Chapter 8

Summary and future perspectives
8.1 Summary

The main objectives and the outcomes of the thesis are shown below:

- **Design of imidazolium based energetic ionic liquids using computational chemistry tools.**

  Thermochemistry of a variety of imidazolium based ILs were predicted accurately using quantum chemical computational studies. The computed heats of formation of all the EILs of 1-ethyl-3-methylimidazolium cation and tetrazolide derivatives, dicyanamide, triazolide, dinitrotriazine, and dinitramide as anions were higher than that of hydrazine. Considering ILs with a suitable oxidizer as a binary monopropellant, Isp of different EILs with varying concentration of HAN was computed. Among the 12 imidazolium based EILs studied, \( [C_{2}\text{MIm}]^{+}[\text{dtrz}]^{-}, \) \( [C_{2}\text{MIm}]^{+}[\text{dn}]^{-} \) and \( [C_{2}\text{MIm}]^{+}[\text{NO}_{2}\text{Otz}]^{-} \) provided the best energetic performance in combination with HAN proposing the title compounds as potential green substitute for hydrazine.

- **Structural studies of ionic liquids using computational methods for organic modification of clay.**

  1-alkyl-3-methylimidazolium ILs were proposed as a replacement for alkyl ammonium salts in clay modification for high temperature applications. Screening of ILs for cation exchange with MMT-Na\(^+\) was done based on computed parameters like HOMO-LUMO energy gap for stability studies, Mulliken charge analysis and MK charge analysis for charge contribution to electrostatic and hydrogen bonding interactions. The stability of \([C_{n}\text{MIm}]^{+}\) cations were assessed based on HOMO-LUMO energy gap (\( \Delta E^{*} \)). \( \Delta E^{*} \) shows drastic decrease in stability after \([C_{4}\text{MIm}]^{+}\) (\( \Delta E^{*} = 6.7 \text{ eV} \)). This change in stability is attributed to shift in HOMO from imidazolium ring to alkyl chain after C4. Chain length of \([C_{n}\text{MIm}]^{+}\) in this study is limited to C16 for thermally stable IL modified organoclay (\( \Delta E^{*} > 4 \text{ eV} \)). \( \Delta E^{*} \) analysis illustrates higher stability for \([C_{n}\text{MIm}]^{+}[\text{BF}_{4}]^{-}\) (6.8 eV) than \([C_{n}\text{MIm}]^{+}[\text{Cl}]^{-}\) (4.1 eV). In \([C_{n}\text{MIm}]^{+}[\text{BF}_{4}]^{-}\), HOMO is diffused between \( \text{BF}_{4}^{-} \) and imidazolium ring and shifted to N2-alkyl group on increasing chain length beyond C14, where as HOMO is located on the Cl\(^-\) anion irrespective of the N2-alkyl chain length in \([C_{n}\text{MIm}]^{+}[\text{Cl}]^{-}\). Compiling all results, \([C_{4}\text{MIm}]^{+}, [C_{6}\text{MIm}]^{+}\) and \([C_{16}\text{MIm}]^{+}\) based ILs were selected for experimental studies.
Synthesis of ionic liquids and experimental validation of predicted properties.

Ionic liquids selected for clay modification, [C₆MIm]⁺[Cl]⁻ and [C₁₆MIm]⁺[Cl]⁻ were synthesized with 95 % yield. The effect of anion on thermal stability of ILs were established using [C₄MIm]⁺[Cl]⁻ (Tₛ = 284 °C) and [C₄MIm]⁺[BF₄]⁻ (Tₛ = 427 °C), and conform to the computed parameters based on HOMO-LUMO energy gap. The decomposition products identified using pyrolysis GC-MS and transition states using DFT method established the higher reactivity of [C₄MIm]⁺[Cl]⁻ over [C₄MIm]⁺[BF₄]⁻ as predicted from the charge transfer analysis. The non-dependency of alkyl chain length on stability of ILs were confirmed by analysing [C₄MIm]⁺[Cl]⁻, [C₆MIm]⁺[Cl]⁻ and [C₁₆MIm]⁺[Cl]⁻. Modification of MMT-Na⁺ with IL was achieved with the lowest processing time of 15 minutes using probe sonication method. The modification was confirmed using FTIR analysis, improved d-spacing in XRD, CHN analysis and TG analysis. The C₆MIm/MMT showed improved thermal stability than conventional alkyl ammonium modified clays. C₁₆MIm/MMT with d-spacing of 18.55 Å and T₁% of 266 °C is proposed as a replacement for Cloisite 25A with d-spacing of 18.65 Å and T₁% of 214 °C. Thermal degradation mechanism of ionic liquid modified clay was elucidated using DFT and experimentally rationalized using pyrolysis GC-MS and ¹³C NMR experiments. For the first time, the predicted carbene mechanism was established by identifying 1-butyl-3-methylimidazol-2-ylidine using ¹³C NMR spectroscopy. The experimental results were conforming to the theoretical studies.

Application of ionic liquid modified clay in the removal of perchlorate ion from water.

1-alkyl-3-methylimidazolium modified clays were used for perchlorate adsorption from water. C₁₆MIm/MMT showed highest adsorption of perchlorate ions (15.6 mg/g of clay) and the conformational changes associated with adsorption were studied using Raman spectroscopy. Experimental data fitted with different adsorption isotherms and kinetic models revealed Freundlich adsorption and pseudo second order kinetics for the adsorption process. On thermal activation 95 % regeneration of clay was observed at 175 °C and regeneration mechanism involving perchloric acid removal was proposed based on DFT studies. The organoclay prepared represents a potential adsorbent for perchlorate with advantage of very low contact time and regenerability of the system.
Preparation and property evaluation of IL modified clay nanocomposites.

The microstructural changes induced in PVDF by ionic liquid modified clay was investigated. Enhancement of electro active β-phase crystallization was observed with increased alkyl chain length of the organic modifier, 1-alkyl-3-methylimidazolium cations in the nanoclay. The PVDF-C4 composite with a self reinforced shish-kebab structure showed superior mechanical properties and retained the thermal stability of pristine PVDF. This work reported a way to prepare PVDF/organoclay composites with enhanced electrical and mechanical properties by adjusting the alkyl chain length of the ionic liquid which offers potential applications in the field of sensors, actuators and batteries.

8.2 Future perspectives

The present investigations extend ample scope for further investigations and future developments, especially to realize ionic liquid based green propellant in space application. Synthesis and characterization of long chain ionic liquid C₁₆MImCl provides, scope for their application as surfactant/soft template in polymerization reactions. The initial studies using C₁₆MImCl as a soft template for copolymerization of aniline and pyrrole resulted in uniform spherical particles with particle size less than 40 nm. AFM images of copolymer of aniline and pyrrole (APC) with and without C₁₆MImCl are shown in Figure 8.1. This opens a promising route for APC synthesis with improved property, especially for sensor application. The use of IL modified clays as thermally stable filler for preparation of different polymer composites are also appealing.

![Figure 8.1](image.png)

Figure 8.1 Topography images of (a) APC and (b) APC in presence of [C₁₆MIm][Cl].