Studies on the Physicochemical Properties of Acidic Ionic Liquids and their Applications

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Chapter 7

Conclusion and Future Scope

7.1 Conclusion

The present thesis attempted to provide an in-depth study into the unique physicochemical properties of N-SO_3H functionalized imidazolium and ammonium based acidic ionic liquids. The variations in their different physicochemical properties (conductivity, polarity, thermal stability, acidity, density, electrochemical stability) 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 investigated elaborately. The knowledge obtained about the physicochemical properties of the N-SO_3H functionalized ILs was then utilized in their applications in catalysis and nanoparticle synthesis.

Chapter 1 of the thesis gave a general introduction on the different classes of ionic liquids. The next part of the chapter provided a comprehensive review on the unique physicochemical properties of the ILs, which include conductivity, viscosity, surface tension, electrochemical and thermal stability, acidity, density, and surfactant-like properties. Additionally, the effects of constituent ions, temperature, concentration, solvent, etc., on these properties were also discussed. A brief discussion on the application of ILs as catalysts in the synthesis of organic products (chalcones, 3-substituted indoles and 2-amino-3-cyanopyridines) was also given in this chapter. Furthermore, this chapter also reviewed the uses of ILs as solvents, templates, or precursors in the synthesis of nanoparticles.

Chapter 2 of this thesis was divided into two parts. The first part outlined the objectives of the current thesis. The next part of the chapter gave a general overview on the spectroscopic and analytical techniques used in the characterization of the synthesized N-SO_3H functionalized ionic liquids, halometallates, organic products as well the nanoparticles. FT-IR and NMR (^1H, ^{13}C & ^{19}F) spectroscopy were used to confirm the structures of the synthesised ILs and organic products. Further, melting point measurements of the solid organic products were also taken. Additionally, ESI-Mass spectrometry was employed to determine the complex metal halide anionic speciation of the halometallates. The physicochemical properties of the ILs were also evaluated using different techniques. Thermal stability and moisture content of these ILs were evaluated by thermogravimetric analysis (TGA). UV-Vis spectroscopy was used to determine the Brønsted acidity of the functionalized ionic liquids. The electrochemical stability windows (ESW) of the RTAILs in molecular solvents were recorded using Cyclic Voltammetry (CV) technique. The conductivity measurements of the ILs in molecular solvents were performed using a digital conductivity meter. Their densities were measured using a pycnometer. In addition, the polarities of some of the ILs were determined by taking the fluorescence emission spectra of pyrene in them. Moreover, the nickel sulphide nanoparticles synthesized using the halometallate ILs, were characterized using analytical techniques like RAMAN, PXRD, SEM, EDX, TEM, BET surface area analysis, XPS, TGA and UV-Visible diffuse reflectance spectra (UV-DRS).

In **Chapter 3**, the first two research objectives were covered with synthesifour members of N-SO_3H functionalized Brønsted acidic 2-alkyl substituted/unsubstituted imidazolium based trifluoroacetate ILs ([DSIM][TFA], [MDSIM][TFA], [EDSIM][TFA] & [BDSIM][TFA]). Following their characterization using (^{1}H & ^{13}C) NMR, FT-IR and elemental analysis techniques, their different physicochemical properties were evaluated. All the four ILs were found to be thermally stable up to 250–260 °C. It was found that the chain length of the 2-alkyl substituents on the imidazolium cation affected the properties like density, Hammett acidity, electrochemical stability, conductivity etc. of the four BAILs. It was found that their densities reduced on increasing the chain length of the C-2 alkyl substituent because addition of -CH_2 group to the imidazolium ring increased the free space between two IL molecules and thus reduced the compactness of the ILs. A similar trend was observed in case of their Brønsted acidity. The increasing +I effect of C-2 alkyl substituents of the imidazolium cation reduced its electron deficient character and hence its acidity. Thus, the Brønsted acidity of the BAILs decreased in the order: [DSIM][TFA]> [MDSIM][TFA]> [EDSIM][TFA]> [BDSIM][TFA]. Furthermore, the Cyclic Voltammetry studies revealed higher electrochemical stability of the four BAILs in the aprotic MeCN compared to protic MeOH. The wider ESWs of the C-2 ethyl and n-butyl substituted 1,3-disulfoimidazolium trifluoroacetate ILs in MeCN can be attributed to the enhancement of electron donating +I inductive effects of the alkyl groups. However, all the four BAILs showed higher ionic conductivities in MeOH as compared to MeCN. The conductivity values of the four BAILs in both the molecular solvents decreased in the following order: [DSIM][TFA]>[MDSIM][TFA]>[EDSIM][TFA] >[BDSIM][TFA]. The increasing bulkiness of C-2 alkyl substituent decreases the mobility of the imidazolium cation and hence conductivity in both the solvents. The reduction in the conductivity values of the

IL solutions at a particular mole fraction with the rise in temperature revealed the self-aggregation tendency of the ILs molecules in presence of the molecular solvents (MeOH & MeCN). The measurement of the conductivities of [MDSIM][TFA] in MeOH by varying the concentration of the (X_{IL} = 0.0052 to 0.2) at room temperature indicated the existence of “Critical aggregation concentration” around X_{IL} = 0.1.

Chapter 4 covered the third and fourth research objectives and investigated the effects of constituent ions on the physicochemical properties of the ionic liquids. Here twelve N-SO_3H functionalized BAILs were synthesized by varying the combinations of cations (2-ethyl-1,3-disulfoimidazolium [EDSIM], N, N-disulfodiethylammonium [DEDSA] and N, N-disulfodibutylammonium [DBDSA]) and anions (Cl^-, CF_3COO^-, OTf^-, BF_4^-). Their characterization using different spectroscopic techniques was followed by comparative studies on their physicochemical properties. Six of the Cl^- and CF_3COO^- anion based ionic liquids showed similar thermal stability up to 250-260°C, whereas the other six BF_4^- and OTf^- anion based ILs were found to be less thermally stable due to the weak coordinating nature of the two anions. Furthermore, the moisture content of the twelve ILs were also evaluated using their TGA and derivative-TGA graphs and the CF_3COO^- anion containing ILs were found to be the most hydrophilic ones. The absence of compact packing in case of linear chain ammonium based ILs was responsible for their lower densities compared to the 2-ethyl-1,3-disulfoimidazolium ILs. Their Brønsted acidity studies revealed comparable acidity of the [DEDSA] and [EDSIM] series of ILs. [DBDSA] series was however found to be slightly less acidic compared to the other two due to the increasing +I effect of the N-butyl substituents on the ammonium cation. It was also observed that the nature of solvent used also affected the electrochemical stability as well as conductivity values of the ILs in them. Cyclic Voltammetry studies showed wider ESWs of the BAILs in aprotic acetone and MeCN as compared to protic MeOH at the same temperature. The ESWs of the [DBDSA] ILs in all the three molecular solvents were found to be slightly higher than the [DEDSA] ILs. This can be related to increasing electrochemical stability of the ILs with increasing size and +I inductive effect of the alkyl chain. The [EDSIM] series had the highest ESW in acetone (3.07-3.45 V) and MeCN (2.75-3.42 V) among the three series of ILs. The fluorescence emission spectra of pyrene in [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 its excimer state. Ionic conductivity of the twelve ILs at a particular concentration (mole fraction x_{IL}= 0.001) and temperature (298.15 K) in the three molecular solvents were affected by the polarity of the respective solvent, size of the ions and presence of ion-pair aggregates. Among the three series of ILs, the imidazolium based ILs ([EDSIM] series) showed the highest conductivity in the three molecular solvents, followed by the [DEDSA] series and then the [DBDSA] series.

After investigating the physicochemical properties of N-SO_3H functionalized imidazolium and ammonium ILs, their catalytic activities were explored in **Chapter 5** which is divided into two parts, **5A** and **5B**. In **Chapter 5A**, the catalytic activities of two series of N-SO_3H functionalized imidazolium ILs i.e. 2-methyl/2-ethyl-1,3-disulfoimidazolium carboxylate ionic liquids [MDSIM][X] and [EDSIM][X], (where, X = CF_3COO^-, CCl_3COO^-, CH_3COO^-) were explored in the one-pot synthesis of 3-substitited indoles. This one-pot sequential route involved the selective formation of chalcones via Claisen-Schmidt condensation in the first step in presence of IL catalyst, which was followed by Michael-like addition of indole to the crude chalcone in the second step. The catalytic activities of the most acidic and thermally stable IL from each series i.e. [MDSIM][TFA] and [EDSIM][TFA] were evaluated in the synthesis of chalcones as well as 3-substituted indoles, by varying their amount as well as reaction temperatures. [MDSIM][TFA] was found to be the best catalyst. The optimized catalyst amount was found to be 5 mol% and the reaction temperature for the first step was found to be 100℃, while that for the second step was 80 ℃. This route provided a simple and efficient acidic ionic liquid catalyzed strategy for preparation of the chalcones and also for the 3-substituted indoles under environmentally safe conditions, avoiding the complicated separation techniques and toxic/or corrosive catalysts/reagents. The solvent-free conditions, easy recycling of catalyst and isolation of products, along with the wide functional group tolerance are a few advantages of this route. **Chapter 5B**, is the continuation of the previous work in **Chapter 5A,** on the exploration of the catalytic properties of N-SO_3H functionalized ILs and the use of chalcones as precursors for synthesis of heterocycles. Here catalytic activities of N-SO_3H functionalized imidazolium, ammonium and piperizinium based ILs [DSIM][TFA], [EDSIM][TFA], [DBDSA][TFA] and [TSPi][Cl]$_2$ were evaluated in the sequential one-pot multicomponent synthesis of 2-amino-3-cyanopyridines. The reaction involved the selective formation of chalcones in the first step as precursors for the multi-component reaction with malononitrile and ammonium acetate in the second step to yield 2-amino-3-cyanopyridine derivatives in presence of the IL catalyst. $[TSPi][Cl]_2$ was found to be the best catalyst for this reaction. The dual solvent-catalyst role of the Brønsted acidic ILs in this two-step one-pot route eliminated the use of toxic organic solvents and metals, tedious chromatographic separations of reaction intermediates/products and strong acidic or basic conditions. Furthermore, this route provided the benefits of selective formation of chalcones /2-amino-3-cyanopyridines, shorter reaction times, easy recycling of catalyst and higher product yields. Amalgamation of multi-component reactions with ionic liquids and solvent-free conditions made the present work more compliant with the protocols of Green Chemistry.

Chapter 6 covered the last three research objectives. Here two new members of N-SO_3H functionalized chloronickellate ionic liquids ($[EDSIM]_x[NiCl_y]$ (1a) & $[EDSIM]_x[NiCl_y]$ (1b) where, x = 2, y = 2,3,4 or 5) were synthesized. The chloronickellate ILs were characterized using (^1H & ^{13}C) NMR, FT-IR spectroscopy, and ESI-mass spectrometry. These halometallates were then utilised as precursor/template in the synthesis of nickel sulphide nanoparticles. The preparation of nickel sulphide nanoparticles were conducted using a simple grinding method, where equimolar amount of $[EDSIM]_x[NiCl_y]/[MDSIM]_x[NiCl_y]$ and sodium sulphide (Na_2S) were grounded in a mortar for 10 minutes at room temperature to form the nickel sulphide nanoparticles 2a/2b. The synthesized nanoparticles (2a & 2b) were characterized using PXRD, RAMAN, TEM, SEM-EDX, XPS, BET and UV-Visible analysis. The EDX spectra of 2a and 2b confirmed the presence of both nickel and sulphur in the nanoparticles. The SEM images of 2a and 2b revealed their sponge-like morphology. The elemental composition and chemical state of the prepared NiS nanoparticles 2a and 2b were studied using X-ray Photoelectron spectroscopy. The Ni 2p XP spectra of both 2a and 2b confirmed the presence Ni^{2+} oxidation state. Furthermore, the S 2p XP spectra of both 2a and 2b indicated the existence of S^{2-} oxidation state. The PXRD pattern of the synthesised nanoparticles 2a and 2b revealed the formation of both the rhombohedral β-NiS phase and orthorhombic α-NiS phase. The TEM analysis revealed the formation nickel sulphide nanosheets and the average particle size was found between 20-35 nm. The BET-surface area analysis of the nanoparticles 2a and 2b revealed their surface area values to be 22.27 m^2/g and 13.68 m^2/g respectively. The band gap values of 2a and 2b were calculated from the Tauc-plots and were found to be 2.39 eV and 2.80 eV respectively. Based on these results, the nanoparticles 2a and 2b were utilised as photocatalysts in the degradation of organic dyes (methylene blue (MB), methyl orange (MO), crystal violet (CV), malachite green (MG) and their mixtures) under sunlight. It was found that 2a exhibited slightly better catalytic activity compared to 2b. These results were consistent with lower band gap values and higher surface area of 2a compared to 2b.

In conclusion, we envision that the above mentioned studies will contribute to increasing the knowledge about various fascinating properties of the ionic liquids. With this knowledge, it becomes easier to design ionic liquids for a specific application as well to find the proper applications of the existing ones.

7.2 Future Scope

The future prospects of our work include:

1) Generation of newer classes of -SO_3H functionalized or non-functionalized ILs by systematic structural variations and combinations of constituent ions to provide greater control over their physicochemical properties.

2) Design and synthesis of functionalized ILs to be used as catalysts, surfactants, ligands in complex synthesis, electrolytes, and capping agents/precursors/templates in nano-synthesis.

3) Investigation of biological activities of chalcones, 3-substituted indoles and 2-amino-3-cyanopyridine derivatives.

4) Synthesis of various types of nanoparticles/quantum dots (QDs)/nanocomposites by utilizing different classes of ILs.