CHAPTER 1

Introduction

1.1 Ionic Liquids

Ionic Liquids (ILs) are the molten salts which are composed of both cation and anion and generally they are liquids below 100 °C (Mecerreyes, 2011). If the melting point of IL is below the room temperature (RT), then the IL is said to be room-temperature ionic liquid (RTIL). ILs, which have been widely promoted as “green solvents” and are attracting much more attention of the researcher in the various fields of chemistry and industry due to their unique features like chemical stability, thermal stability, low vapor pressure, high ionic conductivity, etc. (MacFarlane et al., 2014). Their potential is further highlighted by the fact that their physical and chemical properties can be finely tuned by varying both cation and anion. ILs are composed of different cation and anion (Fig. 1.1).

In the recent years, most of the researchers are attracted towards the ILs, supercritical CO₂ as well as universal solvent water. Among all these materials, ILs has attracted an immense interest in the academic, industrial as well as commercial applications.
RTILs and task-specific ILs with imidazole moiety are relatively expensive, which could hamper their industrial applications. Also, ILs suffers from many disadvantages like its cost, low recovery from the reaction mixture and reusability. The high cost of ILs is one of the most important issues hindering their huge scale application in catalysis, particularly dialkyl imidazolium ILs (Zhang et al., 2011). Also, ILs consist of halogen-containing anions such as [PF$_6$]$^-$, [BF$_4$]$^-$, [CF$_3$SO$_3$]$^-$ and [(CF$_3$SO)$_2$N]$^-$ which in some respect limit their “greenness” (Wasserscheid et al., 2002). The main difficulty associated with the homogeneous catalysis is the recovery of ILs from the reaction mixture. Therefore the techniques have been involved in the separation of product from the reaction mixture is precipitation, extraction using other solvent or distillation with subsequent recovery. But these kinds of workup procedure may result in the deactivation of the catalyst. Conversely, while purifying the compound leaching of the catalyst may occur leading to a loss of the catalyst from the reaction mixture on the other hand further struggle to extract the compound.

Thus, an improvement of less expensive ILs is of great value which could stimulate the large-scale application of ILs in the field of catalysis as well as electrochemistry and separation etc.

In addition, a large amount of expensive IL is needed in homogeneous catalytic processes, which may cause possible toxicological concerns both in the case of imidazole as well as benzimidazole. But due to some distinctive feature of benzimidazole compared to imidazole and another heterocycle, it is necessary to explore them in details to develop the benzimidazolium based ILs. Since, benzimidazolium based ILs have been shown as good thermally stability which is an important characteristic for designing the catalyst (Muskawar et al., 2015).

Therefore recently, PILs is gaining more attention of the researcher not only in the field of catalysis but also in energy and environmental applications, analytical chemistry, materials science and biotechnology.

1.1.1 Literature Reports on Benzimidazolium based Ionic Liquids

Due to its good importance, benzimidazolium based ILs have been attracted in a variety of applications not only in chemistry but also in biology, biological and chemical sensors, corrosion chemistry, biodiesel synthesis and biologically active molecules. Literature reports suggest that many drug molecules containing benzimidazole moiety show potent activity towards the various diseases. ILs
containing benzimidazolium chloride moiety shows antimicrobial activity against the bacteria like cocci, rods, fungi and Bacillus.

Also, when we going towards the metal chemistry of transition metal ions like Palladium complexes derived from N, N-dialkyl-benzimidazolium salts and their application for Suzuki, Heck, Mizoroki-Heck coupling and Suzuki-Miyaura cross-coupling reactions have been studied (Kamisue and Sakaguchi, 2011). Furthermore, benzimidazolium based ILs has been used for the dye-sensitized solar cells (DSSC) by inorganic-organic gel electrolyte with silane substituted benzimidazole (Lee et al., 2009). Also, benzimidazolium based ILs have been used for the preparation of polymer composite and polymerization of styrene with montmorillonite (Cai et al., 2014).

Few literature reports have been published on catalyst based on benzimidazolium cation for the organic reactions. Recently, Iwamoto et al. (2006; 2008) have been studied the benzoin condensation reaction in an aqueous medium using methylene-bridged bis(benzimidazolium)bromide (Fig. 1.2).

![Fig. 1.2 Methylene-bridged bis(benzimidazolium)bromide](image)

The most common catalyst used for such type of reaction is the acid catalyst. Acidic ILs catalysts are of two types one is Lewis acid IL and another is Brønsted acid IL. Therefore many researchers started to introduce the Lewis or Brønsted acidity in ILs by keeping particular functionality and examined their applications. In the Lewis acid, six common ILs including [Bmim]BF$_4$, [Bmim]CF$_3$SO$_3$, ChCl·2SnCl$_2$, ChCl·2ZnCl$_2$, ChCl·2.5SnCl$_2$ and ChCl·2FeCl$_3$ have been used for the synthesis of phytosteryl esters from phytosterols and fatty acids in the presence of ILs with high yield and purity (Yang et al., 2012). Brønsted acid-catalyzed reactions are well known for many years which have shown diverse applications in organic reactions. The catalyst containing -SO$_3$H functionality in the benzimidazolium cation and H$_2$PO$_4$, OTf, OTs and HSO$_4$ counteranion have been reported and shown remarkable catalytic activity in organic reactions.
Wang (2008) has defined the Brønsted acidic task-specific benzimidazolium ILs containing various anion and got the best yield in HSO₄⁻ anion for the mild acetalization of the aromatic aldehyde from a diol (Fig. 1.3).

Also, Li et al. (2011) have demonstrated the sulphonic acid functionalized IL based on benzimidazolium cation for one-pot synthesis of biscoumarine derivatives. Acidities and the catalytic activity depend upon their structures (Fig. 1.4).

Karimi and Vafaezadeh (2012) have reported the SBA-15 functionalized sulphonic acid confined acidic IL as a powerful and water-tolerant catalyst for solvent-free esterification 1. Muskawar et al. (2014) demonstrated the facile esterification of carboxylic acid using amide functionalized benzimidazolium dicationic ILs. The mechanism of this strategy has shown that the amide groups present in the catalyst was expected to form hydrogen bonding with the carboxylic acids and this could facilitate the esterification reactions under mild conditions devoid of any added catalyst or organic solvent 2. The Same author in 2013 has prepared the carboxyl-functionalized benzimidazolium based ILs with various anion including
BF$_4^-$, PF$_6^-$, OMs$^-$ and OTs$^-$. Among all the varied counteranion OTs$^-$ has found to show the more yield 3. Kore et al. (2012) emphasized that the hydration of alkynes using Brønsted acidic ILs in the absence of Nobel metal catalyst/H$_2$SO$_4$ 4 (Fig. 1.5).

**Fig. 1.5 Sulphonic Acid Functionalized ILs**

Further, Kore and Srivastava (2011) have reported the novel imidazole and benzimidazole-based sulfonic acid functionalized Brønsted acidic ionic liquid catalysts (Fig. 1.6) and used for the synthesis of amidoalkyl naphthols, dihydropyrimidinones and synthesis of 1-(phenyl (piperidine-1-yl) methyl) naphthalene-2-ol (Betti base) derivatives.

**Fig. 1.6 Sulphonic Acid Functionalized Brønsted Acidic Ionic Liquid ILs**

Abbasi (2015) have prepared the 1,3-disulfonic acid benzimidazolium chloride (Fig. 1.7) and used for the synthesis of tetrahydropyridine under solvent-free conditions. Hence the benzimidazolium based ILs are good results in the catalysis due to that reason people are using benzimidazolium cation for the synthesis of ILs.
Therefore from the literature reports, we have found that benzimidazole cation is increasingly attracting an interest of researcher in various fields. Hence, in the present thesis work, we have prepared benzimidazolium based PILs for the application of catalysis and as an adsorbent for the adsorption of hexavalent chromium from aqueous solution. The monomer has been used in the entire thesis is 4-vinyl benzyl chloride for the preparation of benzimidazolium based PILs.

1.2 Poly(Ionic Liquid)s

PILs are also referred as polymeric ILs, and it is denoted by a subclass of polyelectrolytes that feature an IL species in each monomer repeating unit, linked to a polymeric backbone to form a macromolecular architecture. Some of the important properties of ILs are incorporated into the polymer chains, which gives rise to a new class of polymeric materials. PILs are attracting increasing interest of the researchers as it is emerging interdisciplinary topic among polymer chemistry, physics, catalysis, materials science, separation, analytical chemistry and electrochemistry. Presently, research on PILs has entered into the long growth stage in which many novel properties and applications have been newly exposed. In the meantime, there is no doubt that PILs have extended the traditional design of solid polyelectrolytes into more complex and versatile directions with pronounced strength in energy, environment and in catalysis applications.

Over the past few years, the introduction of functional groups related to ILs (i.e. cations such as imidazolium, benzimidazolium, pyrrolidinium, pyridinium and anions such as tetrafluoroborate, hexafluorophosphate, hydrogen sulphonate and triflates) into functional polymers is giving rise to a new family of materials with specific properties and exciting applications. Looking at the chemical structure, PILs are polyelectrolytes, the polymers whose repeating unit bear an electrolyte group (cation or anion). Though up to date, there is no clear definition of PILs, we will
consider those polymers synthesized from ILs monomer in apposition to polyelectrolytes which are synthesized from the solid salt monomers.

PILs show some of the unique properties of ILs like ionic conductivity, chemical stability, thermal stability and tuneable solution properties together with the intrinsic polymer properties. Most of the polymers are not soluble in water but they are soluble in polar organic solvents. This may be due to the hydrophobic character of the counterion and the reduced cumbic interactions. As descriptive examples, in the case of cationic polyelectrolyte, the common counteranions are halides such as Cl\(^{-}\), Br\(^{-}\) or I\(^{-}\). However the PILs containing counter anion tetrafluoroborate (BF\(_4\)^{-}), hexafluorophosphate (PF\(_6\)^{-}), Bis(trifluoromethylsulfonyl)amine (CF\(_3\)SO\(_2\)\(_2\)N\(^{-}\)) trifluoromethane sulphonate (CF\(_3\)SO\(_3\)^{-}). Also, different types of copolymers such as random, alternating, block and macromolecular architectures like branched, dendritic or ramified structures are possible.

From the literature survey, it is observed that there is no reports have been published using benzimidazole as a cation for the preparation of PILs. Hence in our work, we have decided to select benzimidazole as a cation for the preparation of PILs. As the benzimidazolium based ILs are more stable towards air, moisture as well as they possess high thermal stability and wide liquid range and also the catalytic activity of the benzimidazolium based ILs have been revealed by the various researcher in the literature (Muskawar et al., 2016).

1.3 Ionic Liquids and Poly(Ionic Liquid)s: A Comparative View

PILs could be soluble in many types of organic solvents ranging from high polar to low polar solvents. This property depends upon the chemical nature of the PILs. The anion part of the PILs plays a significant role in the solubility of the PILs if the PILs is having the same cationic backbone they are generally soluble in different organic solvents which are decided by the anion part of the PIL. The most common technique of the preparation of PIL is the straightforward chain polymerization of IL monomers (Fig. 1.8) although out of the question for researcher those who are working on PIL they are having some confusion about the PILs and ILs periodically in some fields. Therefore we are discussing the similarities and differences between the ILs and PILs in terms of the properties and functions. ILs is organic salts where
the ions are poorly coordinated and melt below 100 °C or even at RT. This inflexible definition excludes certain organic salts with halide anions due to their relatively high melting points. For example, trioctyl-4-vinylbenzyl phosphonium chloride (OPCl) has a melting point (m. p.) near 87 °C and is considered to be an IL according to this definition, whereas the m.p. of tribuyl-4-vinylbenzyl phosphonium chloride (BPCl) is reported to be 125 °C and is therefore strictly not IL (Cheng et al., 2011). The basic concept of PILs is simply and solely based on how they are formed i.e., by the (formal) polymerization of an IL monomer. Hence, PILs similar to common polymers are comprised of the corresponding monomers. Sometimes the physical properties of PILs and ILs are not necessarily related to each other.

![Diagram of PILs and ILs](image.png)

**Fig. 1.8** Schematic Representation of the Relationship between ILs and PILs ILMs: IL Monomers “P” Polymerizable Group

### 1.4 Synthesis of Poly(Ionic Liquid)s

PILs can be synthesized via two basic methods: (Yuan and Antonietti, 2011; Mecerreyes, 2011). One is either 1) Polymerization of IL monomer or 2) Chemical modification of existing polymers (Fig. 1.9) or post polymerization modification as shown in Fig. 1.10. In both the approaches, some polymerization techniques are involved, such as conventional and controlled radical polymerizations, ring opening
metathesis polymerization, step-growth polymerization and other. From a synthetic point of view, each of these methods and polymerization techniques governs different structural parameters of PILs and demonstrate distinct advantages as well as limitations with respect to the molecular design. In the present thesis, we have prepared PILs using both the methods by radical polymerization using Azobisisobutyronitrile (AIBN) as a polymerization initiator. Also, the present thesis especially emphasizes on the preparation of PIL containing benzimidazolium cation for the application of catalysis and adsorption of hexavalent chromium from the aqueous solutions. However, the characteristics of the benzimidazolium based PILs are currently under deep investigation in various significant fields.

![Fig. 1.9 General Schematic Route of Synthesis of PILs](image1)

![Fig. 1.10 Post Polymerization Modification](image2)
1.5 Applications of Poly(Ionic Liquid)s

In similarity with the ILs, PILs are finding applications in numerous different technological fields such as catalysis, Biorelated applications, CO₂ capture or CO₂ separation, sensors, dispersants and stabilizers for metal NPs, polyelectrolytes for electrochemical devices and removal of toxic metals or dye removal and many more. In the following section, some of the applications of PILs have been discussing and it is shown diagrammatically in Fig. 1.11.

In recent times, imidazolium base PILs have shown a broad-spectrum of antimicrobial activities. Riduan et al. (2013) have published the extensive review on imidazolium salts and their polymeric materials for biological applications. These imidazolium salts could be found as a beneficial in bio-related applications including antitumor, antimicrobial and antioxidant.

Isik et al. (2016) have prepared sustainable PILs for CO₂ capture based on deep eutectic monomers properties of the polymers. The synthesized polymer then used as a solid sorbent for CO₂ capture. It has been shown that the polymers prepared with citric acid displayed better performance both experimentally and computationally. The current endeavor showed that sustainable PIL based on deep eutectic monomers can be easily prepared to produce low-energy-cost alternatives to the materials currently being researched for CO₂ capture.

Tang et al. (2005) have been synthesized novel sorbent and membrane materials for CO₂ separation from IL monomers, poly[p-vinylbenzyltrimethyl ammonium tetrafluoroborate] (P[VBTMA][BF₄]) and poly[2-(methacryloyloxy)ethyltrimethylammonium tetrafluoroborate] (P[MATMA][BF₄]) have absorption capacities 7.6 and 6.0 times of those of RTILs, e.g. [bmim][BF₄] respectively with reversible and fast sorption and desorption.

The group of Mecerreyes et al. (2006) built a glucose amperometric biosensor based on the immobilization of glucose oxidase in poly(1-vinyl-3-ethyl-imidazolium tetraborate) or poly(1-vinyl-3-ethyl-imidazolium TFSI) microparticles. The biosensor could be employed in aqueous and non-aqueous media with acceptable results for glucose determination in human serum samples.

Prabhu Charan et al. (2014) have been developed a PILs as “smart” stabilizers for metal nanoparticles. The PILs of the types poly(1-vinyl-3-alkyl imidazolium) X (where alkyl = ethyl, butyl and pentyl; X = Br⁻, OH⁻ they have
synthesized and used for the preparation of various nanoparticles such as silver, gold and nickel nanoparticle in solution. These PILs was found to show the great stability for a longer period without agglomeration.

Doubtless, one of the important applications of PILs is as an electrolyte in electrochemical devices. Thus Lu et al. (2002) revealed that ILs based electrolytes radically improves the performance, speed, cyclability and long-term stability of electrochromic devices and actuators. Additional works prolonged the application of ILs to other electrochemical devices like lithium batteries, dye-sensitized solar cells, fuel cells, supercapacitors, light-emitting electrochemical cells and field effect transistors.

Fig. 1.11 Diagrammatic Representation of Applications of PILs

1.6 Poly(Ionic Liquid)s as a Catalyst and Adsorbent

Benzimidazolium based ILs are well known since last decades as they have been found potential candidates for the various applications and they could bear the typical physical properties that make them interesting as a catalyst for various organic reactions especially condensation reactions. Therefore, the introduction of benzimidazole cation in polymer act as a benzimidazolium based PILs and could act
as a catalyst for the organic reactions and as an adsorbent for the adsorption of various toxic metals and dyes from the aqueous solutions.

(a) Benzimidazolium based PILs have been shown as more thermal stability compared to imidazolium, pyridinium based PILs etc.

(b) It is composed of poorly coordinating ions, so they have the potential to be highly polar yet non-coordinating solvents.

(c) Functionalized benzimidazolium based PILs have been shown to be either heterogeneous or homogeneous catalyst depending upon the substituent and counter anion attached to the polymer matrix.

(d) Past few years various reports have been published on the polymer-based sulphonic acid functionalized Brønsted acid IL catalyst for the various organic reactions including condensation reactions, synthesis of biofuels like 5-Hydroxymethylfurfural (HMF), ethyl levulinate and transesterification of various non-edible oils to get the biodiesel.

(c) Benzimidazolium based PILs are immiscible with a number of organic solvents and provide a nonaqueous polar alternative for two-phase systems.

(f) Benzimidazolium based PILs could be used as an adsorbent as they are thermally stable towards the wide range of temperature. However, they bear the cation and anion part in their structures which could help in the adsorption of some toxic metal ions and dyes via electrostatic interaction or π-π interaction.

(g) Recently, Gao and Gao et al. (2013) have reported the cross-linked PIL bearing –OH and -NH₂ group. These groups could help to improve the adsorption capacity effectively with good adsorption capacity. Because cross-linked PILs are hydrophobic in nature and hydrophobicity of the polymer is more important when it is used as an adsorbent.

(h) They may be used in high vacuum systems and eradicate many contamination problems as they do not evaporate.

1.6.1 Literature Reports

Xu et al. (2010) group have synthesized polystyrene (PS)-supported 1-(propyl-3-sulfonate) imidazolium hydrosulfate acidic IL PSCH₂-[SO₃H-pIM][HSO₄⁻] (Fig. 1.12) catalyst was prepared by supporting the IL onto highly cross-linked chloromethylated polystyrene (PS-CH₂Cl). The resulting catalyst was found to be
thermally stable. The present catalyst could be successfully used for the esterification reaction.

![Figure 1.12](image)

**Fig. 1.12** Polystyrene (PS)-Supported 1-(propyl-3-sulfonate) Imidazolium Hydrosulfate Acidic IL (PSCH$_2$-[SO$_3$H-pIM][HSO$_4$])

Liang (2013) has been demonstrated the synthesis of solid acidic IL polymer (Scheme 1.1) through the copolymerization of acidic IL monomer with divinylbenzene DVB.

![Scheme 1.1](image)

**Scheme 1.1** Solid acidic IL Polymer

The catalyst was used for biodiesel synthesis from waste oils with high free fatty acid (FFA) content was developed (Fig. 1.13). PIL could efficiently catalyze both the transesterification of triglycerides and the esterification of FFAs with a total yield of > 99.0%.

![Figure 1.13](image)

**Fig. 1.13** Solid Acidic IL Polymer
Liang et al. (2013) have demonstrated the efficient procedure for biodiesel synthesis from waste oils using novel solid acidic IL polymer as catalysts.

Li et al. (2014) have been demonstrated the heteropolyanion-based IL-functionalized mesoporous copolymer (Fig. 1.14) catalyst for Friedel–Crafts benzylation of arenes with benzyl alcohol. Keeping to the suitable mesoporous copolymeric structure, P(VB-VMS)PW showed a relatively high yield of benzylating products (96.7%) and it could be facilely recovered and reused.

**Fig. 1.14** Heteropolyanion-based IL-Functionalized Mesoporous Copolymer

Kiasat et al. (2015) have prepared the poly(4-vinyl pyridinium butane sulfonic acid) hydrogen sulfate (Fig. 1.15) P(4VPBSA)HSO$_4^-$, a novel polymeric acidic catalyst by the reaction of cross-linked poly(4-vinyl pyridine) with 1,4-butane sultone and further acidification of the catalyst with sulfuric acid. The catalyst was used for the one-pot preparation of 1,8-dioxo-octahydroxanthenes under solvent-free conditions. Also, the same author has been reported the synthesis of 1-amidoalkyl-2-naphthols and substituted quinolines under solvent-free conditions.

**Fig. 1.15** Poly(4-vinylpyridinium butane sulfonic acid) hydrogen sulfate

Pourjavadi et al. (2012) have synthesized the crosslinked PIL (polysulphonyl IL) as high loaded dual acidic organocatalyst (Fig. 1.16). The (vinyl-3-(3-sulfopropyl) imidazolium hydrogen sulfate [VSim][HSO$_4^-$]) and IL cross-linker (1,4-butanediyl-3,3-bis-l-vinyl imidazolium dihydrogen sulfate) have been copolymerized. The resulting IL heterogeneous catalyst had reported for the synthesis of
Dihydropyrimidines via Biginelli reaction under mild reaction conditions in high yields. Such kind of heterogeneous ILs catalysts is particularly attractive in green chemistry.

Recently, Boroujeni and Shojaei (2013) had synthesized poly(4-vinylpyridine)-supported dual acidic IL: an environmentally friendly heterogeneous catalyst (Fig. 1.17) for the one-pot synthesis of 4,4’(arylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ols).

PILs have been found as potential candidates towards the adsorptive removal of toxic hexavalent chromium (Fig. 1.18) Cr(VI) (Rahman et al., 2013; Mi et al., 2013; and Gao et al., 2014). Wang et al. (2015) had synthesized novel polymeric IL
gel (Fig. 1.19) and investigated its excellent performance for hexavalent chromium removal with maximum adsorption capacity 283 mg g⁻¹.

Pourjavadi et al. (2013) have revealed the synthesis of cross-linked basic nano gel; basic PIL as a heterogeneous catalyst (Fig. 1.20) and it was synthesized by mini-emulsion polymerization of IL monomer 1-ethyl-3-vinylimidazolium bromide [EVim][Br⁻] which was cross-linked by IL-bis-1-vinylimidazolium dibromide (BVD). Finally, Exchange of bromide anions in PIL nano gel with hydroxide produced a supported basic IL catalyst. This catalyst was evaluated for the synthesis of 4H-benzo[b]pyrans by multi-component reaction in water.
Leng et al. (2013) have established the carboxylic acid-functionalized phosphovanadomolybdate-paired ionic polymer (Fig. 1.21) as a green heterogeneous catalyst for hydroxylation of benzene.

![Fig. 1.21 Carboxylic Acid-Functionalized Phosphovanadomolybdate-Paired Ionic Polymer](image)

Boroujeni et al. (2013) have demonstrated the synthesis and application of a novel strong and stable supported IL (Fig. 1.22) catalyst with both Lewis and Brønsted acid sites and used for the synthesis of biscoumarins by two-component one-pot domino Knoevenagel-type condensation/Michael reaction between various aliphatic and aromatic aldehydes with 4-hydroxycoumarin.

![Fig. 1.22 Supported IL](image)

1.7 Research Objectives

Due to the marvelous scope of PILs in the various fields, we have been prompted to:

i) Synthesized sulphonic acid and carboxyl functionalized benzimidazolium based PILs and their characterization using various spectroscopic techniques viz. NMR, IR, elemental analysis, TGA, SEM/EDAX and XRD etc.

ii) To test the sulphonic acid functionalized benzimidazolium based PIL as a heterogeneous catalyst for the Biginelli reaction and to Characterization
synthesized derivative by different spectroscopic tools such as NMR, FT-IR, GC-MS and also by melting point determination.

iii) To test the sulphonic-acid functionalized benzimidazolium based PIL for the Esterification of levulinic acid with ethanol.

iv) To synthesize the carboxyl-functionalized PIL (CFPIL) and its use for the synthesis of β-amino ketones under a solvent-free condition at RT.

v) To evaluate the catalytic activity of the two basic and two acidic ILs catalyst for the transesterification of castor oil with methanol.

vi) To test the sulphonic acid functionalized PIL for the adsorption of hexavalent chromium.

Hence, in the present thesis work, we have attempted to synthesize few PILs and explore their catalytic activity and also the adsorption of hexavalent chromium.

1.8 Scope of Study

Benzimidazolium based PILs are found to play a crucial role as a catalyst for organic reactions and also for the adsorption of toxic metal ions like Cr(VI). In the present thesis work, we have investigated the several parameters like amount of catalyst, reaction time and reaction temperature towards the synthesis of 3,4-dihydropyrimidine-2(1H)-one/thiones derivatives via Biginelli reaction, solvent-free synthesis of β-amino ketones, esterification of levulinic acid and transesterification of castor oil. Moreover, sulphonic acid functionalized PIL has been used as an adsorbent for the adsorption of hexavalent chromium from aqueous solutions.

1.9 Significance of the Work

The contributions of the present research work are as follows:

i) It could overcome some of the environmental issues such as minimization of environmental hazards, toxicity, use of more quantity of solvent and flammability.

ii) The recycling and reusability of the catalyst for the several runs could minimize the tedious catalytic processes.

iii) The simple method of the catalyst, environmentally green process will make the present catalyst beneficial in large-scale synthesis manufacture.
iv) It could minimize the use of a homogeneous catalyst for Biginelli and Mannich reaction.

v) As the process of the purification of the desired product is simple hence it could reduce the time and use of huge amount of solvent.

vi) The cost of the manufacturing could be reduced due to its process simplicity and extraction of product from the reaction mixture.

vii) This work may provide new approaches towards designing of PILs for catalysis application and adsorbents with highly tuneable and desirable characteristics.