

Abstract

Ionic liquids (ILs) are salts containing organic cations and organic or inorganic anions which exists in liquid state with melting point typically below 100 °C, considering the boiling point of water as the point of reference. Poor coordination of the constituent ion-pair i.e. between organic cations with organic or inorganic anions results in liquid state of these organic salts [1]. Physical properties of these ILs like thermal stability, low vapour pressure, melting point, density, viscosity, solubility, conductivity etc. are determined by the combinations of organic cations and anions as well as different substituents added to the constituent ions [2]. Ionic liquids are also termed as designer solvents because of their attractive tuneable physicochemical properties including low vapour pressure, non-volatility, ability to solubilize organic, inorganic, polar, nonpolar species etc., forming biphasic solvent system, acting as dual-solvent catalyst at the same time, acting as co-catalyst. Because of possessing large electrochemical window, they can be used as electrolytes for many studies [3-6].

Ionic liquids, those are designed keeping in mind the application they need to perform are termed as task specific ionic liquids (TSILs). Designing ionic liquids by adding proper substituents, functional groups into the constituent ion-pairs can tune them into homogeneous, heterogeneous or multiphase behaviour of the catalyst [7-10]. Functionalization of the ILs can be done by incorporation of Brønsted acidic functional groups (e.g. -COOH, -SO₃H), basic functional groups into the ion pairs, incorporation of Lewis acidic complex metal halide anions etc. as per necessity to run a chemical reaction. Introducing variation in substituent groups added to cation or anion or both, functionalization in the constituent ions, variation in alkyl chain lengths, results in modification of both physical and chemical properties among ionic liquids [11-13].

One important aspect of using ionic liquid as heterogeneous catalytic system is by immobilization of ionic liquids in various supports. Immobilization transfers the task specific properties of IL into the surface of heterogeneous material and with increase in surface area of active sites reduces the quantity of expensive ionic liquids as catalyst along with easy separation for reuse [6]. The immobilization of ILs into supports is mainly done through formation of covalent bond with the surface of support or by secondary interactions to generate supported liquid phases (SLPs), which does not involve covalent bond interaction between the ionic liquid and the support [14]. Despite all that, immobilization of the ILs is also observed to show a lot of drawbacks. In many cases,

supports like zeolite, structured supports of MCM (Mobil Composition of Matter) family were observed to get structurally destroyed while immobilization is done with task specific ionic liquids [15-18]. Here comes the need for synthesizing ionic liquid based solid catalysts that does not bring any destruction in the resultant structure. Integrating the ion-pair of organic cations with polyoxometalates (POMs) counter anions leads to generation of organic-inorganic hybrids of ionic liquid and polyoxometalate with unique physical and chemical properties. These properties can be tuned as different types of interaction comes into existence according to the functional groups attached to ionic liquid cation that will be combined with the POM anion. Thus, synthesis of ionic liquid based-polyoxometalate not only brings some distinctive characteristic properties in each type of hybrid but also overcomes the limitations of immobilization faced with ionic liquids with supports. It was observed that these hybrids show good results as phase transfer catalysts [19]. The heterogeneous nature introduced in such hybrids was observed to show excellent performance in catalytic reactions [19].

Polyoxometalates are class of early transition metal-oxide clusters, where metals (M = V, Nb, Ta, Mo, W) are present in their highest oxidation state linked by shared oxygen atoms and are well known oxidative catalyst [20]. Their reactivity, thermal and oxidative stability, molecular structural diversity, nucleophilicity, remarkable redox properties and Brønsted acidity is the origin of POMs innumerable application expanding in industry, [21,22] as well as in fundamental studies [23-25]. The use of unmodified pure crystalline POMs in catalytic systems are little hard to process because of their high solubility in polar solvents which makes its recovery laborious [26].

Metal extraction, their recyclability and uses are increasing globally and researchers are developing new technologies for meeting such demands. Ionic liquids and their physico-chemical properties play an important role in metal extraction process and their ionic character leads to many possible metal transfer mechanisms which was not possible using molecular liquids as extraction solvent. Therefore, ionic liquids are considered as relevant alternatives to molecular solvents in case of metal extraction. Biphasic metal extraction from aqueous medium using ionic liquid generally uses ion exchange mechanism.

This thesis work is mainly based on designing task-specific ionic liquids (TSILs) and ionic liquid-polyoxometalate (IL-POM) hybrids by incorporating certain functional groups,

alkyl substituents into the constituent ion pairs. The applications performed are phase transfer catalytic oxidation, metobromuron herbicide degradation, one pot synthesis of 3 substituted indoles, biphasic metal extraction.

Proposed Objectives:

- [1] Synthesis of solvent responsive self-separative Brønsted acidic ionic liquid-polyoxometalate hybrids and exploring their catalytic activity on H₂O₂ mediated oxidation of alcohols.
- [2] Developing ionic liquid based Keggin polyoxometalate hybrids as oxidative degradation catalyst of metobromuron in sunlight and discussing intermediates and its mechanistic aspects.
- [3] Synthesizing variable alkyl bridged Brønsted acidic dicationic imidazolium ionic-liquid based phosphomolybdate hybrids and exploring its efficacy on one-pot sequential synthesis of 3-substituted indole.
- [4] Investigative study on the dual functional behaviour of dicationic task specific imidazolium ionic liquid as extractant as well as hydrophobic biphasic solvent in metal extraction from aqueous medium.

Plan of work

- [1] Design, synthesis and characterization of -SO₃H functionalized diethylamine based ionic liquid cation combined with Keggin polyoxometalate, [DEDSA]₃[PW₁₂O₄₀] and [DEDSA]₃[PMO₁₂O₄₀].
- [2] Exploration of the solvent responsive nature of the above mentioned Brønsted acidic ionic liquid-polyoxometalate hybrids on addition of different solvents and investigating their phase transfer nature for catalytic activity on H₂O₂ mediated oxidation of alcohols.
- [3] Design, synthesis and characterization of another set of -SO₃H functionalized ammonium based dibutylamine ionic liquid cation combined with Keggin polyoxometalate, [DBDSA]₃[PW₁₂O₄₀] and [DBDSA]₃[PMO₁₂O₄₀].
- [4] Exploration of these dibutyldisulphoammonium based ionic liquid and Keggin polyoxometalate hybrids as oxidative degradation catalyst of metobromuron in sunlight, using H₂O₂ as oxidant and discussing intermediates and its mechanistic aspects.

- [5] Synthesizing variable methylene bridged Brønsted acidic dicationic imidazolium based ionic-liquid phosphomolybdate hybrids aiming increased hydrophobicity and thermal stability in the catalysts. Characterization of these synthesized ionic liquids were done with various analytical tools.
- [6] Exploring efficacy of the above synthesized dicationic imidazolium ionic-liquid based phosphomolybdate hybrids as acid catalysts on one-pot sequential synthesis of 3-substituted indole.
- [7] Design and synthesis of two water immiscible, hydrophobic task specific -COOH functionalized dicationic imidazolium chloride ionic liquids.
- [8] Investigative study on the dual functional behaviour of these -COOH functionalized dicationic task specific imidazolium chloride ionic liquids as extractant as well as biphasic solvent in metal extraction from aqueous medium.

Outline of the thesis

This work illustrates design and synthesis of different task specific ionic liquids as well as functionalized ionic liquids and polyoxometalate based hybrids. Further it includes their characterization and applications in various target specific applications. The thesis is divided into **six chapters**.

Chapter 1:

This chapter is divided in to two parts as **Chapter 1A** and **Chapter 1B**

Chapter 1A: General introduction and review of literature

Chapter 1A outlines the broad introduction about ionic liquids, designing them to be task specific by introduction of certain functional groups, substituents etc. It also gives a comprehensive information about the Keggin polyoxometalate used as anion to form organic inorganic IL-POM hybrids. Furthermore, it demonstrates the stability and activity of IL-POM hybrids formed and their uses in oxidation and acid catalyzed reactions. This chapter also illustrates how the choice of cation and incorporation of certain functional groups brings changes in selective solubility, hydrophobicity and active sites etc. Thus, designing task specific ionic liquids is of great importance and developing protocols maintaining overall stability of the individual constituent ions is of potential interest. Thus, our thesis puts an effort on synthesizing counter cation of ionic liquid with desirable functional and substituent groups that brings about changes in physical and chemical

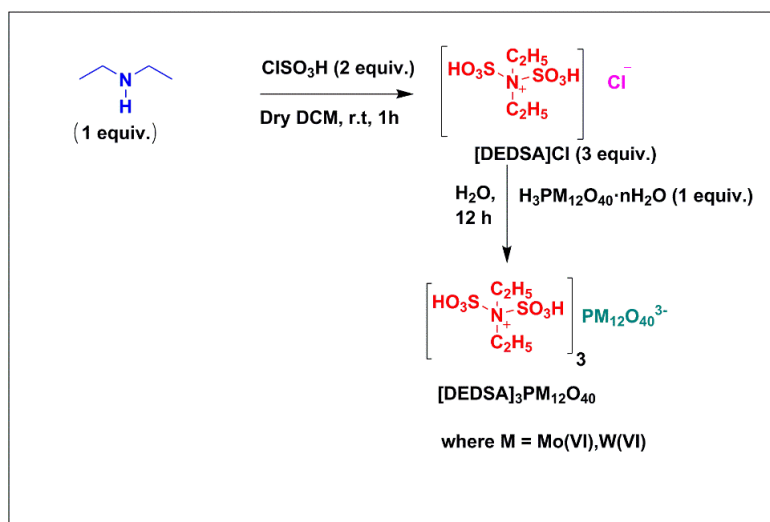
properties while ion exchanging them with polyoxometalates which can turn them into phase transfer catalysts, solvent responsive catalysts, as well as completely heterogenous catalysts. Additionally, designing task specific ionic liquid as metal extractant as well as biphasic extraction solvent was also done with an investigative study of metal extraction.

Chapter 1B: Materials & Methodology

Chapter 1B explains the materials and experimental methods used throughout the research work. For our study two types of Keggin polyoxometalate (heteropolyacids) were selected with general formula $H_3PM_{12}O_{40}$, $M=W$ and Mo . Diethylamine, dibutylamine, 2 methylimidazole were used as the core cations used with specific functionalization for synthesis of the ionic-liquids. This chapter describes different techniques FT-IR, NMR, elemental analysis (CHN, ICP-OES), TGA, Raman, PXRD, UV-DRS, SEM, EDX, AAS, TOC determination, HPLC, GC-MS studies etc. that were utilized for accomplishment of our proposed objectives.

Chapter 2: Solvent responsive self-separative behaviour of Brønsted acidic ionic liquid-polyoxometalate hybrid catalysts on H_2O_2 mediated oxidation of alcohols

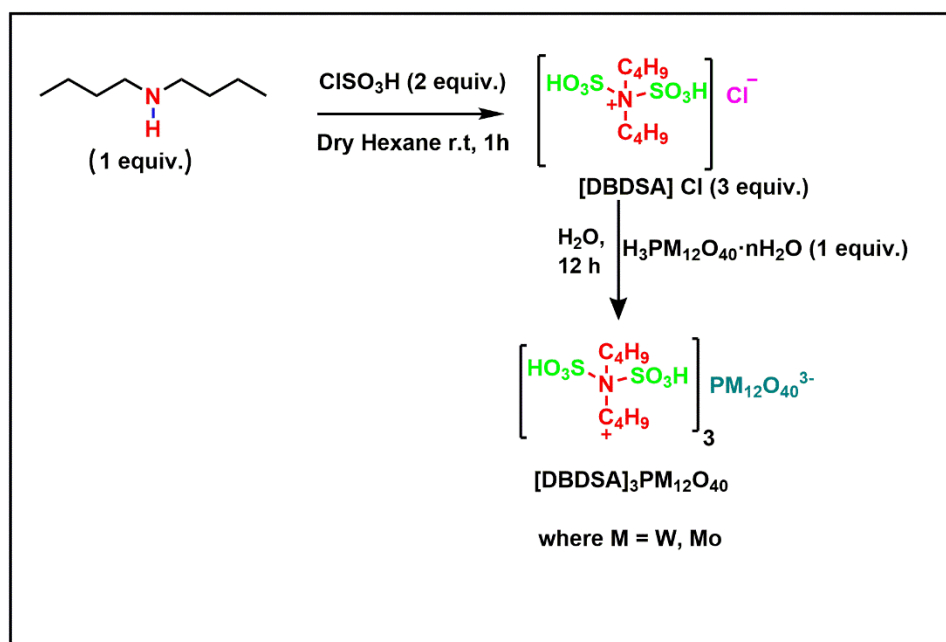
Chapter 2 explains the synthesis of $-SO_3H$ functionalized ammonium based ionic liquid cation combined with Keggin polyoxometalate. $[DEDSA]_3[PW_{12}O_{40}]$ and $[DEDSA]_3[PMo_{12}O_{40}]$ were prepared by anion exchange of diethyldisulphoammonium chloride $[DEDSA]Cl$ with phosphotungstic acid and phosphomolybdic acid respectively. Presence of two hydrophobic ethyl groups tethered to the ammonium cation in combination to Keggin anions along with intermolecular H-bonding interactions involving the $-SO_3H$ groups of the ammonium cation and the POM anion as a whole brings about solvent selective solubility in the hybrids. This IL-POMs based oxidation catalysis facilitate a new type of POM based solvent responsive homogenous to heterogenous phase transfer catalysis process. Due to varied solubility of the hybrids with different solvents, the hybrids can effectively catalyze the oxidation reaction in homogenous condition and then can finally switch back to heterogenous system and convert as self-precipitating catalyst on addition of suitable solvent at the end of the reaction, which made the recovery and reuse of the hybrid very convenient. Properties like water tolerance, high activity, high thermal stability and reusability in these IL-POM hybrid catalytic systems are added advantages in this catalytic system.



Scheme 2.1: Synthesis of [DEDSA]₃PM₁₂O₄₀.

Chapter 3: A mechanistic study on solar energized degradation of herbicide into value-added product using -SO₃H functionalized ionic liquid-polyoxometalate based heterogenous catalyst in aqueous medium

Chapter 3 demonstrates the synthesis of two acidic ionic liquid-based hybrids of polyoxometalate, dibutyldisulphoammonium polyoxometalate, [DBDSA]₃[PM₁₂O₄₀], (M= Mo, W) were prepared by exchanging labile halide ion of parent ionic liquid with Keggin [PM₁₂O₄₀]³⁻ anions. The incorporation of -SO₃H into the ammonium cation results in intra molecular H-bonding with POM anion, which is responsible for preservation of heterogeneity of the catalyst throughout the reaction in aqueous medium. Their catalytic activities were investigated for degradation of metobromuron herbicide in aqueous medium as heterogeneous oxidative catalyst under sunlight using H₂O₂ as oxidant. The isolated active peroxy intermediate was responsible for the reaction. A detailed mechanistic study on degradation of metobromuron into various products at different time intervals was done. The reaction for 8 hours under sunlight removed greater than 70% of TOC and resulted in 1-bromo-4-isocyanatobenzene as the major value-added product. The recyclability experiment showed excellent stability and reusability of the catalyst.

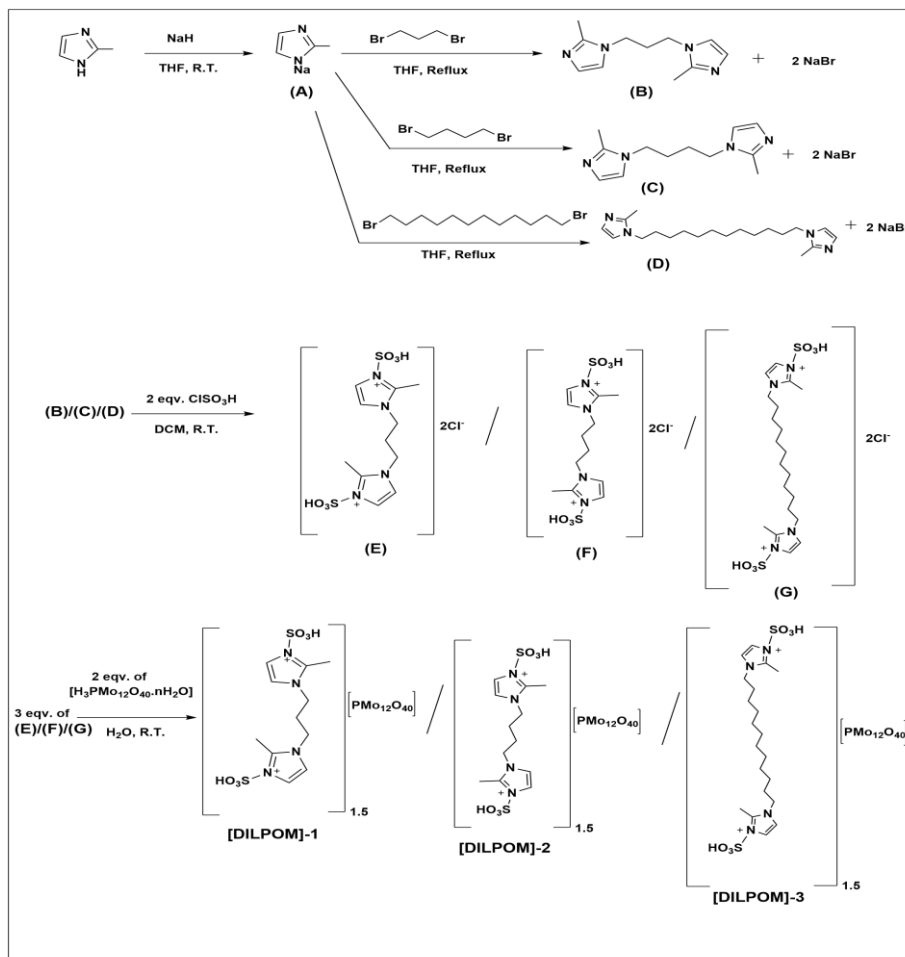


Scheme 3.1: Synthesis of [DBDSA]₃PM₁₂O₄₀ hybrid salt material.

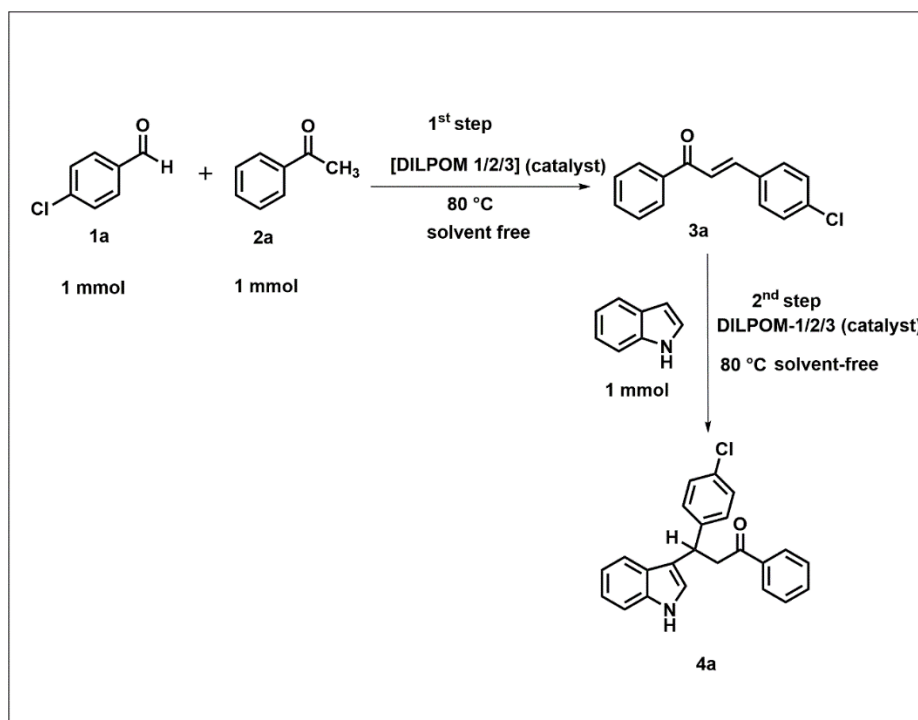
Chapter-4: Study of catalytic activity of methylene bridged dicationic -SO₃H functionalized imidazolium phosphomolybdate hybrids for one pot sequential synthesis of 3-substituted indoles

Chapter 4 explores the catalytic activity of methylene bridged dicationic -SO₃H functionalized imidazolium phosphomolybdate hybrids for one pot sequential synthesis of 3-substituted indoles. Three organic-inorganic hybrids (DILPOM-1/2/3), were synthesized from assembly of -SO₃H functionalized dicationic imidazolium ionic-liquid having variable methylene connecting spacers with inorganic 12-molybdophosphoric acid. DILPOM-1/2/3 are 2-methyl-1-(3-(2-methyl-3-sulfo-1H-imidazol-3-ium-1-yl)propyl)-3-sulfo-1H-imidazol-3-ium phosphomolybdate, 2-methyl-1-(4-(2-methyl-3-sulfo-1H-imidazol-3-ium-1-yl)butyl)-3-sulfo-1H-imidazol-3-ium phosphomolybdate, 2-methyl-1-(12-(2-methyl-3-sulfo-1H-imidazol-3-ium-1-yl)dodecyl)-3-sulfo-1H-imidazol-3-ium phosphomolybdate respectively. Incorporation of various lengths of the connecting spacers make their thermal stability window wider as verified from thermogravimetric analysis and thus can be used as efficient catalysts in high temperature reactions. Extent of hydrogen bond interactions within the -SO₃H group and the PMO₁₂O₄₀³⁻ anion strategically controls the acidic sites. And together with the methylene linkages provide heterogeneous nature to the hybrids making them easily recyclable and thermally stable acid catalyst. The one with longest methylene connecting spacer (n=12), was found to be

more efficient as acid catalyst than the shorter ones towards solvent-free Michael-Like addition of indole with chalcones obtained via Claisen-Schmidt condensation.



Scheme 4.1: Synthesis of [DILPOM]-1/2/3 hybrids.

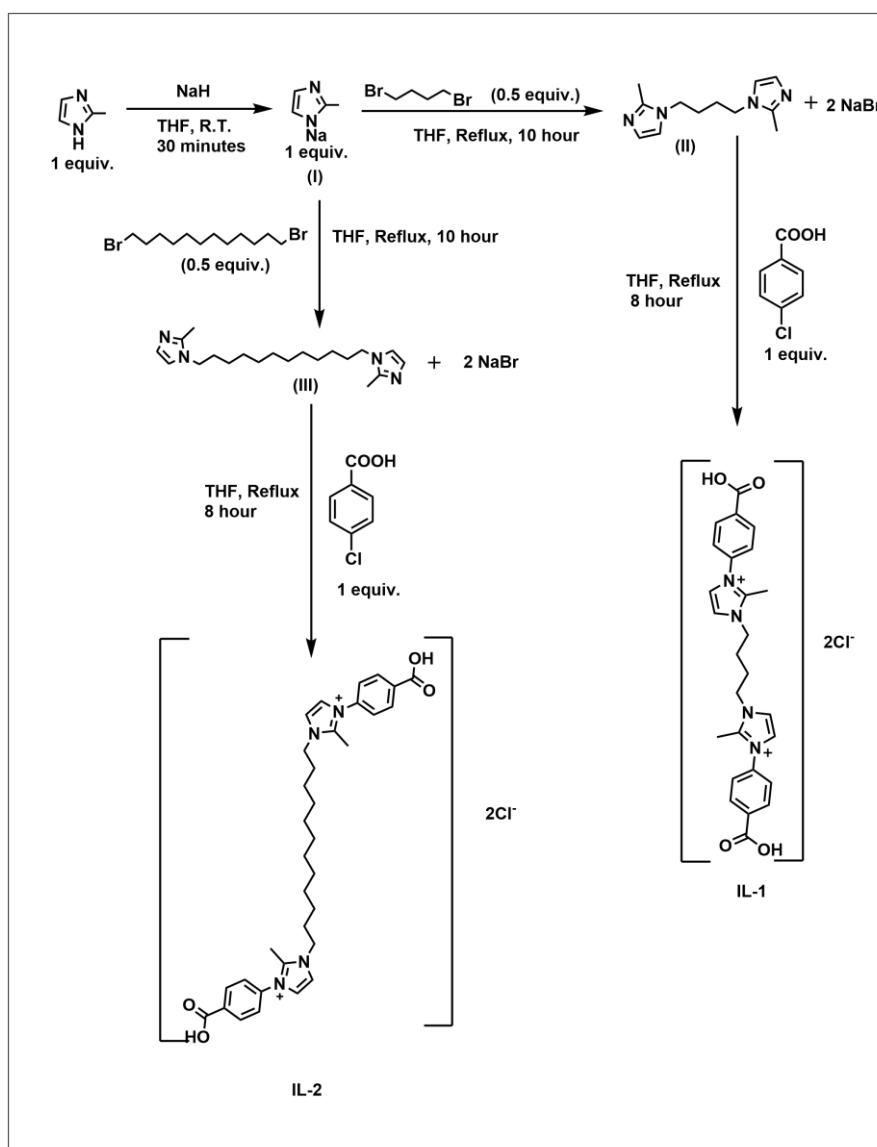


Scheme 4.2: Model reaction for optimization of sequential Claisen-Schmidt condensation followed by Michael-Like addition.

Chapter-5: Investigative study on the dual functional behaviour of dicationic ionic liquid as extractant and hydrophobic biphasic solvent for extraction of Pb(II) in water

Chapter 5 investigates the dual functional behaviour of di-cationic task specific imidazolium ionic liquid as extractant as well as hydrophobic biphasic solvent in Pb(II) extraction from aqueous medium. This work aimed at designing task specific ionic-liquids having limited miscibility with water specifically designed for metal extraction. Water immiscibility in ionic liquids was reached by introducing hydrophobic alkyl spacer ligands connecting the two imidazolium-dication. Furthermore, incorporating carboxylate group via metathesis with *para* chloro benzoic acid and thus addition of an extra phenyl group increases the hydrophobicity preventing solvation of the ionic liquid by water. Two dicationic ionic liquids, **IL-1** named 1,1'-(butane-1,4-diyl)bis(3-(4 carboxyphenyl)-2-methyl-1*H*-imidazol-3-ium) chloride and **IL-2** named 1,1'-(dodecane-1,12-diyl)bis(3-(4carboxyphenyl)-2-methyl-1*H*-imidazol-3-ium)chloride tailored with $(\text{CH}_2)_n$ bridging spacer chains, $n=4$ and $n=12$ respectively were synthesized. The Pb(II) displayed extraction percentages greater than 90% with both the aqueous biphasic system of **IL-1** and **IL-2**. An efficient back-stripping of the Pb(II) metal ion was done using with aqueous

solution of oxalic acid. Calcination of lead oxalate salt obtained showed highest purity of PbO confirmed by PXRD and EDX data. The established experimental condition with the synthesized ionic liquids is a distinguished one as no salting out agent, no extra extracting agents other than the synthesized ionic liquids were used. Moreover, the regeneration of the ionic liquid (**IL-2**), and back stripping of Pb(II) as oxalate salt makes this system an efficient one with negligible loss of the ionic liquid (**IL-2**) into the aqueous medium thus obliging the standards of environment-friendly sustainable development.



Scheme 5.1: Synthesis of IL-1 and IL-2.

Chapter 6: Conclusions and future scopes

Ultimately, **chapter 6** delivers the summary on all the task specific ionic liquids and ionic-liquid based polyoxometalate hybrids those were designed to perform certain types of experiments. After taking a literature survey, the present study explores on designing entirely new sets of TSILs and IL-POM hybrids that are designed to show different characteristic properties based on their structure, the kind of interactions between organic and inorganic units as well as their solvent environment. In order to achieve the goal, ammonium and imidazolium cationic core were selected with functionalization by -SO₃H group as well as -COOH group. For oxidation reactions, Keggin polyoxometalate anions were hybridized with disulphodialkylammonium cation which displayed a solvent responsive solubility resolving the high solubility issue of pure Keggin polyoxometalate. We then present a comprehensive study on the design of Bronsted acidic dicationic imidazolium ionic liquid with variable lengths of methylene alkyl bridge connecting the imidazolium cations for enhancing the hydrophobicity in the catalyst. The combined effect of Bronsted acidity with the variable lengths of methylene chains of the dicationic IL-POMs were explored for synthesis of 3-substituted indole derivatives. By the same token, we proposed designing ionic liquid with limited miscibility in water for biphasic metal extraction from aqueous medium. Incorporating phenyl and carboxylate group into alkyl bridged imidazolium dicationic core rather than sulphonic group completely changed the water sensitivity and solubility of the synthesized ionic liquids. The present work may lead us to wider interest in tuning and designing ionic liquids that specifically satisfies the demands of the task of interest. It may direct us to resolve major issues such as solubility, stability, recyclability, easy recovery and also metal extraction from aqueous medium. Undoubtedly, the results discussed herein may have a broad significance on planning and developing catalytic systems out of ionic liquid that can perform catalytic activities depending upon the user's need for the desired physical, chemical and biological properties. The present report gives an emphasis on the development of TSILs based on the application demand.

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