazolium based ILs and they showed less toxicity with longer alkyl chain length.

As per one of the principles of green chemistry, ILs should not accumulate in the environment after disposal. Biodegradation studies of ILs were carried out as per the guideline lead down by Organisation for Economic Cooperation and Developement (OECD) tests. As per this test, for compound designated as ‘readily biodegradable’ if atleast 60% of degradation occurs within first 10 days out of total 28 days test period. Biodegradability increase, with increase of the alkyl chain length and with the ester functionality and it also depends on the nature of anions. Moreover, reports showed that compare to [MIM] based ILs, [Py] based ILs can be completely degraded and hence they received much attention as green chemicals. In sum up, one can conclude
that the IL with pyridinium based cation with longer alkyl chain length and anions other than fluoride content, could be the promising candidate for DNA isolation, protein extraction, toxicity or cell viability study etc.

1.5.6 Ionic Liquids in Nanoparticle synthesis

Nanoparticles (NPs) have been extensively investigated due to the attraction of their unique physical properties, chemical reactivity and potential applications with high academic and industrial impacts.\textsuperscript{105} Due to their unique physical properties like Plasmon resonance, conductivity, optical absorbance etc. NPs are widely in use for various applications. Scheme 1.2 shows major applications of NPs.

\begin{center}
\includegraphics{scheme12.png}
\end{center}

\textbf{Scheme 1.2} Major applications of Nanoparticles\textsuperscript{106}

As NPs are possessing size dependent properties and size can be controlled during synthesis, its preparation approach is also important. Various synthetic routes for NPs are
shown in Scheme 1.3. Out of all methods depicted in Scheme 1.3, generally NPs are prepared by chemical methods in which the reducing agents are used and a protective agent or phase transfer agents are also required to stabilize the NPs.\textsuperscript{107} Bonnemann et al. first proposed the use of quaternary ammonium salt for stabilizing metal NPs but the NPs are not dispersible in water.\textsuperscript{107a} Dupont et al. have demonstrated the synthesis of Pt, Ir, Rh, and Au NPs in imidazolium based ILs,\textsuperscript{108} where it work as stabilizing agent by surrounding on metal NPs surface. ILs have been successfully employed in the preparation of Au, Pt and bimetallic alloys.\textsuperscript{109} The Au NPs with 1-2 nm size were prepared and stabilizing by an amine-terminated IL.\textsuperscript{109c}

Moreover, the low interfacial tensions of ILs were regarded to be an important property for a high nucleation rate and weak Oswald ripening required for the formation of small NPs.\textsuperscript{110} It has also been documented that NP synthesized in the ILs displayed better dispersion and a smaller particle size than those prepared in aqueous solution.\textsuperscript{109b} Most importantly, from the recent reports it is revealed that nitrogen containing groups such as alkylammonium ions and amidocynogen have a weak interaction with the metal surface.

**Scheme 1.3** Flow map showing the various approaches undertaken for the synthesis of metal nanoparticles
than carbonyl and sulf-hydryl groups, which suggests the potential use of these groups in the synthesis of high-quality “clean” metal NPs.\textsuperscript{109c, 111}

Recently, Zhao et al. reported IL mediated synthesis of “clean” Pd NPs for formic acid electrooxidation.\textsuperscript{112} The formation and stabilization efficiencies of ILs can be tailored by varying the ring structure, the substituting groups in the cations and the counter anions. The anions also play a key role in formation and stabilization of Nanoparticles and can be rationalized by considering the difference in the anion size of surfactants.\textsuperscript{113} Therefore, the designing of ILs, has a promising characteristics to control the size as well as stabilization of NPs.

In view of all these, the first section of the thesis is divided into three Chapters. Chapter 2 covers the detailed synthesis and characterization of ILs based on dodecyl sulphate anion and octyl pyridinium cation, which has hydrophobic character. Chapter 3 is compartmented into three sections; namely 3a, 3b and 3c. Of these three sections, Chapter 3a and 3b covers the use of IL C\textsubscript{8}PyDs, for extraction of metal ions and dyes from aqueous media, while Chapter 3c is composed of the novel ‘Phenol free’ green method for DNA and protein isolation. Moreover, the cytotoxicity and anti oxidant properties of C\textsubscript{8}PyDs will be discussed thoroughly. In Chapter 4, we proposed toxic reducing agent free, block copolymer induced silver nanoparticle (AgNPs) synthesis and checked the influence of ILs with various alkyl chain length and anions on the size and shape of the AgNPs.

\textbf{Section – II}

Amphiphilic block copolymers are a special type of polymers consisting of two or more blocks having different solubility in solvents. These types of block copolymers are classified into various classes on the basis of number of blocks as well as arrangement of blocks. These different amphiphilic block copolymers are shown in Scheme 1.4

The amphiphilic block copolymers self assemble into micelles or aggregates in a selective solvent, i.e. good for one block and poor for the other. Because of this reason amphiphilic block copolymers are self assembled into various liquid crystalline phases namely; cubic, hexagonal (2D and 3D), bicontinuous cubic, lamellar, vesicles etc. (Scheme 1.5).\textsuperscript{114, 115}
Chapter 1

Scheme 1.4 Schematic representation of block copolymer architectures

Simillar morphological structures were observed from the microdomain formation or acting as a structure directing agents with varying composition in solid state.116 This typical property of amphiphilic block copolymer make them more popular for the technological applications, including areas such as; nanotechnology, thin film preparation, ion selective membranes, polymer gel electrolytes, control drug releases for biological systems, etc.117

Water soluble amphiphilic block copolymers may have hydrophilic and hydrophobic moieties and as a result they are analogous to the conventional surfactants and able to form micelles or aggregates. Among the hydrophilic-hydrophobic amphiphilic block copolymers, in most cases poly ethylene oxide (PEO) constitutes as hydrophilic while poly (propylene oxide), poly (butylenes oxide), poly (styrene oxide), polystyrene, poly (methyl methacrylate) etc. are the hydrophobic parts. Among the most studied block copolymers Pluronic® or Poloxamer® Synpluronic® composed of poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) (PEO-PPO-PEO), triblock copolymers are widely studied and commercially available block copolymers. They available in wide range of composition and molecular weight115,118
Scheme 1.5 Various liquid crystalline phases of amphiphilic block copolymers, (A) Monomer, (B) Vesicle, (C) Cubic, (D) Hexagonal (2D), (E) Lamellar and (F) Bicontinuous cubic

When this polymer is put in water, the PEO blocks are selectively solvated by water and micelles are formed from hydrophobic PPO core. The micellization has been very well documented experimentally as well as theoretically in literature.\textsuperscript{119,120} The micellization in general and critical micelle concentrations (CMC) in particular for amphiphilic block copolymers are of interest for many applications including separations, dispersions, detergency, drug and gene delivery, pharmaceutical, cosmetic formulations, agriculture, electrochemistry etc.\textsuperscript{115,118,121} At CMC of block copolymers or surfactants, drastic change in several physical properties such as, surface tension, turbidity, electrical conductivity, osmotic pressure, etc. can take place and therefore, CMC can be determined by measuring any micellar influenced property.\textsuperscript{122} On the basis of these properties, basically there are two types of methods for CMC determination; (i) direct method and (ii) indirect method. In direct method, change in physical property at CMC is directly measured e.g. surface
tension, electrical conductivity, density, light scattering etc. While in indirect method, a probe was supposed to introduce and change in particular property of probe has to be measured at CMC, using methods like dye solubilisation, spectofluorimetry, pulse radiolysis method.

Among all these methods, surface tension (ST) and electrical conductivity (EC) are widely used and popular techniques for determination of CMC of surfactant or block copolymer solutions. It is due to the fact that, ST and EC are easy to operate, less time consuming and the break in the ST/EC vs concentration curve is clear. Out of these two extensively used techniques, ST is suitable for all kinds of surfactant or block copolymers solutions, while EC is useful only for ionic surfactant or mixture of ionic and non ionic surfactants. In other words, EC method is not suitable for the determination of CMC for non ionic surfactants or block copolymers and moreover, ST required sophisticated instrumentation. On the contrary, indirect methods like dye solubilization and fluorescence (dye or fluorescent molecule used as a probe) are less preferable, because it not only contaminate the surfactant/block copolymer solutions but it also affects the CMC values of surfactants. Thus, scientist/researchers are looking for a hybrid method which consist of simple equipment and the tracer or probe should not interfere with CMC values of surfactant or block copolymers.

As discussed earlier in this chapter, ionic liquid (ILs) are interesting class of tuneable solvents with many unique and attractive physicochemical and electrical properties. ILs are melted salts and possess ions which are responsible for electrical conductivity. Moreover, due to tuneable structure, one can develop a IL which have very less or negligible effect on micellization of surfactant or block copolymers and capable to show change in conductivity at CMC for non ionic surfactants or block copolymers. In addition to low melting point and high thermal stability, ILs have several other unique properties like high ionic conductivity and large electrochemical window. These properties are essential for electrolytes and moreover, ILs have attracted considerable interest as potential electrolytes for dye sensitized solar cell, fuel cells and lithium ion batteries. The considerable effort devoted to the gelation of ILs for applications as solid polymer electrolytes and stimuli responsive gels. Therefore, block copolymers and ILs represent very active research area and extent their use in several inter disciplinary science. Both are representing designer compounds which can be tuned as per desire physical and chemical properties. Seperately, block copolymers received interest in
controlling the spontaneous nano scale ordering of their individual molecules by tuning their self assemble structure, while ILs, are useful for control and understanding of their salvation, and other unique properties which received high attention. Self-assembly of amphiphilic copolymers in ILs can produce desirably nanostructures to ILs, which may useful for solubilisation and nanomaterial fabrication. Certain surfactants have been shown to self-assemble into micelles where ILs was used as a solvent. It has been very well documented that micellization of block copolymers in ILs is also promising. In 2008, Zheng et. al. reported aggregation behaviour of pluronic L61((EO)₃(PO)₃₀(EO)₃), L64 ((EO)₁₃(PO)₃₀(EO)₁₃) and F68 ((EO)₇₉(PO)₃₀(EO)₇₉) block copolymers in 1-butyl-3-methyl imidazolium type ILs. The surface tension measurement showed that the dissolution of the copolymers in ILs depressed the surface tension compare to aqueous solutions. The thermodynamic parameters of the micellization of block copolymers in [Bmim][BF₄] and [Bmim][PF₆], suggesting the micellization is a entropy driving process. Same group, reported aggregation behaviour of pluronic P104 ((EO)₂₇(PO)₆₁(EO)₂₇) in aqueous solution of 1-butyl-3-methyl imidazolium bromide (BmimBo). The hydrophobic interaction between PO block of P104 and BMiM⁺ cation was studied by using Nuclear Overhauser Effect (NOE). The detailed micellization along with geometry have been studied by FT-IR spectroscopy, Freeze Fracture Transmission Electron Microscopy (FF-TEM), Dynamic Light Scattering (DLS) and NMR spectroscopy. Moreover, they found that the size of P104 micelles increased with increasing the [Bmim][BF₄] concentration. Very recently, Parmar et al. reported interaction between the IL, 1-alkyl-3-methyl imidazolium tetrafluoroborate and Pluronic P103 micelles in aqueous solutions using DLS, SANS and NMR study. Cloud point data and NMR study support the hydrogen bonding between imidazolium cation and P103 and hydrophobic interaction between PO of PPO core and cation of IL respectively. They also indicated that the presence of ILs hinders the micelle formation of P103 in solution and promotes P103 to orient at air/water interface. Apart from micellization of block copolymer in ILs, there reports on the lyotropic liquid crystalline phases of block copolymers in ILs. Wang et al. found lyotropic liquid crystalline phase of P123 in presence of [Bmim][PF₆]. The polarized optical microscope (POM) and Small Angle X-ray Scattering (SAXS) techniques were used to study these liquid crystalline phases. Similarly, Zhang et al. reported liquid crystalline phases of P123 block copolymers in a room temperature IL in ethyl ammonium nitrate (EAN). Dey et al. reported femtosecond salvation dynamics in a
micron sized aggregate of IL, [Pmim][Br] and P123 triblock copolymers. From DLS measurements, authors found that, addition of RTIL to block copolymer micelle leads to the formation of giant P123-RTIL clusters of size 40 nm. Apart from pluronic block copolymers, a group of Prof. T. P. Lodge demonstrated thermosensitive self assembly of di block copolymers in ILs. In line with the current interest in both ILs and block copolymers, the detailed study on micellization of block copolymers in presence of ILs is desirable. Despite of such requirements, very few reports (as mentioned above) on micellization of aqueous solutions of pluronic block copolymers in presence of IL have been reported.

In view of all this, the Section - II of thesis has been undertaken to get a clear idea on micellization and self assembly, surface association behaviour of pluronic block copolymers in presence of various ILs having different cation, alkyl chain length and anions. The Section - II is composed of two Chapters. Chapter-5 presents our detailed measurements on surface active, viscosity, association behaviour of aqueous solution of pluronic P123 (PEO_{20}-PPO_{70}-PEO_{20}) and F127 (PEO_{97}-PPO_{69}-PEO_{97}) in presence of different types of ILs. The effect of alkyl chain length on cation, cationic head groups, anions and IL concentrations have been explained using various techniques such as Small Angle Neutron Scattering (SANS), Dynamic Light Scattering (DLS), Nuclear Magnetic Resonance (^1H NMR), Viscosity, Surface tension etc. The results are correlated in terms of hydrophobic/hydrophilic character of IL as well as block copolymers and the amount and location of IL in micelles of block copolymers were quantitatively determined using SANS measurements.

In Chapter-6 we, reported novel method for CMC determination of non ionic surfactants/block copolymers using IL by conductometry. The concentration and selection of IL were optimized in such a way that they should have negligible effect on micellization. The method was validated for various surfactants comprised of different hydrophobic part, hydrophilic/hydrophobic ratio, molecular weight etc. and obtained CMC values were compared with one measured using conventional methods like surface tension.

Last Chapter-7 summarizes the complete thesis work and presents the conclusion drawn from our study.
1.7 References:


Chapter 1


Chapter 1


Chapter 1

Chapter 1


Chapter 1


