

**SPECTROSCOPIC INVESTIGATION WITHIN IONIC LIQUID AND
DEEP EUTECTIC SOLVENT BASED SYSTEMS**

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SPECTROSCOPIC INVESTIGATION WITHIN IONIC LIQUID AND DEEP EUTECTIC SOLVENT BASED SYSTEMS

by

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Submitted

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Dedicated to
My Parents

CERTIFICATE

This is to certify that the thesis entitled, “**Spectroscopic Investigation within Ionic Liquid and Deep Eutectic Solvent Based systems**”, being submitted by **Miss Anu Kadyan** 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 reported in the dissertation have not been submitted in part or full to any other University or Institute for the award of any degree or diploma.

Date:

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Almighty and the divine nature.

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ABSTRACT

The fascinating and unique properties of Ionic Liquids (ILs) and of Deep Eutectic Solvents (DESs) coupled to their wide range of applications in various industries and academia render them solvents of utmost importance. However, still not much has been explored about the interactions present within these solvents which restrict their use. In this context, a detailed study of the interactions within neat and cosolvent/salt-modified IL and DES-based systems will help fine tune their physicochemical properties, thereby increasing the overall utility of ILs and DESs.

The thesis entitled ‘Spectroscopic Investigation within Ionic Liquid and Deep Eutectic Solvent Based Systems’ is concerned with the understanding of interactions within neat and cosolvent/salt-modified IL and DES-based systems. The thesis 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. The experimental observations are used to assess the solute-solvent and solvent-solvent interactions within multicomponent IL- and DES-based systems.

The thesis has been divided into seven chapters. Chapter 1 (Background and Introduction) provides a brief introduction to the ILs, DESs, and cosolvent/salt that are employed for the research work along with the motivation behind choosing the particular systems. It also describes the long- as well as short-term aims of the investigation. Chapter 2 titled ‘Materials and Methodologies’ is about chemicals used, purification and storage as well as techniques used during the investigation. Specifically, UV-Vis molecular absorbance, steady-state and time-resolved fluorescence, FTIR absorbance,

Raman spectroscopy, density, and dynamic viscosity measurements are used to acquire the requisite information.

Chapter 3 titled ‘Density, Viscosity and Fluorescence Quenching within Lithium Salt-Added Ionic Liquid Media’ presents excited-state fluorescence lifetime quenching of a popular fluorophore pyrene by well-known quencher nitromethane within LiTf₂N-added IL [emim][Tf₂N] up to 0.40 LiTf₂N mole fraction ($x_{\text{LiTf}_2\text{N}}$) in the temperature range 298.15 to 358.15 K. The main aim of this chapter is to gain insight into the solute diffusion behavior and structural changes in the ionic media with the addition of Li⁺ ions. Chapter 4 titled ‘Microfluidity of Ionic Liquids and Glycol-Modified Ionic Liquids’ provides detailed investigation of various microfluidity probes dissolved within neat ILs and their equimolar mixtures with TEG. The interactions present within the solubilizing media constituted of IL govern the outcomes of chemical processes carried out within such media by controlling the behavior of solutes dissolved therein. The response of spectroscopic microfluidity probes dissolved in IL and IL-based solvents, in this regard, reveals information on both solute-solvent and solvent-solvent interactions present within the system. Chapter 5 titled ‘Photophysical Behavior and Florescence Quenching of L-Tryptophan in Choline Chloride-Based Deep Eutectic Solvents’ presents the detailed investigation of the photophysical properties of L-Trp in two common and popular representative DESs - reline and glyceline - over a temperature range of 298.15-358.15 K. Photophysical properties, such as, absorbance and emission maxima, steady-state anisotropy, fluorescence quantum yield, excited-state intensity and anisotropy decay, and their temperature dependence of L-Trp have potential to offer key insights to the protein dynamics in these neoteric solvents. Further, in this chapter we also reported the outcomes of our investigation of fluorescence quenching of L-Trp within Reline by acrylamide, a well-established electron/charge acceptor quencher; acrylamide is often

used to probe the protein conformation during the quenching of intrinsic L-Trp fluorescence. Chapter 6 titled ‘Spectroscopic Probing of Tetraethylene Glycol Modified (Choline Chloride + Urea) Deep Eutectic Solvent’ explores the effect of cosolvent TEG on the properties of DES reline using solvatochromic probes along with noninvasive techniques, such as, density, viscosity, FTIR and Raman spectroscopy over the complete composition regime within 298 K-358 K. Empirical solvent polarity parameter, E_T^N , obtained using solvatochromic absorbance probe response of a betaine dye, along with Kamlet-Taft parameters suggest the presence of interactions, mainly H-bonded, between TEG and the components of reline. HBA basicity (β) of TEG-modified reline is found to be unusually high. Responses from dipolarity as well as intramolecular charge-transfer fluorescence probes further support these outcomes suggesting a small amount of TEG can effectively alter properties of reline.

Chapter 7 titled ‘Conclusions and Future Prospects’ covers the conclusions drawn from the overall investigation. In brief, it is concluded that addition of a cosolvent or a salt to ILs and/or DESs can result in considerable modification/alteration of physical and physicochemical properties; even favorably enhanced properties can be observed with the appropriate combination of the components. It is suggested that such cosolvent/salt-modified ‘hybrid’ systems may prove to be an inexpensive environmentally benign solubilizing media with potential applications in both academia and industry.

सार

आयनिक लिक्विड (आईएलएस) और डीप यूटेक्टिक सॉल्वेंट्स (डीईएस) के आकर्षक और अद्वितीय गुणों के साथ इनके विभिन्न उद्योगों और शैक्षिक क्षेत्र में प्रयोगिता ने उन्हें अत्यंत महत्व के सॉल्वेंट्स बनाया है। हालांकि, अभी भी इन सॉल्वेंट्स के भीतर मौजूद इंटरैक्शन के बारे में बहुत कुछ नहीं पता चला है जो उनके उपयोग को प्रतिबंधित करते हैं। इस संदर्भ में, नीट और कोसॉल्वेंट/सॉल्ट-संशोधित-आधारित आयनिक लिक्विड (आईएलएस) और डीप यूटेक्टिक सॉल्वेंट्स (डीईएस) सिस्टम के भीतर इंटरैक्शन का एक विस्तृत अध्ययन उनके भौतिक रासायनिक गुणों को ठीक करने में मदद करेगा, जिससे आईएलएस और डीईएस की समग्र उपयोगिता बढ़ जाएगी।

यह थीसिस, जिसका शीर्षक है, “आयनिक लिक्विड और डीप यूटेक्टिक सॉल्वेंट बेस्ड सिस्टम्स के भीतर स्पेक्ट्रोस्कोपिक इनवेस्टिगेशन” का संबंध नीट और कोसॉल्वेंट/सॉल्ट-संशोधित आईएल और डीईएस-आधारित सिस्टम के भीतर इंटरैक्शन की समझ से है। थीसिस में कई ऑप्टिकल स्पेक्ट्रोस्कोपिक तकनीकों के साथ-साथ बल्क प्रॉपर्टी और माइक्रो प्रॉपर्टी मापों का उपयोग करके विवेकपूर्ण रूप से चयनित कोसॉल्वेंट/सॉल्ट-एडेड आईएल और डीईएस मिश्रणों की विस्तृत जांच की गई है। प्रयोगात्मक टिप्पणियों का उपयोग मल्टीकंपोनेंट आईएल और डीईएस आधारित प्रणालियों के भीतर विलय-विलायक और विलायक-विलायक इंटरैक्शन का मूल्यांकन करने के लिए किया जाता है।

थीसिस को सात अध्यायों में विभाजित किया गया है। अध्याय 1 (पृष्ठभूमि और परिचय) आईएलएस, डीईएस और कोसॉल्वेंट/सॉल्ट आधारित का एक संक्षिप्त परिचय प्रदान करता है जो विशेष प्रणालियों को चुनने के पीछे प्रेरणा के साथ शोध कार्य के लिए नियोजित होते हैं। यह लंबी अवधि के साथ-साथ जांच के अल्पकालिक उद्देश्यों का भी वर्णन करता है। अध्याय 2 शीर्षक 'सामग्री और कार्यप्रणाली' रसायनों का उपयोग, शुद्धि और भंडारण के साथ-साथ जांच के दौरान उपयोग की जाने वाली तकनीकों के बारे में है। विशेष रूप से, यूवी-विज़ मॉलिक्यूलर एब्सोर्बंस, स्टेडी-स्टेट और टाइम रेसोल्व्ड फ्लोरोसेन्स, एफटीआईआर एब्सोर्बंस, रमन स्पेक्ट्रोस्कोपी, घनत्व और गतिशील चिपचिपापन माप का उपयोग अपेक्षित जानकारी प्राप्त करने के लिए किया जाता है।

अध्याय 3 शीर्षक 'घनत्व, चिपचिपापन और प्रतिदीप्ति शमन लिथियम सॉल्ट-एडेड आयनिक लिक्विड मीडिया के भीतर' LiTf_2N - एडेड आईएल [emim] $[\text{Tf}_2\text{N}]$ के भीतर एक प्रसिद्ध क्वेंचर नाइट्रोमिथेन द्वारा एक लोकप्रिय फ्लोरोफोर पाइरीन के उत्तेजित-स्टेट फ्लोरोसेंस जीवनकाल को तापमान रेंज 298.15 से 358.15 K ऑन और 0.40 LiTf_2N

मोल अंश तक में प्रस्तुत करता है। इस अध्याय का मुख्य उद्देश्य Li^+ आयनों के साथ आयनिक मीडिया में विलेय प्रसार व्यवहार और संरचनात्मक परिवर्तनों में अंतर्दृष्टि प्राप्त करना है।

अध्याय 4 का शीर्षक “माइक्रोफ़्लूइडीटी ऑफ़ आयनिक लिक्विड्स और ग्लाइकॉल-मॉडिफाइड आयनिक लिक्विड्स”, नीट आयनिक लिक्विड्स और टीईजी के साथ उनके भूमध्यरेखीय मिश्रण के भीतर भंग किए गए विभिन्न माइक्रोफ़्लूइडीटी प्रोब्स की विस्तृत जांच प्रदान करता है।

आईएल को गठित किए गए सॉल्युबलाइजिंग मीडिया के भीतर मौजूद इंटरैक्शन इस तरह के विलेय के व्यवहार को नियंत्रित करके ऐसे मीडिया के भीतर किए गए रासायनिक प्रक्रियाओं के परिणामों को नियंत्रित करते हैं। इस संबंध में आईएल और आईएल-आधारित सॉल्वेंट्स में भंग किए गए स्पेक्ट्रोस्कोपिक माइक्रोफ़्लूइडीटी जांच की प्रतिक्रिया, सिस्टम के भीतर मौजूद विलेय-विलायक और विलायक-विलायक इंटरैक्शन दोनों पर जानकारी प्रकट करती है।

अध्याय 5 का शीर्षक “कोलीन क्लोराइड-आधारित डीप यूक्टेक्टिक सॉल्वेंट्स के भीतर L-Trp का फोटोफिजिकल बिहेवियर और फ्लोरोसेंस कुएन्चिंग”, दो सामान्य और लोकप्रिय प्रतिनिधि डीईएस- रेलीन और ग्लाइसेलीन के फोटोफिजिकल गुणों की 298.15-358.15 K तापमान सीमा में विस्तृत जांच प्रस्तुत करता है - फोटोफिजिकल गुण, जैसे, एब्सोर्बंस और एमिशन मैक्सिमा, स्टेडी-स्टेट एनआइसोट्रोपी, फ्लोरोसेंस क्वांटम उपज, उत्साहित-स्टेट तीव्रता और एनआइसोट्रोपी डीकेय, और L-Trp के उनके तापमान पर निर्भरता इन नवपाषाण सॉल्वेंट्स में प्रोटीन गतिशीलता की प्रमुख अंतर्दृष्टि प्रदान करने की क्षमता है। इसके अलावा, इस अध्याय में हमने एक्रिलामाइड, एक अच्छी तरह से स्थापित इलेक्ट्रॉन / चार्ज स्वीकर्ता क्वेंचर द्वारा रेलीन के भीतर L-Trp की फ्लोरोसेंस कुएन्चिंग की हमारी जांच के परिणामों की रिपोर्ट की; एक्रिलामाइड का उपयोग अक्सर आंतरिक L-Trp फ्लोरोसेंस कुएन्चिंग के दौरान प्रोटीन के विरूपण की जांच के लिए किया जाता है।

अध्याय 6 का शीर्षक “स्पेक्ट्रोस्कोपिक प्रोबिंग ऑफ़ टेट्राथिलीन ग्लाइकोल मॉडिफाइड (कोलीन क्लोराइड + यूरिया) डीप यूक्टेक्टिक सॉल्वेंट” नॉन इनवेसीव तकनीक, जैसे कि घनत्व, चिपचिपापन, एफटीआईआर और रमन के साथ सॉल्वोक्रोमिक जांच का उपयोग करते हुए डीईएस रेलीन के गुणों पर कॉलेवेंट टीईजी के प्रभाव की पड़ताल पूर्ण संरचना शासन और तापमान 298 K-358 K के भीतर करता है। अनुभवजन्य विलायक ध्रुवीयता पैरामीटर, एक बीटेन डाई की सॉल्वेटोक्रोमिक अवशोषक जांच प्रतिक्रिया का उपयोग करके प्राप्त किया जाता है, साथ ही केमलेट-टाफ्ट पैरामीटर, टीईजी और रेलीन के

घटकों के बीच, मुख्य रूप से H- बंधित, इंटरैक्शन की उपस्थिति का सुझाव देते हैं। टीईजी- संशोधित रेलीन की HBA बेसिसिटी (β) असामान्य रूप से अधिक पाई जाती है। द्विध्रुवीयता के साथ-साथ इंट्रामॉलिक्यूलर चार्ज-ट्रांसफर फ्लोरोसेंस जांच के जवाब टीईजी की थोड़ी मात्रा को प्रभावी ढंग से बदलने के लिए इन परिणामों का समर्थन कर सकते हैं।

अध्याय 7 शीर्षक 'निष्कर्ष और भविष्य की संभावनाएं' समग्र जांच से निकाले गए निष्कर्षों को शामिल करता है। संक्षेप में, यह निष्कर्ष निकाला गया है कि कोल्सवैट या सॉल्ट के द्वारा आईएलएस और/या डीईएस के परिणामस्वरूप भौतिक और भौतिक रासायनिक गुणों में काफी संशोधन/परिवर्तन हो सकता है; घटकों के उपयुक्त संयोजन के साथ भी अनुकूल रूप से उन्नत गुण देखे जा सकते हैं। यह सुझाव दिया गया है कि इस तरह के कॉसॉल्वेंट/सॉल्ट-संशोधित सिस्टमस हाइब्रिड 'सिस्टम शिक्षा और उद्योग दोनों में संभावित अनुप्रयोगों के साथ एक सस्ती और पर्यावरणीय सौम्य मीडिया साबित हो सकते हैं।

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LIST OF ABBREVIATIONS

Abbreviation	Full form
IL	Ionic Liquid
DES	Deep Eutectic Solvents
[bmim][PF ₆]	1-butyl-3-methylimidazolium hexafluorophosphate
[bmim][OTf]	1-butyl-3-methylimidazolium trifluoromethylsulfonate
[bmim][BF ₄]	1-butyl-3-methylimidazolium tetrafluoroborate
[bdmim][BF ₄]	1-butyl-2,3-dimethylimidazolium tetrafluoroborate
[bmim][Tf ₂ N]	1-butyl-3-methylimidazolium <i>bis</i> (trifluoromethanesulfonyl)imide
[emim][Tf ₂ N]	1-ethyl-3-methylimidazolium <i>bis</i> (trifluoromethanesulfonyl)imide
[dmpim][Tf ₂ N]	1,2-dimethyl-3-propylimidazolium <i>bis</i> (trifluoromethanesulfonyl)imide
[bmim][TFA]	1-butyl-3-methylimidazolium trifluoroacetate
[bmpip][Tf ₂ N]	1-butyl-3-methylpiperidinium <i>bis</i> (trifluoromethanesulfonyl)imide
[bmpyr][Tf ₂ N]	1-butyl-1-methylpyrrolidinium <i>bis</i> (trifluoromethanesulfonyl)imide
[choline][Tf ₂ N]	<i>N,N,N</i> -trimethylethanolammonium <i>bis</i> (trifluoromethanesulfonyl)imide
TEG	Tetraethylene Glycol
LiTf ₂ N	Lithium <i>bis</i> (trifluoromethanesulfonyl)imide
$E_T(30)$	Transition energy corresponding to betaine dye 30
$E_T(33)$	Transition energy corresponding to betaine dye 33
E_T^N	Normalized E_T values

DENA	<i>N,N</i> -diethyl-4-nitroaniline
NA	4-Nitroaniline
Py	Pyrene
PyCHO	1-pyrenecarboxaldehyde
BPP	1,3- <i>bis</i> (1-pyrenyl)propane
BPD	1,10- <i>bis</i> (1-pyrenyl)decane
PRODAN	6-propionyl-2-(dimethylamino)naphthalene
C-153	Coumarin-153
ANS	1-anilino-8-naphthalene sulfonate
TNS	2-(<i>p</i> -toluidino)naphthalene-6-sulfonate
R6G	Rhodamine 6G
DPH	1,6-diphenyl-1,3,5-hexatriene
DCVJ	9-(2,2-dicyanovinyl)julolidine
L-Trp	L-Tryptophan
LED	Light emitting diode
IRF	Instrument response function
FTIR	Fourier transform infra red
uv	Ultraviolet
vis	Visible