# EFFECT OF IONIC LIQUID ON SURFACTANT AGGREGATION

BY

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*Dedicated to*

*My Family*

# CERTIFICATE

This is to certify that the thesis entitled, "Effect of Ionic Liquid on Surfactant Aggregation", being submitted by Mr. Kamalakanta Behera 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. Kamalakanta Behera 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

Volatile organic compounds (VOCs) which are used in many of the synthetic, catalytic, and polymerization reactions and in various types of separation and extraction processes are generally toxic, hazardous, flammable, and environmentally-damaging in nature. As replacements of these VOCs, recently rediscovered environmentally-benign neoteric ionic liquids (ILs) have emerged as potential alternatives due to their unusual physicochemical properties and potential applications in many fields. Further, aqueous surfactant systems comprising of micellar (or micelle-like) aggregates are a topic of major interest both in academic as well as industrial research due to their unusual physicochemical properties and immense technological applications in different fields such as flow field regulators, solubilizing and emulsifying agents, membrane mimetic media, nanoreactors for enzymatic reactions, among others. Hence, it is of great importance to employ ILs in concert with aqueous surfactant systems forming a new type of hybrid environmentally-benign system composed of water, IL, and surfactant. These hybrid systems will have enormous potential in various fields of science and technology.

The thesis entitled 'Effect of Ionic Liquid on Surfactant Aggregation' deals with the understanding of the formation and properties of molecularly organized assemblies within IL-based solutions. The strategy entails not only an exploration of the influence of the nature of the amphiphile and cosolvents leading to self-assembly in IL-based systems but also the development of a much needed fundamental, molecular-level view of the heterogeneity of such systems. In this context, the main theme is to modulate the key physicochemical properties of surfactant-based systems in favorable fashion by adding ILs. The thesis features detailed investigation into the new type of hybrid environmentally-

benign system composed of water, IL, and surfactant, utilizing various invasive and noninvasive methods.

The thesis has been divided into six Chapters. Chapter 1 (Background and Introduction) provides brief introduction to ILs- and surfactant-based systems. It also entails the long- as well as the 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, electrical conductance, and dynamic light scattering (DLS) techniques are used to obtain required information. Chapter 3 (Effect of Hydrophobic Ionic Liquid on Aqueous Surfactant Aggregation) lays out details of the investigations on the IL-surfactant interactions that lead to changes in the physicochemical properties of aqueous surfactant solutions in the presence of an IL having low aqueous solubility. It is shown that addition of hydrophobic IL 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][$PF_6$]) maximum up to 2 wt% (solubility of this IL in water) results in significant changes in the properties of aqueous anionic sodiumdodecyl sulfate (SDS) and zwitterionic dodecyl sulfobetaine (SB-12) due to strong electrostatic interactions between IL ions and the ionic head groups of the surfactants. Whereas, the properties of aqueous solutions of nonionic surfactant triton X-100 (TX-100) remain almost unaltered by the addition of the IL due to the existence of relatively weak interactions, mainly, H-bonding, ion-dipole, and dipole-dipole interactions. Chapter 4 (Effect of Hydrophilic Ionic Liquid on Aqueous Surfactant Aggregation) lays out details of the investigations on the role of hydrophilic IL on the property modulation of aqueous surfactant solutions. Unlike hydrophobic IL having aqueous solubility limitations, hydrophilic IL can be used in any amount to get desired altered physicochemical properties of aqueous surfactant solution due to their complete aqueous miscibility. It is shown that addition of hydrophilic IL results in significant changes in the physicochemical properties of aqueous surfactant solutions of nonionic, anionic, cationic, and zwitterionic surfactants, respectively. Most importantly, formation of micelles/micelle-like aggregates for each of the above four types of surfactants is observed in the presence of as high as 30 wt% IL in solution. It is observed that in modifying properties of aqueous surfactant solutions, IL at higher concentrations shows cosolvent type behavior, whereas it shows both electrolytic as well as cosurfactant behavior when present at lower concentrations. Most importantly, its behavior is significantly different from that of common electrolytes, cosurfactants, and cosolvents as far as the effectiveness in modifying the properties of aqueous surfactant solutions are concerned. Chapter 5 (Ionic Liquid-Based Microemulsions) lays out details of the investigations on the formation of both IL-in-water (IL/w) and water-in-IL (w/IL) microemulsions, respectively, using hydrophobic IL [bmim][$PF_6$], water, and surfactant. It is shown that both surfactant structure and concentration play important role in formation of each type of microemulsions. Chapter 6 is titled 'Conclusions and Future Perspectives' and it summarizes the work presented in the thesis and presents the key conclusions drawn from the overall investigation. In brief, it is concluded that the important physicochemical properties of an aqueous surfactant solution can be effectively modulated by the addition of IL. In this context, hydrophilic IL is more effective than hydrophobic IL due to its complete aqueous miscibility. The behavior of ILs is significantly different from that of common electrolytes, cosurfactants, and cosolvents, as far as the effectiveness and uniqueness in modulating properties of aqueous surfactant solution is concerned. Also, the use of hydrophobic IL as an oil phase in formation of microemulsions will help in replacing environmentally-damaging VOCs. All-in-all, the main theme is to develop a much needed fundamental, molecular-level view of the heterogeneity of the new type of hybrid environmentally-benign multicomponent systems composed of (IL + water + surfactant), thus opening novel avenues for potential applications of ILs.

# CONTENTS

**Chapter 3: Effect of Hydrophobic Ionic Liquid on Aqueous Surfactant Aggregation**