SPECTROSCOPIC INVESTIGATION WITHIN IONIC LIQUID AND DEEP EUTECTIC
SOLVENT BASED SYSTEMS
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ABSTRACT
To realize the full potential of cosolvent/salt-modified Ionic Liquid (IL)- and Deep Eutectic Solvent (DES)-based systems as alternate solvent media, it is important to understand the nature of solute-solute, solute-solvent and solvent-solvent interactions taking place within these systems. In this work, the approach has been the manifestation and exploration of interactions within neat and cosolvent/salt-modified IL- and DES-based systems. The work features a detailed investigation of judiciously selected cosolvent/salt-added IL and DES mixtures by using various optical spectroscopic techniques along with bulk property and micro property measurements.

In the thesis, the spectroscopic properties of Li salt-added IL \([\text{emim}][\text{Tf}_2\text{N}]\) mixtures which exhibit potential as novel electrolytes for Li-ion batteries were investigated. The fluorescence quenching exhibited by fluorophore-quencher pair of pyrene-nitromethane within LiTf\(_2\)N-added IL \([\text{emim}][\text{Tf}_2\text{N}]\) system is controlled by the molecular-level structural changes within the liquid media beyond the changes in the dynamic viscosity as the Li salt is added to the IL. These structural changes are also supported further by the variation in density and dynamic viscosity of IL \([\text{emim}][\text{Tf}_2\text{N}]\) upon addition of salt LiTf\(_2\)N with temperature and salt concentration. The results strongly support the importance of structural changes beyond viscosity on quenching process. The outcome of these investigations can be used to understand diffusion within Li-salt added IL media.

Solute-solvent interactions depend on the identity and structure of both the probes and the ILs. Attractive electrostatic forces are dominant within an IL and they usually have the largest influence on the dynamic viscosity as they provide high resistance to the shear. On the contrary, inter- and intra-molecular H-bonding is the dominant cause for the presence of shear and thus high dynamic viscosity of the tetraethylene glycol (TEG). When an IL is modified by TEG, inter-species H-bonding between IL and TEG takes place within the system, which, depending on the structure of the IL, may or may not be stronger in strength than the coulombic attraction within neat ILs or H-bonding within neat TEG. In both ILs and (IL + TEG) equimolar mixtures cybotactic regions of the fluorescence probes investigated have lower fluidities than those expected. This hints at the restricted dynamics of the solutes within ILs and IL-glycol mixtures. Importantly, fluorescence microviscosity probe responses do not scale well with the dynamic viscosities of the ILs or (IL + TEG) mixtures. This suggests complex nature of the solute-solvent interactions within these systems that strongly depends on both the identity of the probe as well as the structural features of the IL. The outcomes suggest for a cautious approach in selecting ILs and IL-glycol mixtures and to exercise refrain from any generalization as far as applications requiring viscosity-microviscosity know-how is concerned.

In the thesis, the photophysics of L-Tryptophan (L-Trp) in DESs reline and glyceline was studied and these investigation offered DESs as neoteric media to the rapidly growing field of non-aqueous
enzymology with far reaching consequences in the area of biochemistry and biotechnology.

Photophysical parameters of L-Trp in DESs reline and glyceline are compared with those reported in aqueous and non-aqueous media. Fluorescence quantum yields of L-Trp are found to be significantly higher in reline and glyceline as compared to that in water and several common organic solvents due perhaps to the inherent high viscosity associated to these DESs. Rotational reorientation times of L-Trp within the DESs do not conform to the Debye-Stokes-Einstein formulation suggesting inherent complexity of the DESs as solubilizing media. In these studies, rotational reorientation times of probes of different nature and structure are shown to follow boundary conditions between that of stick and slip or close to slip. However, for L-Trp in DESs, the nonconformity to the Debye-Stokes-Einstein formulation hints at the presence of other complex contributions from the DES to the solute dynamics. Fluorescence quenching of L-Trp by acrylamide within reline is purely dynamic in nature, whereas, in contrast, it is a combination of both dynamic and static effects in water. Role of the solvation environment provided by the DESs on photophysics of L-Trp and quenching of its fluorescence by acrylamide is amply highlighted.

The solvent-solvent interactions present between reline and a judiciously selected green cosolvent TEG were investigated when reline is mixed with TEG. It was observed that its properties can be readily modified by adding an environmentally-benign cosolvent TEG which offers multiple H-bonding possibilities. Solvatochromic probe responses within TEG-added reline highlight the complexity associated with the interactions present within this media. Fluorescence probe behavior further support the modification in the solvation properties as TEG is mixed with reline. The outcomes from excess molar volumes of (reline + TEG) mixtures combined with the positive excess logarithmic viscosities of the mixture leads us to propose the presence of stronger H-bonding interactions between reline and TEG as compared to those between reline and reline and between TEG and TEG. FTIR absorbance and Raman spectroscopic data strongly support the observations that the H-bonding between choline chloride and TEG is increased substantially. Interesting H-bonding reversal due to mixing of TEG to reline is highlighted by our results. These outcomes may open new avenues for DESs and their green cosolvent-modified nonaqueous mixtures in materials synthesis and analytical chemistry.

To conclude, this work provides in-depth details of the importance of the neat as well as cosolvent/salt-added IL and DES mixtures using various invasive and non-invasive techniques. Use of cosolvent/salt which are also industrially important, will help develop IL and DES-based systems with modified physicochemical properties having potential applications in synthesis, biotransformation, polymerization, electrochemistry, among many others. To conclude, the ultimate goal has been to develop these novel and alternate media that are comparatively environmentally-benign and can replace/minimize the use of the traditionally-used volatile organic solvent systems. Therefore, research in this field will encourage the development and utilization of environmentally-benign solvents with superior properties leading towards a sustainable development in science and technology.