MULTI-PROBE SPECTROSCOPIC INVESTIGATION OF IONIC LIQUID-BASED SYSTEMS

BY

ABHRA SARKAR

Department of Chemistry

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CERTIFICATE

This is to certify that the thesis entitled, "Multi-probe spectroscopic investigation of ionic liquid-based systems", being submitted by Mr. Abhra Sarkar 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 him. Mr. Abhra Sarkar 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.

Dr. Siddharth Pandey
Department of Chemistry
Indian Institute of Technology Delhi

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ABSTRACT

The thesis entitled 'Multi-Probe Spectroscopic Investigation of Ionic Liquid-Based Systems' is concerned with the understanding of the interactions within ionic liquid-based complex systems that may help control the properties and applications of these neoteric solvents. Because of their low volatility ionic liquids are being explored as 'green' substitutes for volatile organic solvents. The cosolvents used in our work viz. Tetraethylene glycol, Polyethylene glycols being low-volatile, non-toxic in nature and the other cosolvent water is non-toxic, entirely fulfils the criteria to explore the ionic liquid-based complex 'green' systems. The thesis features detailed spectroscopic investigation utilizing various solvatochromic optical spectroscopic probes to assess solute-solvent and solvent-solvent interactions within cosolvent-modified ionic liquid-based systems. Ionic liquids (ILs) with considerable solubility, miscibility, low volatility, and substantial applications in different fields such as synthesis, catalysis, electrochemistry, polymer/materials science, separation/extraction etc. are becoming substances of paramount importance. In spite of their multifaceted applications, ILs have some serious drawbacks such as limited solubilization ability, higher viscosity and higher cost. IL-based mixed solvent systems may help better tune the physicochemical properties and hence increase the overall utility of ILs. Specifically, the thesis focuses on addition of cosolvents of 'green' nature to obtain IL-based systems with favorable physicochemical properties.

The thesis has been divided into seven chapters. Chapter 1 (Background and Introduction) provides brief introduction to the problems that the thesis addresses along with the strategy opted to solve these problems. It also entails the long- as well as the short-term aims of the investigation. Special emphasis is placed on describing various

electronic absorbance and fluorescence probes used in the thesis. 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 and FTIR absorbance spectroscopies are used to obtain required information. Chapter 3 (Multi-Probe Spectroscopic Investigation within Aqueous 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4])) lays out details of the investigations on aqueous mixtures of water-miscible IL [bmim][BF_4]. It is observed that aqueous mixture of IL [bmim][BF_4] has dramatically modified physicochemical properties as compared to neat IL. Possibility of preferential solvation of the probes by IL [bmim][BF_4] is considered to explain these outcomes. However, changes in solution structure due to interaction(s) between IL and water may not be ignored. Chapter 4 ('Hyperpolarity' within 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) + Tetraethylene Glycol (TEG) Mixture: Multi-Probe Spectroscopic Evidence) reports unusual solvatochromism within IL [bmim][PF_6] + TEG mixtures. The results represent a rare 'synergistic solvent effect' or more specifically 'hyperpolarity' or 'synergetic polarity effect' or 'elevated polarity'. Based on collective probe responses, the primary reason for 'hyperpolarity' is proposed to be the interaction between C2-H of $bmim^+$ and oxygens of TEG, and PF_6^- and hydroxyl hydrogen of TEG (i.e., solvent–solvent rather than solute–solvent) which forms extensive HBD/HBA complexes within the mixture. Chapter 5 titled 'Unusual Solvatochromism within [bmim][PF_6] + Poly(Ethylene Glycol) Mixtures' presents investigation of mixtures of IL [bmim][PF_6] with poly(ethylene glycols) (PEGs) of average molecular weight (MW) 200, 400, 600, 1500. Microscopic solution structuring similar to that proposed within [bmim][PF_6] + TEG is again evoked to explain the experimental outcomes. Chapter 6 (Thermosolvatochromism within Neat and Aqueous Ionic Liquid Systems) describes the effect of temperature on the probe behavior within neat and aqueous IL systems. A rather significant linear decrease in many probe responses on increasing temperature is explained to be caused by a combination of the variation in conductivity, viscosity, density and refractive index within the cybotactic region of the probe along with the probe desolvation. A word of caution is deemed important in analyzing thermosolvatochromic data as specific solute-solvent interactions may result in anomalous temperature dependence within IL-based systems. Chapter 7 is titled 'Conclusions and Future Prospects' and it presents the conclusions drawn from the overall investigation. In brief, it is concluded that addition of a 'green' cosolvent to IL can result in considerable modification/alteration of the physicochemical properties; even enhanced properties can be observed with appropriate combination of the components. Unusual solvatochromic probe behavior is a central theme throughout the thesis. It is suggested that such 'green hybrid' systems could be of potential use to both academia and industry due to their unique properties.

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Chapter 2: Materials and Methodologies