INVESTIGATION OF COSOLVENT-MODIFIED IONIC LIQUID MIXTURES

BY

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CERTIFICATE

This is to certify that the thesis entitled, "Investigation of Cosolvent-Modified Ionic Liquid Mixtures", being submitted by Ms. Shruti Trivedi to the Indian Institute of Technology Delhi for the award of the degree of Doctor of Philosophy in Chemistry is a record of bonafide research work carried out by her. She has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this dissertation have not been submitted in part or full to any other University or Institute for the award of any degree or diploma.

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ABSTRACT

The unique and fascinating properties of ionic liquids (ILs) coupled to their extensive applications in various industries and academia render them substances of utmost significance. However, limited solubilization ability, limited physicochemical properties, high viscosity, and high cost associated with most ILs restrict their overall use. In this context, IL-based multicomponent systems may afford better tuned physicochemical properties and hence increase the overall effectiveness of ILs.

The thesis entitled 'Investigation of Cosolvent-Modified Ionic Liquid Mixtures' is concerned with the understanding of the interactions within cosolvent-modified IL-based systems. The thesis features detailed investigation of judiciously selected cosolvent-added IL systems utilizing various optical spectroscopic techniques along with bulk property and microproperty measurements. The experimental observations are used to assess the interactions within several multicomponent IL-based systems.

The thesis has been divided into seven chapters. Chapter 1 (Background and Introduction) provides a concise introduction to ILs and the problems that this particular research work is based on along with the approaches adopted to answer them. It also describes long- as well as short-term aims of the investigation. Chapter 2 titled 'Materials and Methodologies' is about chemical procurement, purification and storage as well as techniques used during the investigation. Specifically, uv-vis molecular absorbance, molecular fluorescence, excited-state fluorescence intensity decay, FTIR absorbance, and density and viscosity measurements are used to acquire the requisite information. Chapter 3 titled 'Multiprobe Spectroscopic Investigation of (Ionic Liquid + 2,2,2-Trifluoroethanol

(TFE)) and (Ionic Liquid + Propylene Carbonate (PC)) Mixtures' provide details of the solvatochromic probe behavior within (1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) + cosolvent) mixtures with TFE and PC, respectively. Mixtures of [bmim][PF_6] with TFE show rare 'synergistic solvent effect' or 'hyperpolarity' effect which are discussed in terms of coulombic interactions, disruption of TFE multimers, formation of hyper anion preference aggregates, and "free" [bmim]$^+$. In ([bmim][PF_6] + PC) mixtures, spectral behavior of collective probes hint at solute-specific preferential solvation and negligible specific solvent-solvent interaction(s). Chapter 4 titled 'Temperature-Dependent Solvatochromic Probe Behavior within Ionic Liquids and (Ionic Liquid + Water) Mixtures' deals with spectroscopic behavior of absorbance probes and fluorescence dipolarity probes within ILs [bmim][PF_6] and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]), and aqueous mixtures of [bmim][BF_4] as a function of temperature to assess the changes in the physicochemical properties of these interesting systems in the temperature range 10-90 °C. Chapter 5 titled 'Density, Dynamic Viscosity and Probe-Reported Microviscosity of [Ionic Liquid + Poly(Ethylene Glycol) (PEG)] Mixtures and their Temperature Dependence' lays out the details of the bulk property (density and dynamic viscosity) and microproperty (microviscosity) measurements of ([bmim][PF_6] + PEG) mixtures with PEG average molecular weight 200 (PEG200), 400 (PEG400), 600 (PEG600), and 1000 (PEG1000) at different temperatures to assess interactions within these 'hybrid green' systems. Mixtures of ([bmim][PF_6] + PEG1000) and ([bmim][PF_6] + PEG600) show rare 'viscosity synergism' or 'hyperviscosity' which is attributed to the formation of extensive H-bonding between bmim$^+$ and terminal –OH of PEG600/PEG1000 that more than compensates for the losses in coulombic attractive interactions and van der Waals interactions within [bmim][PF_6] and PEG600/PEG1000, respectively. Chapter 6 titled 'Fluorescence Quenching of Polycyclic Aromatic Hydrocarbons by Nitromethane within Ionic Liquid - Added Aqueous Anionic Micellar Solution' explores the applicability of nitromethane as a selective fluorescence quenching agent for discriminating between alternant *versus* nonalternant polycyclic aromatic hydrocarbons (PAHs) within aqueous anionic micellar sodium dodecyl sulfate (SDS) solution in the presence of IL [bmim][BF_4]. Interestingly, in the presence of small amounts of [bmim][BF_4], nitromethane started to selectively quench the fluorescence emission from alternant PAHs even in SDS micellar media. Screening of anionic micellar surface by $bmim^+$ helps nitromethane retain its selective quenching at lower IL concentrations. Chapter 7 titled 'Conclusions and Future Perspectives' highlights the salient features of the overall study. In short, it is concluded that addition of a cosolvent to IL can result in significant modification/alteration of physicochemical properties; even remarkable and unanticipated properties can be observed with appropriate combination of the components. Thus, IL-based multicomponent systems may afford media with favorably altered physicochemical properties thus increasing the overall utility of these interesting substances.

CONTENTS

Chapter 2: Materials and Methodologies

Chapter 4: Temperature-Dependent Solvatochromic Probe Behavior within Ionic Liquids and (Ionic Liquid + Water) Mixtures

Chapter 5: Density, Dynamic Viscosity and Probe-Reported Microviscosity of [Ionic Liquid + Poly(Ethylene Glycol)] Mixtures and their Temperature Dependence

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