Abstract

The concept of Green Chemistry has become quintessential for encouraging sustainable development in laboratories and industries. The twelve principles of green chemistry provide the basic framework for actions that can be taken to make chemical processes and products more environmentally benign. One of the twelve principles of green chemistry states that the use of auxiliary substances such as solvents and separation agents should be made unnecessary and if used should be innocuous. Throughout the recent decades it has been established that conventionally used organic solvents such as halogenated hydrocarbons, n-hexane, tetrachloroethylene, benzene, toluene etc. pose crucial environmental and human health concerns which include atmospheric emissions, contamination of water bodies, carcinogenic risks, reproductive hazards, neurotoxic threats etc. From this perspective, ionic liquids have emerged as a promising environmentally benign alternative to volatile organic solvents.

Ionic liquids comprise an extremely broad class of organic salts and possess wide temperature windows to remain in liquid state. The term “room temperature ionic liquids” (RTILs) is used to represent organic salts which are liquid at room temperature. Ionic liquids (ILs) are also known by several different names like neoteric solvents, designer solvents, ionic fluids, and molten salts. The main advantage of ILs is that their physicochemical properties like polarity, melting points, hydrophobicity, density, ionic conductivity, viscosity, thermal stability, water sensitivity, electrochemical stability, ability to dissolve different solutes as well as miscibility with varied nature of solvents can be tuned by making suitable combinations of organic cations and organic/inorganic anions or through tethering of functionalized side chains to the ions. This has earned them the accolade of ‘designer solvents’ and it is often utilized to design and synthesize ILs for specific uses known as ‘task-specific ionic liquids’ (TSILs). Some of the commonly used organic cations in the ILs are imidazolium, ammonium, pyridinium and phosphonium cations and they are often combined with different inorganic (Cl^-, BF_4^-, PF_6^-, Br^-, OH^-, NO_3^- etc.) and organic (CH_3COO^-, CF_3COO^-, Tf_2N^-, OTf^- etc.) anions. Another important class of ionic liquids is the halometallates. They are usually obtained from reaction between a halide containing IL and a Lewis-acidic metal halide at various molar ratios and are usually solid or semi-solid in nature. The halometallate ionic liquids are generally synthesized from the halides of transition metals like Al, Zn, Sn, Ga, Fe, Co, Ni and lanthanides. Presence of the complex metal halide ions provides the halometallate ILs with an electron accepting ability and hence, they are generally Lewis acidic in nature. However, in the recent decades, dual-functionalized halometallate ILs were developed containing both the Brønsted and Lewis acidic functions. The Brønsted acidity in these halometallate ILs comes from the attachment of functional groups like –SO_3H or –COOH to the organic cations. In comparison to the Lewis-acidic halometallate ILs, the existence of Brønsted acidic function in the organic cation enriches them with several advantages such as higher thermal stability, moisture stability, semi-solid/solid state, higher melting points etc.

In the recent past, ILs have been perceived as a class of prospective material with unique physicochemical properties that originate from their significantly wide range of cation-anion pair combinations at room temperature, their inherent binary nature, the coexistence of distinct local molecular environments that can be controlled through substitution, their complex transport properties, and many other intriguing properties. The ILs have found potential applications in different fields catalysis, analytical chemistry, biomass conversion, nanotechnology, sensors, energy conversion device, polymer science, pharmaceuticals etc. In this context, an in-depth study into the unique physicochemical properties of the ILs which are regulated by their constituent ions can be very beneficial in identification of their specific applications as catalysts, reaction medium, solvents, electrolytes, separation media etc. The present work delves into the synthesis, characterization (NMR, FT-IR, CHN elemental analyses, TGA etc.) and investigation of the various physicochemical properties (conductivity, polarity, thermal stability, acidity, density, electrochemical stability) of N-SO_3H functionalized imidazolium and ammonium cation based Brønsted acidic ionic liquids (BAILs). The variation in the mentioned physicochemical properties of the BAILs with the alteration in factors like nature of constituent cation (alkyl substituted/unsubstituted imidazolium and ammonium), type of anion (Cl^-, BF_4^-, CF_3COO^-,OTf^- etc.), temperature, solvent etc. were studied in detail. Based on the knowledge obtained about various physicochemical properties of the N-SO_3H functionalized BAILs like acidity, thermal stability, polarity, electrochemical stability etc. these BAILs were employed as recyclable catalysts in one-pot sequential Michael-like addition of indole with chalcones via Claisen-Schmidt condensation and one-pot sequential synthesis of 2-amino-3-cyanopyridines. The organic products synthesized belong to classes of compounds having numerous biological and pharmacological properties. Additionally, two new members of dual-functionalized Brønsted-Lewis acidic chloronickellatellate ionic salt systems were developed by incorporating two –SO_3H groups into the imidazolium cation.

These chloronickellate ILs were then utilized as precursors/templates in the synthesis of nickel sulphide nanoparticles. The chloronickellate ILs and the nanoparticles were successfully characterized by various analytical techniques like ^1H NMR, ^{13}C NMR, FT-IR, TGA, RAMAN, PXRD, Mass-spectrometry, TEM, SEM, EDX, UV-Vis spectroscopy, DRS- spectroscopy, BET etc. The nickel sulphide (NiS) nanoparticles were further explored as heterogeneous catalysts in the solar energized degradation of organic dyes methylene blue, methyl orange, malachite green, crystal violet and their mixtures.

The current thesis is divided into seven chapters, four of which summarizes the research findings. The conclusion and future prospective of the study are addressed separately in the end of the thesis in chapter seven.

Chapter 1: General Introduction and Review of Literature

Chapter 1 provides a brief overview on the field of ionic liquids (ILs), including their different classifications and applications. Additionally, it provides a comprehensive review on the unique physicochemical properties of the ILs, like conductivity, viscosity, thermal stability electrochemical stability, acidity, density, surface tension and surfactant properties. A brief discussion on the application of ILs as catalysts in the synthesis of organic products like chalcones, substituted indoles and pyridines is also given. It also further discusses the use of ILs as solvents, templates or precursors in the synthesis of nanoparticles.

Chapter 2: Objectives and Methodology

Chapter 2 presents the objectives of the current thesis. Additionally, it briefly explains general spectroscopic and analytical techniques employed for characterization of synthesized functionalized room temperature ionic liquids (RTILs), halometallates, organic products along with study of physicochemical properties of the ILs. The structures of the synthesized ILs and organic products were confirmed using FT-IR, NMR (^1H, ^{13}C & ^{19}F) spectra and CHN elemental analysis. Additionally, ESI-Mass spectrometry was employed to determine the complex metal halide anionic speciation of

the halometallates. Thermal stability and Brønsted acidity of the functionalized ionic liquids were investigated by thermogravimetric analysis (TGA) and UV-Vis spectroscopy respectively. The electrochemical stability windows (ESW) of the RTAILs in molecular solvents were determined using Cyclic Voltammetry (CV) technique. The conductivity measurements of the ILs in molecular solvents were performed using a digital conductivity meter. Fluorescence spectroscopy was used to determine the polarity of two representative ILs by recording their emission spectrum with pyrene as a probe molecule. Their densities were measured using a pycnometer. The characterization of nickel sulphide nanoparticles synthesized using the halometallate ILs were done by using analytical techniques like FT-IR, RAMAN, PXRD, SEM, EDX, TEM, BET surface area analysis, XPS, TGA and UV-Visible diffuse reflectance spectra (UV-DRS).

Chapter 3: Investigation of the Physical and Electrochemical Behaviour of Direct N-SO_3H Functionalized 1, 3-Disulfo-2-alkyl-imidazolium Trifluoroacetate Ionic Liquids in Molecular Solvents

Chapter 3 discusses the synthesis and characterization of four direct N-SO_3H functionalized 1, 3-disulfo-2-alkyl-imidazolium trifluoroacetate ionic liquids. Detailed investigation on the effects of C-2 alkyl substituent of 2-alkyl (or H)-1, 3-disulfoimidazolium trifluorocetate [RSIM][TFA] ionic liquids (where R = H, CH_3, C_2H_5 and n-C_4H_9) on the values of their ionic conductivity and electrochemical stability window (ESW) in the two molecular solvents MeOH and MeCN were carried out. Further, the effects of the C-2 alkyl substituent of these ILs on their density, thermal stability and Brønsted acidity were also evaluated. Results obtained suggested higher electrochemical stability of the ethyl and n-butyl substitued imidazolium ILs. It was observed that, the sizes of bulkier alkyl substituents decreased the density and conductivity of the [BDSIM] [TFA] and [EDSIM][TFA] ILs. Surfactant like property of these ILs was responsible for the increasing conductivities of IL-molecular solvent mixtures with increasing IL concentration and then showing a gradual decrease after attaining the critical aggregate concentration (CAC) of the ILs. Additionally, the increase in temperature decreased the ionic conductivities of the ILs because of their self-aggregation. +I inductive effect of the C-2 alkyl groups decreased their Brønsted acidity. The Kamlet-Taft solvatochromic parameters of the molecular solvents were used as their polarity indicators and were used to justify the variation of the conductivity values of the

ILs in them. The ILs showed higher ionic conductivities in the polar protic solvent MeOH. However, their electrochemical stability was more in the aprotic MeCN. This research assisted in understanding the effect of $–SO_3H$ group as well as alkyl substituents on the physicochemical properties of imidazolium ILs and the interactions between the molecular solvents with the constituent ion-pairs of the ILs.

Chapter 4: Comparative Study on the Physicochemical Properties of N-SO_3H Functionalized Ammonium and Imidazolium Based Brønsted Acidic Ionic Liquids

Chapter 4 explores the effects of varied combinations of cations (2-ethyl-1,3-disulfoimidazolium, N, N-disulfodiethylammonium and N, N-disulfodibutylammonium) and anions (Cl^-, CF_3COO^-, OTf^-, BF_4^-) on the physicochemical properties of ILs like density, Brønsted acidity, ionic conductivity, electrochemical stability window (ESW), polarity, moisture sensitivity and thermal stability of the ionic liquids. The ionic conductivities and electrochemical stability windows (ESWs) of the 12 Brønsted acidic ionic liquids (BAILs) were measured in three molecular solvents acetone, MeCN and MeOH. The variation of conductivity values of binary mixtures of ILs were correlated to the Kamlet-Taft solvatochromic parameters of these molecular solvents. The results showed that N, N-disulfodiethylammonium [DEDSA] and 2-ethyl-1,3-disulfoimidazolium [EDSIM] BAILs have similar Brønsted acidities. The increase in the alkyl chain length increased the electrochemical stability of the N, N-disulfodibutylammonium [DBDSA] ILs in the molecular solvents compared to the [DEDSA] ILs. Among the three series of ILs, the imidazolium based ILs ([EDSIM] series) showed the highest conductivity in the three molecular solvents, which was followed by the [DEDSA] series and then the [DBDSA] series. The [EDSIM] ILs also showed higher densities compared to the other two IL series. The BF4- and OTf- anion containing ILs showed lower thermal stabilities due to the weakly coordinating nature of the anions. The pyrene fluorescence emission spectra of [EDSIM][Cl] and [EDSIM][TFA] showed a broad structureless band corresponding to excimer emission with its peak around 440-450 nm confirming their highly polar nature, responsible for stabilising the excimer state of pyrene. This research helped in correlating the change in the 6 physicochemical properties of the ILs with the change in molecular structures of the constituent ions and the interactions of constituent ion-pairs of the ILs with the molecular solvents.

Chapter 5A: N-SO_3H functionalized Imidazolium Ionic Liquids Catalysed Sequential Michael-like Addition of Indole with Chalcones via Claisen-Schmidt Condensation

Investigation of the physicochemical properties of the N-SO3H functionalized imidazolium ILs in **chapter 3** revealed their high thermal stability and Brønsted acidity. In **chapter 5A**, we utilized these traits of the N-SO3H functionalized imidazolium BAILs i.e. 2-methyl/2-ethyl-1,3-disulfoimidazolium carboxylate ionic liquids [MDSIM][X] and [EDSIM][X], (where, X = CF_3COO^- (TFA), CCl_3COO^- (TCA), CH_3COO^- (OAc)) for their catalytic application in the sequential Michael-like addition of indole with chalcones via Claisen-Schmidt condensation. Among the six BAILs, [MDSIM][TFA] was found to be the best catalyst. Chalcones formed in the first step of this reaction are known precursors of several heterocycles like oxazoles, isoxazoles, thiazoles etc. The final products of this reaction were 3-substituted indoles which are known to have numerous biological activities. The one-pot approach along with the solvent-free conditions, higher product yields and selectivity, absence of complicated chromatographic separation techniques and toxic solvents/reagents, and shorter reaction time make this approach compliant with protocols of Green Chemistry. 7

Chapter 5B: N-SO_3H Functionalised Ionic Liquid Catalysed Sequential One-Pot Multicomponent Synthesis of 2-Amino-3-cyanopyridines

Chapter 5B compares the catalytic efficiencies of N-SO_3H imidazolium, dibutylammonium and piperizinium based BAILs in one-pot multicomponent synthesis of 2-amino-3-cyanopyridines. The chapter further highlights the use of chalcones as precursors for the synthesis heterocycles. The four BAILs used in this work were N, N, N’, N’- tetrasulfopiperazinium chloride $[TSPi][Cl]_2$, 1,3-disulfoimidazolium trifluoroacetate [DSIM][TFA], 2-ethyl-1,3-disulfoimidazolium trifluoroacetate [EDSIM][TFA], and N,N-dibutyl-disulfo-ammonium trifluoroacetate [DBDSA][TFA]. Among these BAILs, $[TSPi][Cl]_2$ was found to be the most effective catalyst. The products 2-amino-3-cyanopyridine derivatives are known for their various pharmacological properties. This method utilizes the dual solvent-catalyst role of the BAILs and exhibits a broad substrate scope. The catalyst could be easily recycled and reused for at least three times without a significant loss of activity. The multicomponent “one-pot” approach utilized here offers various other advantages like operational simplicity, selective formation of products, minimization of waste generation, shorter reaction times, higher yields, and energy efficiency.

Chapter 6: Investigation of Photocatalytic Activities of Nickel Sulphide Nanosheets Synthesized using Imidazolium Based Chloronickellate Ionic Liquids as Precursor/Template for Photocatalytic Degradation of Organic Dyes

In **Chapter 6**, two new bifunctional Brønsted-Lewis acidic chloronickellatellate ionic salt systems 1a & 1b ($[RSIM]_x[NiCl_y]$, where R = C_2H_5 & CH_3, x = 2, y = 2,3,4 or 5) were developed by incorporating two $–SO_3H$ groups into the imidazolium cation. These chloronickellate ILs were then utilized as precursors/templates for the synthesis of nickel sulphide nanoparticles using a simple grinding method (Scheme 3). Although, there are previous reports available on the synthesis of nickel/nickel sulphide/nickel oxide nanoparticles using ionic liquids as solvents, but no reports on the use of chloronickellate ILs as precursors/templates for the synthesis of nickel sulphide nanoparticles are available till date. The synthesized nickel sulphide nanoparticles were characterized using various analytical tools. The EDX and XP spectra of the nanoparticles confirmed the presence of both nickel and sulphur. The PXRD pattern of the synthesised nanoparticles indicated the existence of both rhombohedral β-NiS phase and orthorhombic α-NiS phase. The TEM analysis revealed the formation of nickel sulphide nanosheets with average particle size between 20-35 nm. The surface area values of the nanoparticles 2a and 2b were evaluated from their nitrogen adsorption-desorption isotherms and were found to be 22.27 m^2/g and 13.68 m^2/g respectively. The estimated band gap value of 2a was found to be 2.39 eV and that of 2b was found to be 2.8 eV. Based on these results, the nanoparticles 2a and 2b were used as photocatalysts in the degradation of organic dyes (MB, MO, CV, MG and their mixtures) under sunlight where 2a exhibited slightly better catalytic activity compared to 2b.

Chapter 7: Conclusion and Future Scope

Chapter 7 summarises the research outcomes of the chapters 3,4,5 and 6. It also discusses the future prospects of ionic liquids and their applications in different fields.

Keywords: *Ionic liquids, Task-specific ionic liquids (TSILs), Room-temperature acidic ionic liquids (RTAILs), Brønsted acidic ionic liquids (BAILs), -SO_3H functionalized ionic liquids, Chloronickellate ionic liquids, Imidazolium ionic liquids, Ammonium ionic liquids, Physicochemical properties, Tunable properties, Surfactant-like properties, Critical aggregate concentration (CAC), Ionic conductivity, Hammett acidity, Electrochemical stability window (ESW), Recyclable catalyst, Chalcones, 3-substituted indoles, 2-amino-3-cyanopyridines, Nickel sulphide nanoparticles, Photocatalyst*