Abstract

This thesis investigates the adsorption of imidazolium and pyrrolidinium based ionic liquids on metallic surfaces. We examine the adsorption dynamics, underlying mechanism, orientation and stability of ionic liquids upon adsorption density functional theory (DFT) calculations and replcia exchange molecular dynamics (REMD) simulations.

Chapter 1 provides a comprehensive introduction to metallic surfaces, followed by interaction of inorganic and organic molecules with metallic surfaces at the interface. The chapter further discuses the importance of ionic liquids, and relevant experimental and computational studies of ionic liquid/metal interfaces are discussed in detail.

Chapter 2 details the computational and theoretical methodologies employed in this thesis to investigate interfacial systems.

Chapter 3 investigates the nature of adsorption of $[C_nMIm]^+$ based cations with varied chain length in combination with $[BF_4]^-$ anion, and $[BMP]^+$ cation with various anions where the role of anion is investigated. All the investigations were conducted using DFT methodology, and the nature of adsorption energy trends along with the structural changes were observed. The strength of adsorption was further correlated with two different charge transfer methods, and correspondingly, which method is more suitable for interfacial systems was also concluded.

Building upon the insights from *Chapter 3*, *Chapter 4* explores the conformational space of a sulfonyl based ionic liquid on platinum based mono and bimetallic surfaces using both DFT and REMD methods. More than 30 conformations of the ionic liquid were identified on both monometallic and bimetallic surfaces. In addition to adsorption energies, factors such as dynamics of ionic liquids, molecule–surface distances, and charge transfer analyses were found to be important indicators for understanding adsorption phenomena.

Chapter 5 investigates the influence of surface heterogeneity on the adsorption of sulfonyl -functionalised ionic liquids using DFT and REMD approach. More than 30 conformations were obtained for Au(111) surface, and Au-Pt-Pt(111) and Pt-Au-Au(111) to observe the effect of changing the top layer atoms of the surface, and how the dynamics of the adsorption varies with the surface modifications. The results were also correlated with d-band center calculations.

Finally, *Chapter 6* provides the conclusion related to the studies conducted in the thesis with a summary of key findings and outlines future research directions.