

**SPECTROSCOPIC INVESTIGATION OF DEEP EUTECTIC
SOLVENTS AND THEIR COSOLVENT–MODIFIED MIXTURES**

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**SPECTROSCOPIC INVESTIGATION OF DEEP EUTECTIC
SOLVENTS AND THEIR COSOLVENT–MODIFIED MIXTURES**

by

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Submitted

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to the



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Dedicated to

My Parents

CERTIFICATE

This is to certify that the thesis entitled, “**Spectroscopic Investigation of Deep Eutectic Solvents and their Cosolvent-Modified Mixtures**”, being submitted by **Mr. Ashish Pandey** 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. He 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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ABSTRACT

The peculiar and beguiling features of deep eutectic solvents (DESs) coupled to their wide range of applications in various industries and academia make them solvents of sheer importance. However, since not much has been explored about these neoteric solvents, overall use of DESs as green media is still restricted. In this context, a detailed study of neat DESs and cosolvent-modified DES systems will help fine tune their physicochemical properties, thereby increasing the overall utility of DESs.

The thesis entitled ‘Spectroscopic Investigation of Deep Eutectic Solvents and their Cosolvent–Modified Mixtures’ is concerned with the understanding of the interactions within neat DESs as well as cosolvent-modified DES–based systems. The thesis presents a detailed analysis of the solubilizing ability of popular DESs and judiciously selected cosolvent-added DESs systems utilizing various optical spectroscopic and other techniques. The experimental observations are used to assess the interactions within several multicomponent DES-based systems.

The thesis comprises of seven chapters. Chapter 1 (Background and Introduction) presents a compact introduction of DESs and the issues that lead to this particular research work along with approaches to resolve them. It also describes the long- as well as 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, excited-state fluorescence intensity decay and fluorescence correlation spectroscopy (FCS) measurements coupled with non-invasive techniques such as FTIR absorbance and

Raman spectroscopies, and density and dynamic viscosity measurements are used to acquire the necessary information.

Chapter 3 titled ‘Polarity of Choline Chloride-Based Deep Eutectic Solvents’ provides an estimate of the polarity associated to these solvents. Detail knowledge of the dipolarity of DESs is essential for the development of them as green media. The solvatochromic optical spectroscopic response of various uv-vis absorbance and molecular fluorescence probes has been used to assess the polarity of DESs. Information on the cybotactic region that surrounds several solvatochromic probes within four common and popular choline chloride based DESs, named Ethaline, Glyceline, Reline and Maline, is obtained and used to assess the effective dipolarity afforded by each of these DESs. Chapter 4 (Solvatochromic Probe Behavior within Choline Chloride–Based Deep Eutectic Solvents: Effect of Temperature and Water) deals with the changes in the spectroscopic behavior of absorbance probes and fluorescence dipolarity probes with temperature within the DESs– Ethaline, Glyceline and Reline and their aqueous mixtures. Variations in temperature and addition of water, a benign cosolvent, can alter the physicochemical properties of a DES.

Chapter 5 titled ‘Fluorescence Quenching of Polycyclic Aromatic Hydrocarbons within Deep Eutectic Solvents and their Aqueous Mixtures’ explores the applicability of nitromethane as a selective fluorescence quenching agent for the analysis of polycyclic aromatic hydrocarbons (PAHs) within Glyceline and Reline. Interestingly, the different PAHs dissolved in Glyceline and Reline were differentiated into two groups based on their quenching efficiencies. Diffusion dynamics of pyrene in aqueous mixtures of both the DESs has also been discussed and shown to be independent of the identity of the

solute. Chapter 6 (Hydrogen Bond Donor/Acceptor Cosolvent-Modified Choline Chloride Based Deep Eutectic Solvents) provides details of the solvatochromic probe behavior within Glyceline and Reline on addition of HB donor/acceptor cosolvents– TFE and HMPA, respectively. Addition of cosolvents TFE and HMPA having contrasting features of very high HB donating acidity and HB accepting basicity, respectively, significantly modifies the physicochemical properties of Glyceline and Reline. Addition of HB donor/acceptor cosolvent appears to disturb the salt-HB donor equilibria within DES via complex interplay of interactions within the system.

‘Conclusions and Future Perspectives’ are presented in the final chapter (chapter 7) of the thesis where the inferences withdrawn from the overall study are discussed. In short, it is concluded that DESs are effective solvents with solvation capability similar to many ionic liquids and other conventional solvents. Also, the addition of a cosolvent to DESs may significantly modify/change the physicochemical properties of the DES; task-specific DES-based multicomponent systems with favorably enhanced physicochemical properties can thus be developed. The work done towards this thesis will increase the overall effectiveness of the newly developed DESs.

सार

विभिन्न उद्योगों और शिक्षाविदों में उनके व्यापक आवेदनों के साथ डीप इयूटेक्टिक सॉल्वेंट्स (डीईएस) की अनोखी और भ्रामक विशेषताएं उन्हें महत्व के सॉल्वेंट्स बनाती हैं। हालांकि, चूंकि इन नये सॉल्वेंट्स के बारे में ज्यादा नहीं पता लगाया गया है, डीईएस का संपूर्ण उपयोग ग्रीन मीडिया के रूप में अभी भी प्रतिबंधित है। इस संदर्भ में, स्वच्छ डीईएस और कॉसोलेंट-संशोधित डीईएस सिस्टम का एक विस्तृत अध्ययन उनके भौतिक गुणों को बेहतर बनाने में मदद करेगा, जिससे डीईएस की समग्र उपयोगिता बढ़ जाएगी।

“डीप इयूटेक्टिक सॉल्वेंट्स स्पेक्ट्रोस्कोपिक इनवेस्टिगेशन और उनके कॉसोलेंट-संशोधित मिश्रण” नामक शोध निपुण डीईएस के साथ-साथ कॉसोलेंट-संशोधित डीईएस सिस्टम की समझ के साथ संबंध है। थीसिस लोकप्रिय डीईएस की सुलभ क्षमता का विस्तृत विश्लेषण और विभिन्न ऑप्टिकल स्पेक्ट्रोस्कोपिक और अन्य तकनीकों का उपयोग करने वाले विवेकपूर्ण रूप से चयनित कॉसोलेंट-डीईएस सिस्टम को प्रस्तुत करता है। प्रयोगात्मक अवलोकनों का उपयोग कई मल्टी-कॉम्पोनेंट डीईएस-आधारित प्रणालियों के भीतर होने वाले इंटरैक्शन का आकलन करने के लिए किया जाता है।

थीसिस में सात अध्याय शामिल हैं अध्याय 1 (पृष्ठभूमि और परिचय) डीईएस के कॉम्पैक्ट परिचय और उन समस्याओं को सुलझाने के दृष्टिकोण के साथ इस विशेष अनुसंधान कार्य के लिए आगे बढ़ता है। यह जांच के लंबे और साथ ही लघु-अवधि के उद्देश्यों का भी वर्णन करता है। अध्याय 2 नामक 'सामग्री और पद्धतियां' रासायनिक खरीद, शुद्धि और भंडारण के साथ-साथ जांच के दौरान इस्तेमाल की जाने वाली तकनीकों के बारे में है। विशेष रूप से, यूवी-विज आणविक अवशोषण, आणविक प्रतिदीप्ति, उत्साहित-राज्य प्रतिदीप्ति तीव्रता क्षय और प्रतिदीप्ति सहसंबंध स्पेक्ट्रोस्कोपी (एफसीएस) मापन जैसे कि गैर-इनवेसिव तकनीक जैसे एफटीआईआर शोष और रमन स्पेक्ट्रोस्कोपी, और घनत्व और गतिशील चिपचिपाहट माप का उपयोग आवश्यक जानकारी प्राप्त करने के लिए किया जाता है।

अध्याय 3 नामक 'पोलरेटी ऑफ क्लोइन क्लोराइड-बेसेड डीप इयूटेक्टिक सॉल्वेंट्स' इन सॉल्वेंट्स से जुड़े ध्रुवीकरण का एक अनुमान प्रदान करता है। डीईएस के द्विध्रुवीकरण का विस्तृत ज्ञान उन्हें हरे रंग की मीडिया के रूप में विकसित करने के लिए आवश्यक है। विभिन्न यूवी-विज अवशोषण और आणविक प्रतिदीप्ति जांच के सोल्वेटोक्रोमिक ऑप्टिकल स्पेक्ट्रोस्कोपिक प्रतिक्रिया डीईएस की ध्रुवीकरण का आकलन करने के लिए उपयोग किया गया है। चार सामान्य और लोकप्रिय कोलिन क्लोराइड आधारित डीईएसएस, एथैलीन, ग्लासेलेन, रिलेन और मैलेन नाम के भीतर कई सल्वेटोक्रोमिक जांच के चारों ओर से घेरे वाले साइबेटेक्टिक क्षेत्र की जानकारी प्राप्त की जाती है और इनमें से प्रत्येक डीईएस द्वारा प्राप्त प्रभावी द्विध्रुवीय का आकलन करने के लिए उपयोग किया जाता है। अध्याय 4 (क्लोइन क्लोराइड के भीतर सोल्वेटोक्रोमोमिक प्रोब बिहेवियर- बर्ज डीप इयूटेक्टिक सॉल्वेंट्स: तापमान और पानी का प्रभाव) अवशोषण जांच के स्पेक्ट्रोस्कोपिक व्यवहार में परिवर्तन और डीईएसएस एथैलीन, ग्लासेलेन और रिलेन के भीतर तापमान और प्रतिदीप्ति द्विध्रुवीय जांच में परिवर्तन से संबंधित है और उनके जलीय मिश्रण। तापमान और पानी के जोड़ में बदलाव, एक सौम्य कॉसोलेंट, डीईएस के भौतिक गुणों को बदल सकते हैं।

अध्याय 5 नामक 'फ्लोरेन्सेंस क्वेंकिंग ऑफ पॉलिकेक औरैमेटिक हाइड्रोकार्बन इन डीप इयूटेक्टिक सॉल्वेंट्स एंड एक्जुस मिस्क्वर्स' ने ग्लिसेलेन और रिलेन के अंदर पॉलिलिकिक सुगन्धित हाइड्रोकार्बन (पीएच) के विश्लेषण के लिए एक चयनात्मक प्रतिदीप्ति शमन एजेंट के रूप में नाइट्रोमेथेन की प्रयोज्यता की खोज की है। दिलचस्प बात यह है कि, ग्लासेलेन और रिलेन में अलग-अलग पीएच भंग कर उनकी शमन की क्षमता के आधार पर दो समूहों में विभेद किया गया। दोनों डीईएस के जलीय मिश्रण में प्यूरिन की गतिशीलता की गतिशीलता पर भी विचार-विमर्श किया गया है और

इसे सॉल्यूट की पहचान से मुक्त करने के लिए दिखाया गया है। अध्याय 6 (हाइड्रोजन बॉन्ड डोनर / एसेप्टोर कॉसोलेंट -संशोधित क्लोइन क्लोराइड बेस गेट एयूटेक्टिक सॉल्वेंट्स) क्रमशः एचबी डोनर / स्वीकर्ता कॉसोल्वेन्ट्स टीएफई और एचएमपीए के अलावा ग्लासेसेन और रिलेन के भीतर सोल्वेट्रोक्रोमिक जांच के विवरण का विवरण प्रदान करता है। कोसोल्वेन्ट्स टीएफई और एचएमपीए को जोड़कर बहुत उच्च एचबी दान देने वाली एसिडिटी और एचबी को मूलभूतता स्वीकार करने की सुविधाओं के विपरीत, क्रमशः ग्लासेलेन और रिलेन के भौतिक गुणों को संशोधित करता है। एचबी दाता / स्वीकर्ता कॉसोलेंट को जोड़ना प्रणाली के भीतर बातचीत के जटिल परस्पर क्रिया के माध्यम से डीईएस के भीतर नमक-एचबी दाता संतुलन को परेशान करने लगता है।

'निष्कर्ष और भविष्य के परिप्रेक्ष्य' को अंतिम अध्याय (अध्याय 7) में प्रस्तुत किया गया है, जहां पर समग्र अध्ययन से निकाले गए निष्कर्ष पर चर्चा की जाती है। संक्षेप में, यह निष्कर्ष निकाला है कि डीईएस कई आयनिक तरल पदार्थ और अन्य पारंपरिक सॉल्वेंट्स के समान सॉल्वेशन क्षमता वाले प्रभावी सॉल्वेंट्स हैं। इसके अलावा, डीईएस में कॉसोलेंट जोड़ने से डीईएस के भौतिक गुणों को संशोधित / बदल सकते हैं; कार्य-विशिष्ट डीईएस-आधारित बहुसंख्यक प्रणालियों के साथ अनुकूल बड़े हुए भौतिक गुणों को विकसित किया जा सकता है। इस थीसिस के लिए किए गए काम से नव विकसित डीईएसएस की समग्र प्रभावशीलता में वृद्धि होगी।

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Bio-data

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LIST OF ABBREVIATIONS

Abbreviation	Full form
DES	Deep Eutectic Solvents
[bmim][PF ₆]	1-butyl-3-methylimidazolium hexafluorophosphate
[bmim][BF ₄]	1-butyl-3-methylimidazolium tetrafluoroborate
TFE	2,2,2– Trifluoroethanol
HMPA	Hexamethylphosphoramide
$E_T(30)$	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
PRODAN	6-propionyl-2-(dimethylamino)naphthalene
ANS	1-anilino-8-naphthalene sulfonate
TNS	2-(<i>p</i> -toluidino)naphthalene-6-sulfonate
PAHs	Polycyclic aromatic hydrocarbons
FCS	Fluorescence Correlation Spectroscopy
LED	Light emitting diode
IRF	Instrument response function
FTIR	Fourier transform infra red

uv

Ultraviolet

vis

Visible