

**SURFACTANT AND DYE AGGREGATION WITHIN DEEP
EUTECTIC SOLVENT-BASED SYSTEMS**

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by

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Department of Chemistry

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Dedicated to

My Parents

CERTIFICATE

This is to certify that the thesis entitled, “**Surfactant and Dye Aggregation Within Deep Eutectic Solvent-Based Systems**”, being submitted by **Mr. Mahipal** 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 unusual and fascinating features of the molecular aggregation of surfactants and dye within 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 the surfactants and dye aggregation within these neoteric solvents, overall use of DESs as green media is still restricted. In this context, a detailed study of neat DESs and water added DES systems will help fine tune their physicochemical properties, thereby increasing the overall utility of DESs.

The thesis titled ‘Surfactant and Dye Aggregation within Deep Eutectic Solvent-Based Systems’ is concerned with the understanding of the molecular aggregation within DES media. The thesis features detailed investigation of the aggregation of popular surfactants and common carbocyanine dyes within neat and water added DESs using various optical spectroscopic and other techniques. Chapter 1 ‘Background and Introduction’ provides a brief overview of the various systems that are investigated in this work. It also provides concise introduction to the problems that this particular research work is based on along with the strategies adopted to solve them. Both long- and short-term objectives of the investigation are also discussed. The basic intent of the work is to understand the aggregation of surfactants and carbocyanine dyes within DES-based solubilizing media.

However, the basic science involved with fully characterizing these DESs as solvent systems is still in its infancy, holding back more efficient utilization of these “*green*”

solvents. Phenomenon of molecular aggregation within DES-based solvent systems is of great importance due to its immense application potential in various fields.

Chapter 2 titled ‘Materials and Methodologies’ is about chemical procurement, preparation, purification and storage as well as techniques used during the investigation. Specifically, uv-vis molecular absorbance, steady-state and time-resolved fluorescence, refractometer, DLS (dynamic light scattering), SAXS (small-angle X-ray scattering), transmission electron microscopy (TEM), conductometry, density and dynamic viscosity as well as surface tension measurements were used to gather requisite information. Chapter 3 is titled ‘Self-Aggregation of Surfactants within Choline Chloride Derived Deep Eutectic Solvents’. In this chapter, we have presented self-aggregation of cationic surfactants within (choline chloride + glycerol) DES. Specifically, self-aggregation of cationic surfactants of the *n*-alkyltrimethylammonium family within an archetypical DES glyceline was found to take place spontaneously. Estimated thermodynamic parameters suggest this self-aggregation process to be less entropically driven than that in water. The self-assembly process was found to be thermodynamically favorable.

The responses of fluorescence dipolarity and microfluidity probes, pyrene and 1,3-bis-(1-pyrenyl) propane, respectively, were used to establish the existence of these aggregates. Surface tension, electrical conductivity, DLS, SAXS, TEM, density, and dynamic viscosity measurements were effectively used to characterize the aggregates (e.g., micelles and/or microemulsions). We next present clear lines of evidence for self-aggregation of a popular anionic surfactant within a DES containing a small fraction of water. Namely, well-defined assemblies of sodium dodecyl sulfate (SDS) apparently form in the archetype DES reline. Significant enhancement in the solubility of organic

solvents that are otherwise not miscible in choline chloride-based DESs was achieved within reline in the presence of SDS. The remarkably improved solubility of cyclohexane within SDS-added reline is attributed to the presence of spontaneously formed oil-in-DES microemulsions by SDS under ambient conditions. The novel water-free self-assemblies presented in this work might serve as dynamic soft templates to direct the growth of size- or shape-tailored nanoparticles within water-restricted media under ambient conditions. Chapter 4 titled ‘Properties of Aqueous Micellar Solutions in the Presence of Deep Eutectic Solvents’, presents changes in the physicochemical properties of aqueous surfactant solutions above their critical micelle concentrations (cmc) as DESs reline and glyceline, respectively, are added. It is shown that the properties of aqueous surfactant solutions can be tuned in favorable fashion by adding appropriate amount of DES. The main emphasis of this investigation is to establish the versatile role of DESs in modifying properties of aqueous surfactant solutions which may enhance the applications of aqueous surfactant systems; potential applicability of DESs will increase as well.

Further, for comparison sake, the effect of IL addition on the physicochemical properties of aqueous micellar solutions of various surfactants is also assessed. The overall outcomes of this work infers that appropriate addition of DES can result in desirable changes in the physicochemical properties of surfactant solutions. Chapter 5 is titled ‘Aggregation of Carbocyanine Dyes in Choline Chloride-Based Deep Eutectic Solvents in the Presence of Aqueous Base’. The self-aggregation behavior of two common and popular carbocyanine dyes, 5,5',6,6'-tetrachloro- 1,1'-diethyl- 3,3'-di(4-sulfobutyl)-benzimidazole carbocyanine (TDBC) and 5,5'-dichloro-3,3'-di(3-sulfopropyl)-9-methyl-benzothiacarbocyanine (DMTC), was investigated within DES

glyceline and reline, under ambient conditions. Effect of the addition of aqueous base on aggregation was explored. The optical spectroscopic responses of uv-vis absorbance and molecular fluorescence probes mentioned above indicate that both DESs in the presence of base are found to support J-aggregates of TDBC. Under similar conditions, DMTC forms fluorescent H-aggregates along with J-aggregates within the above DES-based systems. A comparison of the carbocyanine dye behavior in various aqueous base-added DES systems to that in aqueous basic media reveals contrasting aggregation tendencies and/or efficiencies. Surfactants as additives were demonstrated to control and modulate carbocyanine dye self-aggregation within DES-based media.

Chapter 6 titled ‘Conclusions and Future Prospects’ presents the summary of the overall investigation. In brief, it is concluded that common anionic and cationic surfactants and popular carbocyanine dyes within DES-based systems can self-aggregate. These novel, non-toxic, and inexpensive solubilizing media present themselves as alternate diverse systems that sustain surfactant and cyanine dye aggregation. The overall outcomes of this work may help establish the surfactant and dye aggregation within DES-based systems as novel heterogeneous media for various application. It is particularly interesting to apply these novel surfactant self-assemblies as soft templates for nanomaterials synthesis, chemical analysis, extractions, material synthesis, and electrodeposition. The work done towards this thesis will increase the overall effectiveness of the molecular aggregation of surfactants and dye within the newly developed DESs.

सार

विभिन्न उद्योगों और अकादमिक क्षेत्रों में अनुप्रयोगों की विस्तृत श्रृंखला के साथ-साथ गहरे ईयूटेक्टिक सॉल्वेंट्स (डीईएस) विदीन सर्फैक्टेंट्स और डाई के आणविक एकत्रीकरण की असामान्य और आकर्षक विशेषताएं उन्हें गंभीर महत्व के सॉल्वेंट बनाती हैं। हालांकि, चूंकि इन सूक्ष्म सॉल्वेंट्स की विदीन सर्फैक्टेंट्स और डाई एकत्रीकरण के बारे में ज्यादा जानकारी नहीं मिली है, इसलिए डीईएस का समग्र उपयोग हरी मीडिया के रूप में अभी भी प्रतिबंधित है। इस संदर्भ में, नीट डीईएस और पानी के अतिरिक्त डीईएस सिस्टम का विस्तृत अध्ययन उनके भौतिक रसायन गुणों को अच्छी तरह से ट्यून करने में मदद करेगा, जिससे डीईएस की समग्र उपयोगिता बढ़ जाएगी।

डीप ईयूटेक्टिक सॉल्वेंट-आधारित सिस्टम विदीन 'सर्फैक्टेंट एंड डाई एग्रीगेशन' नामक थीसिस डीईएस मीडिया विदीन आणविक एकत्रीकरण की समझ से संबंधित है। थीसिस में लोकप्रिय सर्फैक्टेंट्स और सामान्य कार्बोसाइनिन डाई के एकीकरण की विस्तृत जांच की सुविधा है, जिसमें नीट और पानी विदीन विभिन्न ऑप्टिकल स्पेक्ट्रोस्कोपिक और अन्य तकनीकों का उपयोग करके डीईएस जोड़ा गया है। अध्याय 1 'पृष्ठभूमि और परिचय' इस काम में जांच की गई विभिन्न प्रणालियों का एक संक्षिप्त अवलोकन प्रदान करता है। यह उन समस्याओं के संक्षिप्त परिचय भी प्रदान करता है जो इस विशेष शोध कार्य को हल करने के लिए अपनाई गई रणनीतियों के आधार

पर आधारित हैं। जांच के लंबे और अल्पकालिक उद्देश्यों दोनों पर भी चर्चा की गई है। काम का मूल उद्देश्य डीईएस-आधारित घुलनशील मीडिया विदीन सर्फैक्टेंट और कार्बोसाइनिन डाई के एकत्रीकरण को समझना है।

हालांकि, विलायक प्रणालियों के रूप में इन डीईएस को पूरी तरह से चित्रित करने के साथ शामिल बुनियादी विज्ञान अभी भी अपने बचपन में है, जो इन "हरे" सॉल्वेंट्स के अधिक कुशल उपयोग को वापस रखता है। विभिन्न क्षेत्रों में इसकी विशाल अनुप्रयोग क्षमता के कारण डीईएस-आधारित सॉल्वेंट सिस्टम विदीन आणविक एकत्रीकरण की घटना बहुत महत्वपूर्ण है।

'सामग्री और पद्धति' शीर्षक वाला अध्याय 2 रासायनिक खरीद, तैयारी, शुद्धिकरण और भंडारण के साथ-साथ जांच के दौरान उपयोग की जाने वाली तकनीकों के बारे में है। विशेष रूप से, यूवी-विज्ञ आणविक अवशोषण, स्थिर-स्थिति और समय-हल फ्लोरोसेंस, रिफ्रेक्ट्रोमीटर, डीएलएस (गतिशील प्रकाश बिखरने), SAXS (छोटे-कोण एक्स-रे स्कैटरिंग), ट्रांसमिशन इलेक्ट्रॉन माइक्रोस्कोपी (टीईएम), आचरणमिति, घनत्व और गतिशील चिपचिपाहट साथ ही आवश्यक जानकारी इकट्ठा करने के लिए सतह तनाव माप का उपयोग किया गया था। अध्याय 3 का शीर्षक है 'कोलाइन क्लोराइड व्युत्पन्न डीप यूटैक्टिक सॉल्वेंट्स' विदीन सर्फैक्टेंट्स का आत्म-पृथक्करण। इस अध्याय में, हमने (कोलाइन क्लोराइड + ग्लिसरॉल) डीईएस विदीन cationic surfactants का आत्म-पृथक्करण प्रस्तुत किया है। विशेष रूप से, एक archetypical डीईएस

ग्लाइसेलीन विदीन एन-एल्काइलट्रिमथिलैमोनियम परिवार के cationic surfactants के आत्म-पृथक्करण स्वचालित रूप से होने के लिए पाया गया था। अनुमानित थर्मोडायनामिक पैरामीटर सुझाव देते हैं कि इस आत्म-एकत्रीकरण प्रक्रिया को पानी में उससे कम गतिशील रूप से संचालित किया जाए। आत्म-असंबली प्रक्रिया थर्मोडायनामिक रूप से अनुकूल पाया गया था।

इन समेककों के अस्तित्व को स्थापित करने के लिए प्रतिदीप्ति द्विध्रुवीयता और माइक्रोफ्लुलिटी जांच, पायरिन और 1,3-बीआईएस ((1-पायरेनिल) प्रोपेन के प्रतिक्रियाओं का जवाब क्रमशः उपयोग किया जाता था। भूतल तनाव, विद्युत चालकता, डीएलएस, एसएक्सएस, टीईएम, घनत्व, और गतिशील चिपचिपाहट माप प्रभावी रूप से समेकित (उदाहरण के लिए, माइक्रेल और / या सूक्ष्मदर्शी) को दर्शाने के लिए उपयोग किए जाते थे। हम एक डीईएस विदीन पानी के एक छोटे से हिस्से वाले एक लोकप्रिय एनीओनिक सर्फैक्टेंट के आत्म-एकत्रीकरण के लिए साक्ष्य की स्पष्ट रेखाएं प्रस्तुत करते हैं। अर्थात्, सोडियम डोडसील सल्फेट (एसडीएस) की अच्छी तरह से परिभाषित असंबली स्पष्ट रूप से आर्केटाइप डीईएस रेलाइन में बनती है। कार्बनिक सॉल्वेंट्स की घुलनशीलता में महत्वपूर्ण वृद्धि जो अन्यथा कोलाइन क्लोराइड आधारित डीईएस में मिसाल नहीं है, एसडीएस की उपस्थिति में रेखांकित विदीन हासिल की गई थी। एसडीएस-जोड़ा रेलाइन विदीन साइक्लोहेक्सेन की उल्लेखनीय रूप से बेहतर घुलनशीलता परिवेश स्थितियों के तहत एसडीएस द्वारा स्वचालित रूप से गठित तेल-इन-डीईएस माइक्रोमैल्शन की उपस्थिति के

लिए जिम्मेदार है। इस काम में प्रस्तुत उपन्यास जल मुक्त आत्म-असंबली गतिशील नरम टेम्पलेट्स के रूप में काम कर सकते हैं ताकि आकार-या आकार के अनुरूप नैनोकणों को परिवेश की स्थिति के तहत पानी से प्रतिबंधित मीडिया विदीन निर्देशित किया जा सके। डीप ईटक्टिक सॉल्वेंट्स की उपस्थिति में जलीय माइकलर सॉल्यूशंस की गुणधर्मों का शीर्षक अध्याय 4, क्रमशः डीईएस रेलाइन और ग्लाइसेलीन के रूप में उनके महत्वपूर्ण माइकल सांद्रता (सेमीसी) के ऊपर जलीय सर्फैक्टेंट समाधान के भौतिक रसायन गुणों में परिवर्तन प्रस्तुत करता है। यह दिखाया गया है कि जलीय सर्फैक्टेंट समाधान के गुणों को उचित मात्रा में डीईएस जोड़कर अनुकूल फैशन में ट्यून किया जा सकता है। इस जांच का मुख्य जोर जलीय सर्फैक्टेंट समाधानों के गुणों को संशोधित करने में डीईएस की बहुमुखी भूमिका स्थापित करना है जो जलीय सर्फैक्टेंट सिस्टम के अनुप्रयोगों को बढ़ा सकता है; डीईएस की संभावित प्रयोज्यता भी बढ़ेगी।

इसके अलावा, तुलनात्मक रूप से, विभिन्न सर्फैक्टेंट्स के जलीय सूक्ष्म समाधान के भौतिक रसायन गुणों पर आईएल अतिरिक्तता का प्रभाव भी मूल्यांकन किया जाता है। इस काम के कुल परिणामों में अनुमान है कि डीईएस के उचित जोड़ के परिणामस्वरूप सर्फैक्टेंट समाधानों के भौतिक रसायन गुणों में वांछनीय परिवर्तन हो सकते हैं। अध्याय 5 का नाम 'जलीय बेस की उपस्थिति में कोलाइन क्लोराइड-आधारित डीप यूटक्टिक

सॉल्वेंट्स में कार्बोसाइनिन डाई का एकत्रीकरण' है। दो आम और लोकप्रिय कार्बोसाइनिन डाई का आत्म-संयोजन व्यवहार, 5,5', 6,6'-टेट्राक्लोरो- 1,1'-डायथिल -3,3'-डी (4-सल्फोबूटिल) -बेन्ज़ीमिडाज़ोल कार्बोसाइनिन (टीडीबीसी) और 5,5'-डिक्लोरो-3,3'-डी (3-सल्फोप्रोपील) -9-मेथिल-बेंजोथियाकार्बोसाइनिन (डीएमटीसी) की जांच डीईएस ग्लाइसेलीन विदीन की गई थी और परिवेश की स्थितियों के तहत रेखांकित किया गया था। एकत्रीकरण पर जलीय आधार के अतिरिक्त प्रभाव का पता लगाया गया था। उपरोक्त वर्णित यूवी-विज़ अवशोषण और आणविक प्रतिदीप्ति जांच के ऑप्टिकल स्पेक्ट्रोस्कोपिक प्रतिक्रियाएं इंगित करती हैं कि बेस की उपस्थिति में दोनों डीईएस टीडीबीसी के जे-एग्रीगेट्स का समर्थन करने के लिए पाए जाते हैं। इसी तरह की स्थितियों के तहत, डीएमटीसी उपरोक्त डीईएस-आधारित प्रणालियों विदीन जे-एग्रीगेट्स के साथ फ्लोरोसेंट एच-एग्रीगेट्स बनाता है। जलीय मूल मीडिया में विभिन्न जलीय बेस-एडेड डीईएस सिस्टम में कार्बोसाइन डाई व्यवहार की तुलना विपरीत समेकन प्रवृत्तियों और / या क्षमता को दर्शाती है। डीईएस-आधारित मीडिया विदीन कार्बोसाइन डाई स्व-एकत्रीकरण को नियंत्रित और संशोधित करने के लिए additives के रूप में सर्फैक्टेंट का प्रदर्शन किया गया था।

'निष्कर्ष और भविष्य संभावनाएं' शीर्षक वाला अध्याय 6 समग्र जांच का सारांश प्रस्तुत करता है। संक्षेप में, यह निष्कर्ष निकाला गया है कि डीईएस-आधारित प्रणालियों विदीन आम एनीओनिक और cationic surfactants और लोकप्रिय कार्बोसाइनिन रंग स्वयं अलग हो सकते हैं। ये उपन्यास, गैर विषैले, और सस्ती घुलनशील मीडिया स्वयं को वैकल्पिक विविध प्रणालियों के रूप में प्रस्तुत करते हैं जो सर्फैक्टेंट और साइनाइन डाई एकत्रीकरण को बनाए रखते हैं। इस काम के कुल परिणाम डीईएस-आधारित प्रणालियों विदीन सर्फैक्टेंट और डाई एकत्रीकरण को विभिन्न अनुप्रयोगों के लिए उपन्यास विषम मीडिया के रूप में स्थापित करने में मदद कर सकते हैं। इन उपन्यास सर्फैक्टेंट स्व-असेंबली को नैनोमटेरियल संश्लेषण, रासायनिक विश्लेषण, निष्कर्षण, सामग्री संश्लेषण, और इलेक्ट्रोडोप्शन के लिए मुलायम टेम्पलेट्स के रूप में लागू करना विशेष रूप से दिलचस्प है। इस थीसिस की ओर किए गए काम से नए विकसित डीईएस विदीन सर्फैक्टेंट्स और डाई के आणविक एकत्रीकरण की समग्र प्रभावशीलता में वृद्धि होगी।

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LIST OF ABBREVIATIONS

Abbreviation	Full form
DES	Deep Eutectic Solvent
[bmim][PF ₆]	1-butyl-3-methylimidazolium hexafluorophosphate
BPP	1,3-Bis(1-pyrenyl)propane
cmc	Critical micelle concentration
CPyB	Cetylpyridinium bromide
CTAB	Cetyltrimethylammonium bromide
DLS	Dynamic light scattering
CTAC	Cetyltrimethylammonium chloride
EC	Electrolyte conductivity
HeTAB	<i>n</i> -Hexyltrimethylammonium bromide
HPLC	High-performance liquid chromatography
IL	Ionic liquid
o/w	Oil-in-water
POE	Polyoxyethylene
Py	Pyrene
SB-12	<i>n</i> -Dodecyl sulfobetaine
SDS	Sodiumdodecyl sulfate
TDS	Total dissolved solids
TX-100	Triton X-100
Uv	Ultraviolet

Vis	Visible
VOC	Volatile organic compound
w/o	Water-in-oil
TDBC	5,5',6,6'-Tetrachloro-1,1'-diethyl-3,3'-di-(4-sulfobutyl)-benzimidazolocarbocyanine
DMTC	5,5'-Dichloro-3,3'-di(3-sulfopropyl)-9-methylbenzothia Carbocyanine
SAXS	Small angle X-ray scattering
DLS	Dynamic light scattering
TEM	Transmission electron microscopy
HBD	Hydrogen bond donors
TCSPC	Time-correlated single photon counting
CCD	Charge coupled device
ATC	Automatic temperature compensation
SDBS	Sodium dodecyl benzene sulphonate
TTAB	Tetradecyltrimethylammonium bromide
DTAB	Dodecyl trimethylammonium bromide
DeTAB	Decyl trimethylammonium bromide
OTAB	Octadecyltrimethylammonium bromide
CTATS	Hexadecyltrimethylammonium toluenesulfonate
PDI	Polydispersity index
cac	Critical aggregation concentration
N _{agg}	Aggregation number