

# **Strategic design and utilization of task-specific ionic liquids and ionic liquid-polyoxometalate hybrids**

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## *Chapter-6*

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# Conclusions and Future Scopes

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## 6.1 Conclusions

As discussed in the preceding chapters, TSILs are an important class of ILs as it is possible to synthesize ILs with specific compositions to impart desired properties and reactivities. It was observed that the incorporation of functional groups into the ILs modifies the solvent parameters of the ILs. The inclusion of functional groups and the overall composition of the ionic liquid change properties like polarity, viscosity, hydrogen bonding ability, acidity etc. Furthermore, it was also observed that the functional group can catalytically activate the substrate and hence help the reaction to proceed.

Above all green and solid catalysts are preferred more in industries for their heterogeneous nature. Therefore, the solidification of ionic liquids by various means has drawn great attention. Therefore, this thesis explores a method of solidification of the ionic liquids by electrostatically exchanging labile halide anions of the ILs against inorganic Keggin anions. Herein Keggin polyoxometalates are chosen as an anion of interest keeping in mind the reactions to be performed and the remarkably tuneable properties of POMs. The combination of TSILs and Keggin polyoxometalate was an approach to integrate the advantages of both heterogeneous and homogeneous catalysts. This thesis also delivers the concept of carrying out experiments by synthesizing TSILs and IL-POM hybrids as metal-extracting solvents or catalysts with desired properties for the reaction under study. The activity of ILs and hybrids with different solvents was also studied.

To accomplish our 1<sup>st</sup> objective, we designed and presented two solvent-responsive thermally stable -SO<sub>3</sub>H functionalized ammonium-based Keggin polyoxometalate hybrids, [DEDSA]<sub>3</sub>[PMo<sub>12</sub>O<sub>40</sub>] and [DEDSA]<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>]. The introduction of sulfonic groups and hydrophobic groups i.e. ethyl groups in the cationic counterpart and their interactions like H-bonding, ion-dipole interactions etc. with the anion as well as solvent molecules resulted in solvent responsive nature in the hybrids. The ability of solvent selective solubility and precipitation of the catalysts proved as a great advantage while separating the catalysts from the reaction medium. And this property also led to generation of two solvent-responsive phase transfer catalysts. Both the catalysts were used as efficient catalysts for oxidation of substituted benzylic alcohol to aldehydes and acyclic secondary alcohol to keto compounds using hydrogen peroxide as a green oxidant in CH<sub>3</sub>CN. The catalysts were inactive for oxidation of cyclic secondary alcohol.

It also acted as chemoselective oxidant for oxidation of secondary alcohol containing double bond to keto compound with rearrangement of the double bond in  $\alpha$ ,  $\beta$  position to the carbonyl group. Because of the high thermal stability, high catalytic activity and ease in recovery and reuse, this protocol is an environment-friendly one for oxidation of alcohols to aldehydes and ketones. Thus, it was possible to design solvent-responsive self-separative catalysts with strategic design of cationic core by inclusion of proper functional groups and alkyl substituents in IL-POM hybrids.

By the same token, in order to carry out our 2<sup>nd</sup> objective, two water-insoluble heterogeneous IL-POM catalysts, [DBDSA]<sub>3</sub>[PMo<sub>12</sub>O<sub>40</sub>] and [DBDSA]<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>] with dibutyl disulfoammonium cation were synthesized. Both served as efficient oxidative degradation catalyst for degradation of phenyl urea herbicide when used with H<sub>2</sub>O<sub>2</sub> as oxidant in presence of sunlight in aqueous medium. This research may supply new insight into development of functionalized heterogeneous IL-POM systems, which is cost effective in which heterogeneity is preserved throughout the reaction in aqueous medium. Study of advanced oxidation activity of IL-POM hybrids in aqueous medium was possible without having any trouble in loss of heterogeneous nature. The reaction resulted in 1-bromo-4-isocyanatobenzene as the major product which is a value-added product as it is used as one of the substrates for synthesis of various unsymmetrical disubstituted urea derivatives by many scientists [1]. The efficiency of these catalysts, both in presence and absence of sunlight was monitored by the results obtained from TOC removal data. The strong electrostatic interactions, hydrogen bonding within -SO<sub>3</sub>H functional group and POM anion are the main driving forces for the structural stability of the hybrid materials and retention of heterogeneity throughout the reaction. The ability to design and incorporate functional groups into parent ionic liquid cation that serves the purpose specific to the need of task provides great potential in usage of these functionalized IL-POM hybrids as oxidative catalyst in presence of H<sub>2</sub>O<sub>2</sub> as oxidant. This method proves to be an eco-friendly approach in degradation studies of phenylurea (metobromuron) herbicide in aqueous medium.

Altogether, while accomplishing our first two objectives and from the data obtained from chapter 2 and 3, it was concluded that a calculated change in structure and strategic inclusion of substituents in the parent ILs hugely impacts the overall physical and chemical properties of any TSILs as well as TSILs derived organic-inorganic hybrids. The

reactivities of TSILs and IL-POM hybrids with different structures and influence of solvents on the solubility of these materials due to interactions present were explored. From this study, it is seen that reactivities of IL-POM hybrids with H<sub>2</sub>O<sub>2</sub> as oxidant in water and the other one in acetonitrile as two different solvents was different. This is based on the theory that the hydroxyl radicals if generated in oxidation reactions are stabilized by hydrogen bonding to water which is not possible while using acetonitrile as solvent [2].

The 4<sup>th</sup> chapter discusses the synthesis and characterization of -SO<sub>3</sub>H functionalized three organic-inorganic solid hybrid materials of IL-POM [DILPOM-1/2/3] with variable lengths of the methylene bridged imidazolium dications and Keggin anion [PMo<sub>12</sub>O<sub>40</sub>]<sup>3-</sup>. For these three organic-inorganic solid hybrid materials, [DILPOM]-1 as 2-methyl-1-(3-(2-methyl-3-sulfo-1H-imidazol-3-ium-1-yl)propyl)-3-sulfo-1H-imidazol-3-ium phosphomolybdate, [DILPOM]-2 as 2-methyl-1-(4-(2-methyl-3-sulfo-1H-imidazol-3-ium-1-yl)butyl)-3-sulfo-1H-imidazol-3-ium phosphomolybdate, [DILPOM]-3 as 2-methyl-1-(12-(2-methyl-3-sulfo-1H-imidazol-3-ium-1-yl)dodecyl)-3-sulfo-1H-imidazol-3-ium phosphomolybdate were synthesized with variable lengths of the methylene bridged imidazolium dications and Keggin anion [PMo<sub>12</sub>O<sub>40</sub>]<sup>3-</sup>. The cationic composition in the organic part of the hybrid and the interactions of -SO<sub>3</sub>H functional groups present with the anionic PMo<sub>12</sub>O<sub>40</sub><sup>3-</sup> results in the overall acidity, solubility in solvent. Since the cationic part comprises of the -SO<sub>3</sub>H group, so the cationic part is responsible for the general acidity in the hybrid. Presence of acidic sites in the hybrids were determined by NH<sub>3</sub>-TPD and FT-IR studies using pyridine as probe molecule. [DILPOM]-3 was observed to show highest yield of 3-substituted indoles compared to [DILPOM]-1 and 2. These results infer that due to presence of longer carbon chain in [DILPOM]-3, steric hindrance increases which weakens the interactions between the subunits resulting in a greater number of free -SO<sub>3</sub>H groups which resulted in highest acidic sites in [DILPOM]-3. The catalytic activity of these acidic heterogeneous hybrids was explored in the sequential Claisen-Schmidt condensation followed by Michael-Like addition of indole with chalcone to prepare 3-substituted indoles as single product in one pot method without isolation of the intermediate chalcones using 10 mol % of the catalyst at 80 °C within 3-4 hours for different substrates in neat conditions. The catalyst was recycled for four runs and slight decrease of catalytic activity was observed. No oxidative products were isolated during reaction which clearly displayed preferential role of Brønsted acidity of the hybrid for the acid catalysed reaction. The acidic nature of the IL-

POM hybrids can be explored to conduct variety of Brønsted acid catalysed organic reactions. However, structural change of the catalyst over 4<sup>th</sup> catalytic cycle was observed in this case.

From chapter 2, 3, 4, we can conclude that the composition and design of the ionic liquid cation and their interactions with polyoxometalate anion have a great impact on their resultant physical and chemical properties, their structural and thermal stability, stimuli responsive nature, hydrophobicity etc. And these properties can be modified by varying the composition of ions in ILs and IL-POM hybrids.

In chapter 5, our objective was to design a type of extractant and biphasic hydrophobic solvent for extraction of metals in water that can replace organic solvents used conventionally for this purpose. To achieve this goal, we synthesized two 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-(4 carboxyphenyl)-2-methyl-1*H*-imidazol-3-ium)chloride. TSILs with inbuilt carboxylic acid chelates and limited water miscibility which is a necessary condition for metal extraction from aqueous medium was achieved. The hydrophobicity in both the ionic liquids are introduced because of hydrophobic alkyl spacer ligands added while designing cationic part and extended intramolecular hydrogen bonding. An investigative study was performed on the dual functional behaviour of di-cationic task specific imidazolium ionic liquid as extractant as well as organic phase to extract Pb(II) from aqueous solution of Pb(NO<sub>3</sub>)<sub>2</sub>. Greater than 90% extraction efficiency was observed with both the ionic liquids as biphasic extraction solvent in this case. Apart from that, comparative and selective extraction experiments of Pb(II), Ni(II) and Co(II) also showed the highest extraction percentage for Pb(II) in comparison to Ni(II) and Co(II), using very less amount **IL-2**. The results obtained from FT-IR spectra suggested metal exchange via deprotonation of carboxylic acid functional group in the IL forming a hydrophobic metal-IL complex, solubilized in ionic liquid phase. The **IL-2** was extracted back in DCM and evaporation of the solvent under reduced pressure reproduced the **IL-2** back which was reused in the next cycle. Moreover, the metal oxalate salt obtained via oxalic acid precipitation method is also calcinated to its oxide. Thus, the metal extracted from water is converted into its oxide form thus reducing the metal waste which can be used in fields like in battery uses. None of the compound goes into the sink as the extracted metal is also converted into its oxide in its purest form. The

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task-specific ionic liquid designed is quite efficient for extraction, as metal is extracted at a high extraction percentage and the back extraction with oxalic acid do not destroy the TSIL (**IL-2**). This study thus concludes that use of long alkyl chain spacer in dicationic imidazolium based ionic liquids with inbuilt carboxylic acid functionalization as observed in **IL-2** served as a good choice for extraction of the Pb(II) metal ion from aqueous medium.

## 6.2. Future scopes

Task specific ionic liquids have extensive range of properties and applications to be explored and have enormous possibilities of growth in near future. Similarly, POMs possess properties that have great usage in electrochemical, catalytic, energy conversion and storage, molecular magnetism [3]. POMs in their pure solid and crystalline state have many limitations because of their restricted processability. In this context modification of POMs into different forms for e.g. gel nature, thermo-responsive nature, stimuli responsive solubility etc. results in wide applicability of POMs. One way to do this is by modification of POMs with specifically designed series of IL based functionalized cations to prepare new types of hybrid materials [4].

i. With a huge library of cations and anions present to synthesize plenty of structures of TSILs, fine tuning of properties like viscosity, hydrophobicity, structural stability etc. have unknown potentials yet to get explored as extractants. In order to use these TSIL based extraction systems to find implementation in industrial separation and purification, proper choice of cation and anion for designing TSILs, checking cost of synthesis are needed. These extraction systems have great potential to replace conventional solvents used for liquid-liquid extraction commercially in future [5].

ii. Modification of POMs by ionic liquid cations leads to generation of new POM functionalized hybrids with gel type nature [4,6,7]. These gel type materials can be easily shaped and proper tuning of the cationic core of ionic liquids can bring characteristic properties in the resultant hybrids like temperature responsive behaviour. Synthesis of these soft materials are important because they can be used as electrolytes and in electrochemical capacitors and fuel cells etc. [8,9].

iii. Nowadays studies are going on synthesis of ionic liquids with specific cationic core, substituents, and their confinement into nanopore. These studies are relevant as

TSILs and POM-ILs have potential application in electrochemical double layer capacitors (EDLCs) [10-17]. As EDLCs have structure similar to batteries can complement the capabilities of internal combustion engines, fuel cells, and batteries in hybrid vehicles, industrial equipment, and electronic devices. Therefore, understanding the thermal properties like melting range, ion conductivity, etc. of ILs and POM-ILs confined into nano-pore help in usage of such systems in electrochemistry [18]. Understanding the behaviour of ILs confined inside nanopores is also relevant to the development of nanoparticles based on organic salts [19,20]. These nanomaterials have potential uses in biomedical applications ranging from magnetic hyperthermia cancer treatment to medical imaging [21-25].

iv. Lastly, the acidic or basic functionalization in TSILs can be extended for synthesis of biologically relevant heterocyclic compounds via multicomponent approach.

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