Chapter 2

Objectives and Methodology

2.1 Objectives of the present work

As already discussed, ionic liquids (ILs) owing to their unique physicochemical properties have evolved as environmentally friendly alternatives to volatile organic solvents [1,2]. The name 'designer solvents' has been allotted to the ILs because of their unique ability to tune their physicochemical properties like polarity, hydrophobicity, ionic conductivity, viscosity, thermal stability, water sensitivity, electrochemical stability, solubility of diverse solutes in them, and miscibility/immiscibility with a wide range of solvents by making suitable combinations of cation and anion or by functionalizing the side chains of the ions [3-6]. Based on this context, the recent years have seen the development of a specific class of ionic liquids called the 'task-specific ionic liquids' (TSILs). TSILs are synthesized with specific properties for applications in a particular field like catalysis [7-11], analytical chemistry [12], biomass conversion [13.14], nanotechnology [15,16], sensors [17,18], energy conversion device [19], polymer science [20], pharmaceuticals [21] and so on. Most of these TSILs have a functional group anchored to the cation or anion of an ionic liquid. Based on the nature of the functional group attached to it, the TSILs can be acidic, basic, chiral, metal-containing, or polymeric [8, 9, 22-25]. Furthermore, these TSILs have become attractive candidates for catalysts in the field of organic synthesis because of the several advantages they provide like green reaction conditions, higher product yield, higher product selectivity, easy work-up procedures, energy efficient processes etc. [4, 7-10, 26-28].

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 the 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. Chalcones are biologically viable compounds having versatile pharmacological activities such as antibacterial, antituberculosis, antifungal, antimalarial, antiviral, antioxidant, anti-inflammatory, and anticancer [29-32]. They are also precursors for formation of flavonoids and isoflavonoids. The traditional synthetic routes of chalcones involving Claisen-Schmidt condensation between acetophenone derivatives and aromatic aldehydes involve strong acidic or basic reagents/catalysts like NaOH, KOH, $AlCl_3$ HCl etc [32-35]. These methods have some serious drawbacks like catalyst recovery, less product selectivity, longer reaction time, extreme reaction conditions and complex work-up procedures, formation of side products etc [33,35]. The BAILs catalysed synthesis of chalcones however overcomes all these shortcomings by providing a green and efficient procedure as well as high product selectivity in the formation of Michael addition products. Moreover, the Michael addition products of chalcones with indole are found abundantly in nature as flower scents, perfume coal tar etc. and are known to possess antiviral, antifungal, antimicrobial, anti-inflammatory and analgesic activities [36-38]. Similarly, the pyridine ring is an important scaffold in heterocyclic chemistry due to its presence in many significant biological molecules like Vitamin B6, nicotinic acid, dipicolinic acid etc. Moreover, the substituted pyridines like the 2-amino-3-cyanopyridines have garnered considerable research interest as they are known to exhibit anti-bacterial activity, IKK-β inhibition, A_{2A} adenosine receptor antagonistic properties, HIV-1 integrase inhibition, carbonic anhydrase inhibition, antifungal, anti-inflammatory, anticancer and anti-parkinsonism properties [39-45]. All the synthesized products were characterized by analytical techniques like ^1H NMR, ^{13}C NMR, FT-IR, melting point measurements etc.

Another important class of ionic liquids is the halometallates. They are usually obtained from the reaction between a halide containing IL and a Lewis-acidic metal halide at various molar ratios. A dynamic equilibrium mixture of various complex metal-halide anions either in molten, semi-solid or in solid states are often generated based on the various molar ratios of the metal halides to ILs used. Presence of the complex metal halide ions provide the halometallate ILs with an electron accepting ability and hence, are generally Lewis acidic in nature [3]. The early reports of halometallate ILs were the chloroaluminate ILs, which existed in the liquid state and were highly moisture unstable [3, 46, 47]. However, over the time, the halometallate ionic liquids containing transition metals like Zn, Sn, Ga, Fe, Co, Ni and lanthanides were also developed and were found to be moisture stable and existed in semi-solid/ solid state [8, 48-51]. Furthermore, in the recent decades, dual-functionalized halometallate ILs were developed containing both the Brønsted and Lewis acidic functions [4, 51]. 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. Since this evolution of the halometallate ILs from hygroscopic compounds to more moisture stable and functionalized compounds, they have found applications in diverse fields like catalysis, nano-particle synthesis, energy-conversion devices, separation media etc. [15, 17, 49-51]. In this regard, we have utilized these properties of functionalized halometallate ILs in nanoparticle synthesis. Already ILs have been successfully utilized as solvents and capping agents in the synthesis of nanoparticles [52-55]. However, there exist only few reports on the utilisation of the ILs as precursors/templates in nanoparticle synthesis [15, 55-58]. In our present work, we have synthesised N-SO_3H functionalized imidazolium based chloronickellate ILs and used them as precursors/solvents/template for the synthesis of nickel sulphide (NiS) nanoparticles. The ILs and the nanoparticles were successfully characterized by various analytical techniques like ^{1}H 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.

2.1.1 Objectives

The present work envisions developing new categories of task-specific –SO_3H functionalized ILs and finding their potential applications by performing a comprehensive study on their physicochemical properties. In this regard, we designed our objectives in the following way:

[1] Synthesis and characterization of –N-SO_3H functionalized ionic liquids of imidazolium in combination with simple organic/non-metallic inorganic anions.

[2] Investigation of the physicochemical properties like conductivity, thermal stability, acidity, self-aggregation tendencies, density and electrochemical stability of the synthesized imidazolium ionic liquids.

[3] Synthesis and characterization of –N-SO_3H functionalized ionic liquids of acyclic ammonium cations in combination with simple organic/non-metallic inorganic anions.

[4] Investigation of the physicochemical properties like conductivity, thermal stability, acidity, self-aggregation tendencies, density, and electrochemical stability of the synthesized ammonium ionic liquids.

[5] Exploration of the catalytic activities of the synthesized –N-SO_3H functionalized ionic liquids in one-pot synthesis of indole derivatives and 2-amino-3-cyanopyridines.

[6] Synthesis and characterization of –N-SO_3H functionalized imidazolium based chloronickelatte ionic liquids.

[7] Application of the synthesized chloronickelatte ionic liquids as precursors/templates in the synthesis of nickel sulphide (NiS) nanoparticles.

[8] Application of the synthesized nickel sulphide (NiS) nanoparticles in the solar energized degradation of organic dyes.

2.2 Methodology

This section briefly explains general spectroscopic and analytical techniques employed for characterization of synthesized N-SO_3H functionalized room temperature ionic liquids (RTILs), halometallates, organic products along with study of physicochemical properties of the ILs. As already mentioned earlier, the structures of the synthesized ILs were confirmed using FT-IR, NMR (^{1}H, ^{13}C & ^{19}F) spectra and CHN elemental analysis. The characterization of organic products obtained from the IL catalysed organic reactions, were done through FT-IR and NMR (^{1}H & ^{13}C). In case of the solid organic products, their melting points were also determined. Additionally, ESI-Mass spectrometry was employed to determine the complex metal halide anionic speciation of the N-SO_3H functionalized imidazolium based chloronickellates. Thermal stability and

Brønsted acidity of the functionalized ionic liquids were investigated by thermogravimetric analysis (TGA) and UV-Vis Hammett acidity studies respectively. The electrochemical stability windows (ESWs) 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 few representative RTAILs 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 N-SO_3H functionalized imidazolium based chloronickellates were done by using analytical techniques like RAMAN, PXRD, SEM, EDX, TEM, BET surface area analysis, XPS, TGA and UV-Visible diffuse reflectance spectra (UV-DRS).

2.2.1 Required Materials

The required chemicals were purchased from various commercial suppliers like MERCK, Alfa Aesar and TCI chemicals. They were used directly without any further purification.

2.2.2 Analytical methods

The various analytical methods used in the characterization of the ionic liquids, organic products and nanoparticles are listed below:

2.2.2.1 Fourier Transform Infrared (FT-IR) spectroscopy

The FT-IR spectra of all the liquid as well as solid samples were recorded on Perkin Elmer MIR-FIR FT-IR spectrophotometer using KBr pellets. The FT-IR spectra of the ionic liquids provided valuable information regarding the attachment of –SO_3H group through nitrogen atom of the ammonium and imidazolium ILs. Further the presence of various functional groups in the organic products as well in the ILs could be confirmed from their stretching and bending vibrations in the fingerprint region (450-2000 cm^{-1}) of their respective FT-IR spectra. The information regarding O-H, N-H stretching vibrations and also existence of inter- or intra-molecular hydrogen bonding interactions could be obtained from 2500-4000 cm^{-1} region of the FT-IR spectrum.

2.2.2.2 Nuclear Magnetic Resonance spectroscopy (NMR)

The NMR spectra (^1H NMR, ^{13}C NMR, ^{19}F) of all the synthesized ILs and the organic products of catalytic reactions (chalcones, 3-substituted indoles and 2-amino-3-cyano pyridines) were recorded on JEOL 400 MHz spectrophotometer (δ in ppm) using DMSO-d_6 (or $CDCl_3$) as solvent and TMS as internal standard. The ^{19}F NMR was taken in case of BF_4^- anion containing ILs to confirm the presence of the BF_4^- anion.

2.2.2.3 Thermogravimetric analysis (TGA)

The thermal stabilities of the prepared ILs were determined by performing their thermogravimetric analysis in the Shimadzu TGA-50 analyser. The thermogravimetric analysis data of the room temperature acidic ILs were also employed to determine their moisture content.

2.2.2.4 CHN Elemental analysis

The CHN elemental analysis of the prepared ILs and organic products were carried out on PerkinElmer 20 analyser.

2.2.2.5 UV-Visible spectroscopy

The Hammett acidity study of the synthesized room-temperature acidic ionic liquids (RTAILs) and the kinetic studies for the degradation of organic dyes using nickel sulphide nanoparticles were carried out in Shimadzu UV 1800 spectrophotometer. The Hammett acidity studies of the RTAILs were conducted to determine their Brønsted acidity strength. It was done by calculating their Hammett functions H^o from their UV-Visible Hammett plots using **Equation 1.4** from **chapter 1**. 4-nitroaniline was used as a basic indicator and the H^o was calculated by measuring of absorbance differences $[I]/[HI]^+$ on UV–Vis spectrophotometer in ethanol solution [9,10].

$$\mathbf{H^o = pK(IH^+)\,(aq) + \log[I]/[IH^+]} \qquad \textbf{(Equation 1.4)}$$

Here pK(I)aq. expresses pKa value of the basic indicator in aqueous solution. The procedure was carried out with mixing of equal concentration of the indicator (5 mg L^{-1}, pKa = 0.99) and IL (5 mmol L^{-1}) in ethanol solution [9, 10]. The absorbance of the basic indicator [I] in the IL solutions decreased with increasing acidity of the ILs. The protonated form $[HI]^+$ of the indicator never appeared because of its lower molar absorptivity. Thus, with the increasing acidity of the BAILs, their H^o values become smaller.

2.2.2.6 Raman spectroscopy

The Raman spectra of the nickel sulphide nanoparticles were recorded using RENISHAW spectrophotometer equipped with an Ar laser of excitation wavelength of 514 nm.

2.2.2.7 Mass spectrometry

The electron spray ionisation mass spectra of the imidazolium chloronickellate ILs were recorded on Synapt G25 (Waters) liquid chromatography mass spectrometer to determine their complex metal halide anionic speciation.

2.2.2.8 Powder-X-ray Diffraction (PXRD) analysis

Powder X-ray diffraction spectra of the nickel sulphide nanoparticles were recorded on Rigaku–Multiflex instruments using a nickel filtered CuK (0.15418 nm) radiation source and scintillation counter detector. This technique was used to confirm the structure of the nickel sulphide nanoparticles.

2.2.2.9 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analysis

Scanning electron microscopy of the nickel sulphide nanoparticles was performed on a JEOL JSM-6390LVSEM, equipped with energy dispersive X-ray analyser (EDX). The scanning electron microscopy (SEM) analysis of the nickel sulphide nanoparticles provided information about their surface morphology. The EDX analysis is a technique of elemental analysis that is based on the generation of characteristic X-rays in atoms of the specimen by incident beam electrons. The EDX analysis of the nanoparticles provided information regarding their composition. This technique gives an overall mapping of the sample by analysing near-surface elements and estimates the elemental proportion at different positions.

2.2.2.10 Transmission Electron Microscopy (TEM) analysis

Transmission electron microscopy (TEM) is another useful tool for characterization of the nanoparticles. It is a quantitative method to determine the particle size, shape, and distribution. TEM also enables images of nanoparticles to be captured at high resolution. The high-resolution TEM images (HRTEM) of the nickel sulphide nanoparticles were recorded in JEOL 2100F field emission transmission microscope.

2.2.2.11 UV-Visible Diffuse Reflectance Spectroscopy

The electronic spectra of the nickel sulphide nanoparticles were recorded using Hitachi U-3400 spectrophotometer with a diffuse reflectance apparatus equipped with an integrating sphere (60 mm inner diameter). The optical band gaps of the prepared nanoparticles for photocatalytic applications were analysed from their UV−visible diffuse reflectance spectra. From the UV data, the Tauc plot has been drawn to calculate the band gap values of the prepared nanoparticles using the following equation:

$$(\alpha h\upsilon)^{1/n} = \beta\,(h\upsilon - Eg) \qquad \text{(Equation 2.1)}$$

where α, h, υ, β and E_g are the coefficient of absorption, Planck’s constant, frequency of incident photon, constant of band tailoring parameter and E_g is the energy of optical bandgap for direct (n = 1/2) or indirect transition (n = 2) [59, 60]. The power factor of transition mode ‘n’ is dependent on nature of solid material. The plotting of photo energy hυ versus $(\alpha h\upsilon)^2$ provides a straight line in certain regions by assuming all transitions as direct transitions.

2.2.2.12 The Brunauer - Emmett – Teller (BET) analysis

The Brunauer - Emmett – Teller (BET) analysis was performed to investigate the surface area data of the nickel sulphide nanoparticles. The BET surface areas of the nanoparticles were determined using nitrogen (N_2) sorption data measured at 77K using Antor Paar Autosorb iQ MP-AG (2 STAT) BET surface area analyser.

2.2.2.13 Fluorescence measurements

Steady state fluorescence analyses of the representative RTILs were performed on a Hitachi F-2700 FL spectrophotometer by using pyrene as probe molecule. Appropriate amount of the pyrene was dissolved in neat ILs to prepare the solutions for emission (10^{-}

^{4} M). The excitation wavelength of pyrene was set at 345 nm. The fluorescence spectra provided information regarding the polarity of the RTAILs.

2.2.2.14 Conductivity measurements

The ionic conductivities of synthesized room temperature ILs in molecular solvents (MeOH, MeCN and acetone) were measured on Eutech PC7700PH/mV/Conductivity/°C/°F Bench Meter. The instrument provides a full-scale resolution of 0.5% and an accuracy of ±1% and can measure conductivity in the ranges from 0 to 2000 μS and 0 to 200.0 mS. It was calibrated with 0.1M KCl solution, both before and after the measurements were taken. The effect of change in temperature and the mole fraction of the RTAILs in their binary mixtures with molecular solvents were also studied from their conductivity measurements.

2.2.2.15 Cyclic Voltammetry technique

The electrochemical stability windows (ESWs) of the ILs in molecular solvents (MeOH, MeCN and acetone) were measured using the Cyclic Voltammetry (CV) technique in CHI600E Electrochemical Workstation/Analyzer. The CV plots for 0.1 M solution of the ILs in molecular solvents (MeOH, acetone and MeCN) were recorded using glassy carbon as the working electrode, platinum as the counter electrode and non-aqueous Ag/Ag^{+} as the reference electrode.

2.2.2.16 Melting point measurements

The melting point of the organic products (chalcones, Michael adducts and 2-amino-3-cyanopyridines) were recorded on BUCHI M-560 digital melting point.

2.2.2.17 X-ray photoelectron spectroscopy (XPS)

The elemental composition and chemical state of the prepared NiS nanoparticles were studied using X-ray Photoelectron spectroscopy. The XP spectra were recorded using Thermoscientific NEXA Surface analyser.

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