DYE AGGREGATION AND PROBE BEHAVIOR WITHIN AQUEOUS IONIC LIQUID SOLUTIONS

BY

MAROOF ALI

DEPARTMENT OF CHEMISTRY

SUBMITTED

IN FULFILLMENT OF THE REQUIREMENTS OF THE DEGREE OF

DOCTOR OF PHILOSOPHY

TO THE

INDIAN INSTITUTE OF TECHNOLOGY DELHI

NOVEMBER 2010

CERTIFICATE

This is to certify that the thesis entitled, "Dye Aggregation and Probe Behavior within Aqueous Ionic Liquid Solutions", being submitted by Mr. Maroof Ali 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. Maroof Ali 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

ACKNOWLEDGEMENTS

I would like to thank is my supervisor Dr. Siddharth Pandey. His over enthusiasm and integral view on research has made a deep impression on me. I owe him lots of gratitude for having me shown this way of research. He encouraged me to think independently and develop newer ideas regarding my research work. I am deeply indebted to Dr. Siddharth Pandey for providing me state-of-art facilities and a research oriented environment along with his relentless encouragement and support.

I extend my sincere thanks to all the past and present Heads of the Department of Chemistry, and all other teaching and nonteaching members of the Department for providing me necessary help, support and suggestions during my research work.

I would like to express my sincere thanks and gratitude to Dr. Gary A. Baker, Oak Ridge National Laboratory (USA) Dr. (Mrs.) Shubha Pandey, Dr. G. V. Prakash, Dr. N. D. Kurur, Dr. Shashank deep (all from IIT Delhi), Prof. Anwar Ali, Prof. Amir Azam, (JMI, Delhi), Dr. Nafees-ur-Rehman and Dr. Aminul Islam (AMU, Aligarh) for their help and continuous guidance during my research period.

I express my sincere thanks to my labmates, Abhra, Kamalakanta, Shruti, Vinod, Rewa, Hari Om, Raj Kumar, Mintu, Robin, Chhavi, Poulami, and Ambika for their unconditional help, support, and affection towards me. Without their cooperation it would be difficult to achieve this goal.

I would also like to thank to Javed Iqbal, Dr. Sohel Dalal, Mr. Shahid Naeem, Ashhar Iqbal, Jahangeer, and Gulam Mohd with whom I have shared my feelings. I also thank my friends Drs. Mohd Tariq, Altaf, Khalid, Naved, Md. Naushad, Md. Naeem, Masoom, Showkat, Firdoos Itto, Prince Firdaus, Mohd. Rafat, Abrar, Mohd Qamar, Tanveer, and Zia

for their precious help, expertise, generous with this time and memorable moments. Finally, thanks to all IITD friend for their kind hospitality during my stay in IIT Delhi.

Words are no measure to describe the forbearance and fortitude with which my family has encouraged me. I express my sincere gratitude towards my parents, other family members, and my uncle for their unconditional love, support, and blessings which have brought me to reach this destination. I greatly appreciate the love, patience and encouragement received from them. This journey would have been very difficult or rather impossible without their spiritual support to me.

I would also like to express my sincere thanks to University Grant Commission (UGC), India for financial assistance, and Indian Institute of Technology Delhi for providing me other necessary facilities during my research career.

Maroof Ali

ABSTRACTS

ILs are receiving increased attention from both academia and industrial research communities due to their unusual features. Many chemical processes demonstrate effects and outcomes that are very different within a milieu constituted of *only* ions as opposed to molecular solvent. Almost every named chemical reaction has been reported in ILs. ILs also show increased applicability in a variety of analytical methodologies encompassing electroanalysis, separation, extraction, spectrometry, and sensing. The recent investigations on ILs are partly due to their *potential* environmentally-benign nature.

Recent studies by numerous researchers, including our own group, have demonstrated the potential of ILs in altering the behavior of dyes and probes. The hypothesis that ILs and aqueous ILs afford altered (and perhaps unusual) outcomes towards dye aggregation and probe behavior is tested in this thesis. With the help of these studies, different patterns of aggregation and prototropic behavior along with the modes of different solute-solvent and/or solvent-solvent interactions present in IL-based solutions have been unveiled effectively. The thesis also provides insights into the role of the solutes in exploring the physicochemical properties of the IL-based solutions.

The chapter titled "Aggregation Behavior of *meso*-Tetrakis(4-sulfonatophenyl) porphyrin (TSPP) in a hydrophilic IL [bmim][BF_4] and its aqueous mixtures" is divided into two parts. The first part describes that the addition of low amount of [bmim][BF_4] to an aqueous solution of TSPP favors the formation of J-aggregates at low solution pH; further increasing the amount of [bmim][BF_4] leads to destabilization of these aggregates. Addition of IL to higher pH solutions favors the formation of the TSPP-[bmim][BF_4]

complex. The second part details the aggregation and photophysical behavior of TSPP in neat [bmim][BF_4] and in the presence of aqueous HCl. The addition of aqueous HCl results in the efficient formation of J-aggregates of TSPP within neat [bmim][BF_4]. An increase in the formation of aggregates is observed with increase in the strength of aqueous HCl as well as increase in the TSPP concentration. The chapter titled “Prototropism of Fluorescein within Neat and Aqueous Mixtures of Ionic Liquid” deals with the study of the behavior of fluorescein in IL [bmim][BF_4] and its water mixtures. Several important outcomes are obtained from the study of the prototropic behavior of fluorescein in IL [bmim][BF_4]-based solutions. The addition of IL [bmim][BF_4] causes the lactonization of the fluorescein at lower pH while no such effect is observed at higher pH. In neat [bmim][BF_4], no absorbance and fluorescence is observed due to the presence of neutral form of fluorescein. Addition of buffer to IL [bmim][BF_4] causes conversion of the neutral form to the different forms which depends upon the pH of the added buffer. The solvatochromic behavior of the dianion species of the fluorescein is also studied. The emission from the cationic species of the fluorescein is observed in the presence of IL [bmim][BF_4] within dilute HCl which is otherwise to be observed only from highly concentrated HCl or H_2SO_4 solution.

The chapter (Behavior of various dyes and probes within dilute aqueous IL solutions) presents interesting outcomes of IL addition to aqueous dye solutions. The first part of the chapter describes the precipitation and re-dissolution of cationic dyes within dilute aqueous IL solutions. It is observed that the addition of only ~1.7 wt% of ILs [bmim][BF_4] and [bmim][PF_6], respectively, to aqueous solutions of six popular cationic dyes results in the quantitative precipitation of each dye from its aqueous solution. The unusual outcome of dilute aqueous solutions of [bmim][PF_6] prompted us to investigate certain physicochemical properties of this solution. With considerably modified physicochemical properties, dilute aqueous IL solutions may find use in a variety of chemical applications. Specifically, we have measured important physical properties, such as the density, viscosity, and refractive index of dilute aqueous [bmim][PF_6] with up to 2 wt% IL and found these properties to be significantly different from those of pure water. The Chapter (Fluorometric assay of water within ILs) deals with fluorometric estimation of small amounts of water within ILs. It is well known that water is one of the impurities present in ILs due to the hygroscopic nature of most of these neoteric solvents. The stability and physicochemical properties of ILs are highly affected by the presence of water. Water detection and estimation in several ILs is carried out using two fluorescence probes, DMABN and pyranine. Fluorescence emission behaviors of pyranine and DMABN are found to be considerably different with trace amount of water in ILs. Changes in the emission behaviors with varying amount of water provide the means for water estimations.

Chapter titled 'Conclusions and future prospects' presents the conclusions drawn from the overall investigation. In brief, it is concluded that ILs used in our studies are unique in affecting behavior of dyes and probes in their aqueous solutions. Further, it is emphasized that the photophysical behavior of probes and dyes in IL-added systems is different than that in conventional organic solvents. All-in-all, the findings of this work will help understand the different types of molecular-level interactions within IL-based systems and could be of potential use to both academia and industry.

CONTENTS

Chapter 1: Introduction and Background

Chapter 2: Materials and Methodologies

Chapter 3: Aggregation Behavior of *meso*-Tetrakis(4-sulfonatophenyl)porphyrin in a Hydrophilic Ionic Liquid and its Aqueous Mixtures

Chapter 4: Prototropism of Fluorescein within Neat and Aqueous Mixtures of Ionic Liquid

Chapter 5: Behavior of Various Dyes and Probes within Dilute Aqueous Ionic Liquid Solutions

Chapter 6: Fluorometric Assay of Water within Ionic Liquids