Abstract

Room Temperature Ionic Liquids (RTILs) are a new class of solvents receiving increasing attention for their possible use as alternative solvent/electrolyte to conventional electrolytes in electrochemical setups. Due to their wide electrochemical window, appreciable conductivity, ability to dissolve wide range of organic and inorganic substrates, low vapour pressure, high chemical and thermal stability and above all ability to stabilize transient species, RTILs are considered as excellent media for ecofriendly, innovative and sustainable electrochemistry. Besides all the advantageous features RTILs do have, their wide spread use for electrochemical investigations and applications is yet to be realized. Some practical concerns associated with use of RTILs in electrochemical setups and a lack of complete understanding about their role as solvent/electrolytes in electron transfer and the associated reactions are the main reasons that currently hamper their use for electrochemical investigations and applications. In this regard some fundamental aspects related to RTILs, like equilibrium and transport properties of pure RTILs and alteration of these properties through use of cosolvents or variations in experimental parameters, specialities of electrode/RTIL interfaces over that of the electrode/conventional electrolyte solution interfaces, impact of RTIL specific effects on heterogeneous electron transfer and associated chemical reactions need some detailed investigations. Work presented in this thesis is an attempt to have a better understanding about some of these challenges one comes across, while working with RTIL based electrochemical setups. Electrochemistry of model redox systems was explored to test the validity of established theories in RTILs and to realize the potential advantages of RTILs over conventional solvents. Solvent dynamic control over transport, charge transfer processes and ion pair effects are discussed. The advantageous aspects due to solvent specific effects of RTILs over thermodynamic, kinetic and mechanistic aspects of heterogeneous electron transfer and associated reactions are also discussed. The thesis has been organized in seven chapters.

Chapter 1: Room Temperature Ionic Liquids for Electrochemistry: A Review

This chapter provides a brief introduction about RTILs and their potential advantages as solvents in electrochemistry. A brief account about the current art of research in the field of RTIL based electrochemical investigations and applications is presented in light of published research reports.
Chapter 2: Synthesis and Physicochemical Characterization of Imidazolium Based Ionic Liquids

This chapter presents details about the synthesis, purification and characterization of RTILs viz., 1−butyl−3−methylimidazolium tetrafluoroborate ([BMIM][BF₄]), 1−butyl−3−methylimidazolium hexafluorophosphate ([BMIM][PF₆]), 1−butyl−2,3−dimethylimidazolium tetrafluoroborate ([BDMIM][BF₄]) and 1−butyl−2,3−methylimidazolium hexafluorophosphate ([BDMIM][PF₆]). Effect of temperature and acetonitrile as cosolvent on the surface and bulk characteristics viz. surface tension, conductance, absorption and emission characteristics of these RTILs is also discussed.

Chapter 3: Current Transients across Electrode/Ionic Liquid Interface

In this chapter we present an approximate theoretical model for diffusion-limited processes on realistic fractal interfaces and its use for the quantification of current responses corresponding to potential steps at electrode/RTIL interface. The model includes a complete set of realistic fractal morphological characteristics and gives information about various morphological features of electrode surface. A comparison of Cottrell equation with the present model to account for the experimentally recorded current transients across electrode/RTIL interface is also presented. The new result explains experimental findings of the temporal scale invariance as well as deviation from this in transition region with better accuracy than the conventionally used Cottrell equation.

Chapter 4: Electrochemistry of Model Redox Systems in Imidazolium Based Ionic Liquids

This chapter presents a discussion about electrochemistry of model redox systems viz. ferrocene, ethylferrocene and chloride ion in 1−butyl−3−methylimidazolium tetrafluoroborate ([BMIM] [BF₄]) and 1−butyl−3−methylimidazolium hexafluorophosphate ([BMIM] [PF₆]) RTILs. The transport and charge transfer parameters for the redox moieties have been estimated. A brief discussion about solvent dynamic control on kinetic and thermodynamic parameters for transport and electron transfer in RTILs is presented.

Chapter 5: Ion Pairing and its Impact on Electron Transfer Reactions in Imidazolium Based Ionic Liquids

This chapter presents a discussion about ion pair effect in RTILs. Redox behaviors of standard redox systems have been explored to understand the effect of ionic liquid molecular structure over the ion pair effect. The implications of the ion pair effect over the
kinetic, thermodynamic and mechanistic aspects of electron transfer initiated bond dissociation in halohydrocarbons are discussed.

Chapter 6: Quinones in Imidazolium based Room Temperature Ionic Liquids: An Electrochemical Investigation

This chapter presents voltammetric investigations on quinone-hydroquinone redox couple in 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) room temperature ionic liquids (RTILs). Mechanistic and kinetic aspects of quinone/hydroquinone equilibrium and its potential use for ammonia sensing are discussed. The chapter also includes a discussion about voltammetric investigations, aimed to probe the potential use of Pd²⁺ plus benzoquinone in [BMIM][BF₄] as green alternative to Wacker type catalytic systems.

Chapter 7: Summary and Future Scope

In this chapter we present concluding remarks and future scope of the entire work presented in the thesis.