

**INVESTIGATION OF SURFACTANT AGGREGATION WITHIN
IONIC LIQUID, DEEP EUTECTIC SOLVENT, AND FLUOROUS
SOLVENT-BASED MEDIA**

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IONIC LIQUID, DEEP EUTECTIC SOLVENT, AND FLUOROUS
SOLVENT-BASED MEDIA**

by

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SUBMITTED

IN FULFILLMENT OF THE REQUIREMENTS OF THE
DEGREE OF DOCTOR OF PHILOSOPHY

to the



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Dedicated to
My Parents, Siblings and the
Almighty God

CERTIFICATE

This is to certify that the thesis entitled, “**Investigation of Surfactant Aggregation within Ionic Liquid, Deep Eutectic Solvent and Fluorous Solvent-Based Media**”, being submitted by **Ms. Anjali** 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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ABSTRACT

Amphiphilic aggregation into micellar and non-micellar assemblies constitutes a major area of both academic and industrial research, owing to its wide range of physicochemical characteristics and technological utilities. These include enhanced detergency, efficient solubilization and emulsification, membrane-mimetic environments, and the formation of nanoreactors for enzymatic and catalytic processes. The emergence of unconventional solvent systems, particularly ionic liquids (ILs), deep eutectic solvents (DESs), and fluorous liquids (FLs) has created newer avenues to expand the scope of such amphiphile-based soft materials. These alternative media not only remove environmental challenges but also have emerged as promising substitutes for conventional organic solvents and traditional aqueous systems, offering distinctive and easily tunable physicochemical properties that render them highly versatile in diverse chemical processes. The judicious selection of such media enables precise control over aggregation behavior and paves the way for more advanced, yet sustainable, soft-matter architectures. Consequently, demonstrating amphiphilic aggregation within these unconventional solvents is a critical endeavour for revealing their untapped practical applications and shaping the future design of soft-matter systems.

The thesis titled **‘Investigation of Surfactant Aggregation within Ionic Liquid, Deep Eutectic Solvent, and Fluorous Solvent-Based Media’** focuses on the effect of dispersion medium on amphiphilic aggregation in unconventional solvents such as ionic liquids (ILs), deep eutectic solvents (DESs) and fluorous solvents (FLs). It also reports the formation and characterization of environmentally-benign surfactant-free water-in-DES microemulsions (MEs) (along with their physicochemical properties) and surfactant-assisted nonaqueous solvent-in-fluorous MEs. The thesis also features the modulation of the physicochemical properties of type-V DESs by non-surfactant small amphiphilic molecule, i.e., hydrotrope, which creates favorable conditions for the formation of water-in-oil MEs in hydrophobic type-V DESs.

The thesis has been divided into eight chapters. **Chapter 1 (Background and Introduction)** introduces the emerging field of unconventional solvent systems, namely, ILs, DESs, and FLs, highlighting their growing academic and industrial relevance. It also features the advances in the field made by the scientific community as well as an overview of the limitations that encouraged our work and potential solutions to circumvent the present problems. The overarching objective of the thesis is to investigate amphiphile aggregation behavior in these non-traditional solvents, thus establishing the groundwork for their application in various relevant fields. Amphiphile self-assembly, including micellization, vesicle formation, and monolayer organization, is well-studied in conventional aqueous and hydrocarbon systems. However, its behavior in alternative solvents remains underexplored. This research aims to fill this gap by systematically studying amphiphile aggregation in ILs, DESs, and FLs to deepen our understanding of solvent–surfactant interactions and broaden the scope of amphiphile-based applications in novel solvent environments.

Chapter 2 titled ‘**Materials and Methodologies**’ provides an in-depth description of all the techniques and protocols involved in the procurement/synthesis of chemicals as well as the investigative procedures followed. Specifically, uv-visible molecular absorbance spectroscopy, steady-state/time-resolved fluorescence spectroscopy, fluorescence correlation spectroscopy (FCS) along with certain non-invasive techniques, such as dynamic light scattering (DLS), small-angle X-ray scattering (SAXS), differential scanning calorimetry (DSC), Fourier-transform infrared (FTIR) spectroscopy, rheometry, electrical conductivity, surface tension, density (ρ), and dynamic viscosity (η) measurements are exercised to obtain the desired information.

Chapter 3 titled ‘**Mixed Micelle Formation by Sodium Dodecylsulfate and Dodecyltrimethylammonium Bromide in Aqueous Ionic Liquid Media**’ explores how the IL [C₂C₁im][EtSO₄] influences (SDS + DTAB) mixed micellization. In water, limited miscibility led to precipitation due to poor charge screening.⁵ However, introducing even a small amount of

IL eliminated this problem, enabling clear solutions across all compositions. Using pyrene fluorescence, the critical aggregate concentration (CAC) was measured at 90°C. In water, strong synergism between SDS and DTAB lowered the CAC, but increasing IL content reduced attractive interactions, reflected in rising CAC values and less negative (eventually positive at higher IL composition) interaction parameters (β), estimated using Rubingh's model. The micelle composition also shifted with IL content, aligning more closely with ideal behavior. IL ions penetrated the micellar palisade layer, altering solvation and increasing micelle dipolarity. Overall, the study demonstrates how ILs can fine-tune surfactant interactions by screening electrostatic forces, enabling more flexible micelle design.

Chapter 4 titled '**Aggregation of Mixed (Cationic + Anionic) and (Cationic + Nonionic) Surfactant Systems within a (Lanthanide Salt : Urea) Deep Eutectic Solvent**', marks the first experimental investigation of mixed micellization within a type-IV lanthanide salt-based DES, which has water-like solvating properties and moderate ionic strength.⁶ Surfactant aggregation of DTAB with SDS and TX-100 was monitored using fluorescence (PyCHO probe) and subsequently confirmed through DLS study. CAC values of both (DTAB + SDS) and (DTAB + TX-100) surfactant mixtures lied between the CACs of the respective surfactants in the mixture. This observation suggested that the ionic nature of the (La : U) DES effectively screened the charges on the surfactant headgroups. The estimated thermodynamic parameter revealed that DES facilitated the self-aggregation of mixed micellization of (DTAB + SDS) over the complete composition range of the surfactant mixture at ambient conditions. This was in contrast to IL, which facilitated mixed micellization at higher temperatures than room temperature, imposing restrictions on their use.⁵ Results of the investigated surfactant mixture compared with the aqueous system (characterized by low ionic strength) and IL (characterized by high ionic strength) systems, and a striking contrast was observed, particularly for the (cationic + anionic) mixture, likely due to the presence of lanthanide metal ions that screen the charges on the surfactant headgroups. Aggregation numbers and solvation environments were also studied,

showing that (La : U) DES enables favorable, tunable micellization under mild conditions. Overall the work highlighted that (La : U) DES with its moderate ionic strength, not only facilitates favorable thermodynamics at ambient conditions but also modulates the synergistic effect, and hence, allows better tunability in mixed micellization.

Chapter 5 titled ‘**Formation of Ethanolamine-Mediated Surfactant-Free Microemulsions Using Hydrophobic Deep Eutectic Solvents**’, focuses on replacing the traditional surfactants and conventional organic solvents used in the MEs. This study introduces a novel, surfactant-free strategy using ethanolamine (ETA) as a hydrotrope to facilitate the mixing of immiscible phases. In this study, five novel and green hydrophobic DESs (HDESs) were synthesized using DA and five (5) structurally different terpenoids [thymol, L(–)-menthol, linalool, β -citronellol, and geraniol] in a molar ratio 1 : 1. These DESs were used as oil phase, and water as the aqueous phase. Optimal ETA concentrations were determined using Bèizer interpolation. The resulting surfactant-free MEs (SFMEs) were characterized through FTIR absorbance, interfacial tension, electrical conductivity, DLS, UV-vis absorbance, and fluorescence, revealing stable nanoaggregates (8–30 nm) with low polydispersity and a strong dependence on water content. UV-vis absorbance and DLS analyses further supported the formation of water-rich domains. Nile red fluorescence suggested core–shell structures, and the system successfully solubilized the insoluble metal salts like $K_3Fe(CN)_6$. Density (ρ) and viscosity (η) studies (293–343 K) revealed non-ideal behavior. Viscosity showed non-Arrhenius temperature dependence, following the VFT model, and exhibited a non-linear trend with water content, initially decreasing, then increasing due to growing nanoaggregate size. These findings emphasized nanoaggregate formation as a key mechanism for water solubilization in SFMEs.

Chapter 6 titled ‘**Ethanolamine-mediated Microstructural Transitions within Terpenoid- and Fatty Acid-based Deep Eutectic Solvents**’ presents the modulation of physicochemical properties of the fatty acid-based DESs with the addition of a small amphiphilic

ETA molecule, which created the favorable conditions for the formation of water-in-oil ME within aforementioned V DESs. The type-V DESs presented in the study were composed of terpene [menthol (Men) or thymol (Thy)] and a fatty acid (DA)]. For comparative purposes, a non-DA-based DES composed of Thy and Men was selected. The addition of ETA led to a monotonic increase in ρ across all systems. However, a striking divergence in η behavior was observed, while the η of the non-DA system increased gradually, DA-based DESs exhibited an unusual, exponential increase in η . This phenomenon, referred to as η synergism, is rarely reported in non-aqueous systems and is herein demonstrated for the first time in DES media. Temperature dependence of η shows a better correlation to VFT equation rather than Arrhenius model. Despite an increase in η , rheology measurements confirmed the DES retained the Newtonian fluid characteristics ($R^2 \geq 0.997$), ruling out gelation. A concurrent sharp rise in electrical conductivity was observed in DA-based DES system, hinting the induced ionic interactions leading to increased η . In contrast, a negligible change in electrical conductivity (κ) in non-DA DES implied that DA played a crucial role in bringing microstructural changes in DA-based DESs, especially its carboxylic acid functionality. This was further supported by UV-vis and FTIR absorbance, and DSC studies, all indicating enhanced ionic interactions and extended H-bonding networks. Cybotactic regions of the fluorescence microfluidity probes [BPP - an intramolecular excimer forming probe as well as perylene and DPH - well-established anisotropy probes] also manifested the unprecedented increase in η of the DA-based DES system upon ETA addition, indicating that observed structural changes are molecular interaction-driven. Solvatochromic probe analysis (via DENA, NR, and NA probes) further showed the microstructural transitions with ETA addition. Overall, the study demonstrated that the carboxylic acid functionality of the DA played a crucial role in bringing microstructural transition upon ETA addition driven by a combination of enhanced ionic interactions and extended H-bonding. While in non-DA DESs, extended H-bonding networks dominated and derived the synergistic viscosity behavior.

Chapter 7 titled ‘**Perfluorinated Surfactant-Assisted Polar-in-Fluorous Nonaqueous Microemulsions: Formation and Solute Solvation**’ is focused on providing the first experimental evidence of ME formed by dispersing polar nonaqueous solvents within a fluoruous continuous phase using PFMC as the bulk medium. The study encompassed EtOH, EG, formamide, and DMF as the non-aqueous components and PFHA as an emulsifier. The MEs were characterized using steady-state absorbance and fluorescence spectroscopy, time-resolved fluorescence anisotropy, fluorescence correlation spectroscopy (FCS), DLS, and small-angle X-ray scattering (SAXS), confirming the formation of polar-solvent-rich nonaqueous domains. The structural integrity of ME strongly depended on the polarity, hydrogen-bonding capability, and functional groups of the polar solvent. A dual-dye comparison using coumarin dyes (C102 and C153) provided insights into both bulk and interfacial structures. C153 responded predominantly to variations in the interfacial microenvironment, governed by surfactant organization, whereas C102 reflected changes in the bulk fluoruous phase. This dual-dye approach offered complementary insight into both interfacial structuring and bulk-phase dynamics within these novel fluoruous solvent-based MEs.

Chapter 8 titled ‘**Conclusions and Future Perspectives**’ lays down the conclusions drawn from the overall investigation and the future scope of the work. This chapter summarizes the key findings of the study and outlines promising directions for future research. This study explored unconventional solvents - ILs, DESs, and FLs - for surfactant self-assembly. IL [C₂C₁im][EtSO₄] and hydrated metal salts effectively supported mixed-surfactant aggregation. Ethanolamine-based DESs can offer environmentally-friendly alternatives to toxic surfactants. Surfactant-free MEs in DESs can demonstrate sustainable formulation strategies. Fluoruous-phase MEs provide water-free systems for advanced dispersion phase engineering, potentially opening a new direction in fluoruous-phase chemistry.

सारांश

एम्फीफिलिक सिस्टम जिसमें माइक्रेलर (या मिसेल जैसा) समुच्चय शामिल हैं, अकादमिक और औद्योगिक अनुसंधान दोनों में रुचि का एक प्रमुख क्षेत्र बने हुए हैं। उनकी स्व-असेंबली भौतिक-रासायनिक और तकनीकी अनुप्रयोगों की एक विस्तृत श्रृंखला को रेखांकित करती है, जिसमें डिटर्जेंसी, घुलनशील और पायसीकारी एजेंट, झिल्ली-मिमेटिक मीडिया और एंजाइमेटिक प्रतिक्रियाओं और उत्प्रेरक प्रक्रियाओं के लिए नैनोरिएक्टर शामिल हैं। अपरंपरागत विलायक प्रणालियों, विशेष रूप से आयनिक तरल पदार्थ (आईएल), गहरे यूटेक्टिक सॉल्वेंट्स (डीईएस), और फ्लोरस तरल पदार्थ (एफएल) के उद्भव ने उभयचर-आधारित नरम पदार्थ के दायरे का विस्तार करने के नए अवसर पेश किए हैं। ये मीडिया पारंपरिक कार्बनिक सॉल्वेंट्स और पारंपरिक जलीय प्रणालियों के लिए उल्लेखनीय विकल्प साबित हुए हैं, जो विशिष्ट भौतिक-रासायनिक गुणों की पेशकश करते हैं जो उन्हें विविध रासायनिक प्रक्रियाओं में अत्यधिक बहुमुखी प्रदान करते हैं। इस तरह के मीडिया का विवेकपूर्ण चयन एकत्रीकरण व्यवहार को तैयार करने और टिकाऊ रसायन विज्ञान को आगे बढ़ाने के लिए नए रास्ते खोल सकता है। इसलिए इन वैकल्पिक मीडिया के भीतर उभयचर एकत्रीकरण की क्षमता का प्रदर्शन करना उनके अप्रयुक्त व्यावहारिक अनुप्रयोगों को उजागर करने और सॉफ्ट-मैटर डिज़ाइन के भविष्य को आकार देने के लिए एक महत्वपूर्ण प्रयास है।

'आयनिक लिक्विड, डीप यूटेक्टिक सॉल्वेंट और फ्लोरस सॉल्वेंट बेस्ड मीडिया के भीतर सर्फैक्टेंट एग्रीगेशन की जांच' शीर्षक वाली थीसिस आयनिक तरल पदार्थ (आईएल), डीप यूटेक्टिक सॉल्वेंट्स (डीईएस) और फ्लोरस सॉल्वेंट्स (एफएल) जैसे अपरंपरागत सॉल्वेंट्स में एम्फीफिलिक एकत्रीकरण पर फैलाव माध्यम के प्रभाव पर केंद्रित है। यह पर्यावरण-सौम्य सर्फैक्टेंट-मुक्त वाटर-इन-डीईएस माइक्रोइमल्शन (एमई) (उनके भौतिक-रासायनिक गुणों के साथ) और सर्फैक्टेंट-असिस्टेड नॉन-एक्वाक्सियस सॉल्वेंट-इन-फ्लोरस एमई के गठन और लक्षण वर्णन की भी रिपोर्ट करता है। थीसिस में गैर-सर्फैक्टेंट छोटे एम्फीफिलिक अणु, यानी हाइड्रोट्रोप द्वारा टाइप-वी डीईएस के भौतिक-रासायनिक गुणों का

मॉड्यूलेशन भी शामिल है, जो हाइड्रोफोबिक टाइप-वी डीईएस में वाटर-इन-ऑयल एमई के निर्माण के लिए अनुकूल परिस्थितियों का निर्माण करता है।

थीसिस को आठ अध्यायों में विभाजित किया गया है। **अध्याय 1 (पृष्ठभूमि और परिचय)** अपरंपरागत विलायक प्रणालियों के उभरते क्षेत्र का परिचय देता है, अर्थात्, आईएल, डीईएस और एफएल, उनकी बढ़ती शैक्षणिक और औद्योगिक प्रासंगिकता पर प्रकाश डालता है। इसमें वैज्ञानिक समुदाय द्वारा किए गए क्षेत्र में प्रगति के साथ-साथ उन सीमाओं का अवलोकन भी शामिल है जिन्होंने वर्तमान समस्याओं को दरकिनार करने के लिए हमारे काम और संभावित समाधानों को प्रोत्साहित किया। थीसिस का व्यापक उद्देश्य इन गैर-पारंपरिक सॉल्वेंट्स में उभयचर एकत्रीकरण व्यवहार की जांच करना है, इस प्रकार विभिन्न प्रासंगिक क्षेत्रों में उनके आवेदन के लिए आधार तैयार करना है। माइसेलाइजेशन, पुटिका गठन और मोनोलेयर संगठन सहित एम्फीफाइल स्व-असेंबली, पारंपरिक जलीय और हाइड्रोकार्बन प्रणालियों में अच्छी तरह से अध्ययन किया जाता है। हालाँकि, वैकल्पिक सॉल्वेंट्स में इसका व्यवहार कम खोजा गया है। इस शोध का उद्देश्य आईएल, डीईएस और एफएल में एम्फीफाइल एकत्रीकरण का व्यवस्थित रूप से अध्ययन करके इस अंतर को भरना है ताकि विलायक-सर्फैक्टेंट इंटरैक्शन की हमारी समझ को गहरा किया जा सके और उपन्यास विलायक वातावरण में एम्फीफाइल-आधारित अनुप्रयोगों के दायरे को व्यापक बनाया जा सके।

अध्याय 2 शीर्षक 'सामग्री और कार्यप्रणाली' रसायनों की खरीद/संश्लेषण में शामिल सभी तकनीकों और प्रोटोकॉल के साथ-साथ अपनाई गई जांच प्रक्रियाओं का गहन विवरण प्रदान करता है। विशेष रूप से, यूवी-दृश्यमान आणविक अवशोषण स्पेक्ट्रोस्कोपी, स्थिर-अवस्था / समय-हल प्रतिदीप्ति स्पेक्ट्रोस्कोपी, उत्तेजित उत्सर्जन कमी माइक्रोस्कोपी (एसटीईडी), प्रतिदीप्ति सहसंबंध स्पेक्ट्रोस्कोपी (एफसीएस) कुछ गैर-इनवेसिव तकनीकों के साथ-साथ गतिशील प्रकाश बिखरने (डीएलएस), छोटे-कोण एक्स-रे बिखरने (SAXS), डिफ्रेंशियल स्कैनिंग कैलोरीमेट्री (DSC), फूरियर-ट्रान्सफॉर्म इन्फ्रारेड (FTIR) स्पेक्ट्रोस्कोपी, उत्तेजित उत्सर्जन कमी माइक्रोस्कोपी (STED), रियोमेट्री, विद्युत चालकता, सतह तनाव, घनत्व (ρ) और गतिशील चिपचिपाहट (η) माप वांछित जानकारी प्राप्त करने के लिए प्रयोग किए जाते हैं।

अध्याय 3 शीर्षक 'जलीय आयनिक तरल मीडिया में सोडियम डोडेसिलसल्फेट और डोडेसिलट्रिमीथाइलमोनियम ब्रोमाइड द्वारा मिश्रित मिसेल फॉर्मेशन' इस बात की पड़ताल करता है कि आईएल [सी₂सी₁₁आईएम][ईटीएसओ₄] (एसडीएस + डीटीएबी) मिश्रित माइकलाइजेशन को कैसे प्रभावित करता है। पानी में, सीमित मिश्रणशीलता के कारण खराब चार्ज स्क्रीनिंग के कारण वर्षा हुई।⁵ हालाँकि, थोड़ी मात्रा में IL भी पेश करने से यह समस्या समाप्त हो गई, जिससे सभी रचनाओं में स्पष्ट समाधान संभव हो गया। पाइरीन प्रतिदीप्ति का उपयोग करते हुए, महत्वपूर्ण मिसेल एकाग्रता (सीएमसी) को 90 डिग्री सेल्सियस पर मापा गया था। पानी में, एसडीएस और डीटीएबी के बीच मजबूत तालमेल ने सीएसी को कम कर दिया, लेकिन आईएल सामग्री में वृद्धि ने आकर्षक इंटरैक्शन को कम कर दिया, जो बढ़ते सीएसी मूल्यों और कम नकारात्मक (अंततः उच्च आईएल संरचना पर सकारात्मक) इंटरैक्शन पैरामीटर (β) में परिलक्षित होता है, जिसका अनुमान रुबिंग के मॉडल का उपयोग करके लगाया जाता है। मिसेल संरचना भी आईएल सामग्री के साथ स्थानांतरित हो गई, जो आदर्श व्यवहार के साथ अधिक निकटता से संरेखित हो गई। आईएल आयनों ने माइक्रेलर पोलिसडे परत में प्रवेश किया, जिससे सॉल्वेशन बदल गया और मिसेल द्विध्रुवीयता बढ़ गई। कुल मिलाकर, अध्ययन दर्शाता है कि कैसे आईएल इलेक्ट्रोस्टैटिक बलों की स्क्रीनिंग करके सर्फेक्टेंट इंटरैक्शन को ठीक कर सकते हैं, जिससे अधिक लचीले मिसेल डिजाइन को संभव किया जा सकता है।

अध्याय 4 शीर्षक 'मिश्रित (धनायनित + आयनिक) और (धनायनित + गैर-आयनिक) सर्फेक्टेंट सिस्टम के भीतर (लैथेनाइड नमक: यूरिया) डीप यूटेक्टिक सॉल्वेंट' शीर्षक से एक टाइप-IV लैथेनाइड नमक-आधारित डीईएस के भीतर मिश्रित माइसेलाइजेशन की पहली प्रयोगात्मक जांच को चिह्नित करता है, जिसमें पानी जैसे घोलने वाले गुण और मध्यम आयनिक ताकत होती है।⁶ एसडीएस और टीएक्स-100 के साथ डीटीएबी के सर्फेक्टेंट एकत्रीकरण की निगरानी प्रतिदीप्ति (पायसीएचओ जांच) का उपयोग करके की गई थी और बाद में डीएलएस अध्ययन के माध्यम से पुष्टि की गई थी। दोनों (डीटीएबी + एसडीएस) और (डीटीएबी + टीएक्स-100) सर्फेक्टेंट मिश्रण के सीएसी मान मिश्रण में संबंधित सर्फेक्टेंट के

सीएसी के बीच झूठ बोले गए थे। इस अवलोकन ने सुझाव दिया कि (ला: यू) डीईएस की आयनिक प्रकृति ने सर्फैक्टेंट हेडग्रुप पर आरोपों की प्रभावी ढंग से जांच की। अनुमानित थर्मोडायनामिक पैरामीटर से पता चला है कि डीईएस ने परिवेश की स्थितियों में सर्फैक्टेंट मिश्रण की पूरी संरचना सीमा पर (डीटीएबी + एसडीएस) के मिश्रित मिश्रणीकरण के स्व-एकत्रीकरण की सुविधा प्रदान की। यह आईएल के विपरीत था, जिसने कमरे के तापमान की तुलना में उच्च तापमान पर मिश्रित मिश्रणीकरण की सुविधा प्रदान की, जिससे उनके उपयोग पर प्रतिबंध लगा दिया गया।⁵ जलीय प्रणाली (कम आयनिक शक्ति की विशेषता) और आईएल (उच्च आयनिक शक्ति की विशेषता) प्रणालियों की तुलना में जांच किए गए सर्फैक्टेंट मिश्रण के परिणाम, और एक हड़ताली विपरीत देखा गया था, विशेष रूप से (धनायनित + आयनिक) मिश्रण के लिए, संभवतः लैथेनाइड धातु आयनों की उपस्थिति के कारण जो आवेशों को स्क्रीन करते हैं सर्फैक्टेंट हेडग्रुप पर। एकत्रीकरण संख्या और समाधान वातावरण का भी अध्ययन किया गया, यह दर्शाता है कि (ला: यू) डीईएस हल्की परिस्थितियों में अनुकूल, ट्यून करने योग्य माइसेलाइजेशन को सक्षम बनाता है। कुल मिलाकर काम ने इस बात पर प्रकाश डाला कि (La: U) DES अपनी मध्यम आयनिक शक्ति के साथ, न केवल परिवेश की स्थितियों में अनुकूल ऊष्मप्रवैगिकी की सुविधा प्रदान करता है, बल्कि सहक्रियात्मक प्रभाव को भी नियंत्रित करता है, और इसलिए, मिश्रित micellization में बेहतर ट्यूनेबिलिटी की अनुमति देता है।

अध्याय 5 शीर्षक 'हाइड्रोफोबिक डीप यूटेक्टिक सॉल्वेंट्स का उपयोग करके इथेनॉलमाइन-मध्यस्थता सर्फैक्टेंट-मुक्त माइक्रोइमल्शन का गठन', एमई में उपयोग किए जाने वाले पारंपरिक सर्फैक्टेंट और पारंपरिक कार्बनिक सॉल्वेंट्स को बदलने पर केंद्रित है। यह अध्ययन एक अमिश्रणीय चरणों के मिश्रण को सुविधाजनक बनाने के लिए हाइड्रोट्रोप के रूप में इथेनॉलमाइन (ईटीए) का उपयोग करके एक उपन्यास, सर्फैक्टेंट-मुक्त रणनीति का परिचय देता है। इस अध्ययन में, पांच उपन्यास और हरे हाइड्रोफोबिक डीईएस (एचडीईएस) को डीए और पांच (5) संरचनात्मक रूप से अलग-अलग टेरपेनोइड्स [थाइमोल, एल (-)-मेन्थॉल, लिनालूल, β -सिट्रोनेलोल, और गेरानियोल] का उपयोग करके दाढ़ अनुपात 1: 1 में संश्लेषित किया गया था। इन डीईएस का उपयोग तेल चरण के रूप में किया जाता था, और पानी का

उपयोग जलीय चरण के रूप में किया जाता था। इष्टतम ईटीए सांद्रता Bèizer प्रक्षेप का उपयोग करके निर्धारित की गई थी। परिणामी सर्फैक्टेंट-मुक्त एमई (एसएफएमई) को एफटीआईआर अवशोषण, इंटरफेसियल तनाव, विद्युत चालकता, डीएलएस, यूवी-विज़ अवशोषण और प्रतिदीप्ति के माध्यम से विशेषता थी, जो कम पॉलीडिस्पर्सिटी और पानी की मात्रा पर एक मजबूत निर्भरता के साथ स्थिर नैनोएग्रीगेट (8-30 एनएम) का खुलासा करता था। यूवी-विज़ अवशोषण और डीएलएस विश्लेषण ने पानी से भरपूर डोमेन के निर्माण का समर्थन किया। नील लाल प्रतिदीप्ति ने कोर-शेल संरचनाओं का सुझाव दिया, और सिस्टम ने $K_3Fe(CN)_6$ जैसे अघुलनशील धातु लवणों को सफलतापूर्वक घुलनशील किया। घनत्व (ρ) और चिपचिपाहट (η) अध्ययनों (293-343 K) ने गैर-आदर्श व्यवहार का खुलासा किया। चिपचिपाहट ने वीएफटी मॉडल का पालन करते हुए गैर-अरहेनियस तापमान निर्भरता दिखाई, और पानी की मात्रा के साथ एक गैर-रैखिक प्रवृत्ति का प्रदर्शन किया, शुरू में कम हो गया, फिर बढ़ते नैनोएग्रीगेट आकार के कारण बढ़ रहा था। इन निष्कर्षों ने एसएफएमई में जल घुलनशीलता के लिए एक प्रमुख तंत्र के रूप में नैनोएग्रीगेट गठन पर जोर दिया।

अध्याय 6 शीर्षक 'टेरपेनॉइड- और फैटी एसिड-आधारित डीप यूटेक्टिक सॉल्वेंट्स के भीतर इथेनॉलमाइन-मध्यस्थता माइक्रोस्ट्रक्चरल ट्रांजिशन' एक छोटे एम्फीफिलिक ईटीए अणु के साथ फैटी एसिड-आधारित डीईएस के भौतिक-रासायनिक गुणों के मॉड्यूलेशन को प्रस्तुत करता है , जिसने उपरोक्त वी डीईएस के भीतर वाटर-इन-ऑयल एमई के गठन के लिए अनुकूल परिस्थितियों का निर्माण किया। अध्ययन में प्रस्तुत टाइप-वी डीईएस टेरपीन [मेन्थॉल (पुरुष) या थाइमोल (थाय)] और एक फैटी एसिड (डीए)] से बना था। तुलनात्मक उद्देश्यों के लिए, एक गैर-डीए-आधारित डीईएस का चयन किया गया था जो आपके और पुरुषों से बना था। ईटीए के जुड़ने से सभी प्रणालियों में एक नीरस वृद्धि हुई ρ । हालांकि, व्यवहार में एक हड़ताली विचलन η देखा गया था, जबकि η गैर-डीए प्रणाली में धीरे-धीरे वृद्धि हुई, डीए-आधारित डीईएस ने η में असामान्य, घातीय वृद्धि का प्रदर्शन किया। यह घटना, जिसे सहक्रियता के रूप में जाना जाता η है , शायद ही कभी गैर-जलीय प्रणालियों में रिपोर्ट की जाती है और यहां डीईएस मीडिया

में पहली बार प्रदर्शित की जाती है। टी-निर्भरता η अरहेनियस मॉडल के बजाय वीएफटी समीकरण के लिए बेहतर सहसंबंध दिखाती है। वृद्धि के बावजूद η , रियोलॉजी माप ने पुष्टि की कि डीईएस ने न्यूटनियन द्रव विशेषताओं ($R^2 \geq 0.997$) को बरकरार रखा, जिससे जेलेशन को खारिज कर दिया गया। डीए-आधारित डीईएस प्रणाली में विद्युत चालकता में समवर्ती तेज वृद्धि देखी गई, जो प्रेरित आयनिक इंटरैक्शन से η में वृद्धि का संकेत देती है। इसके विपरीत, गैर-डीए डीईएस में विद्युत चालकता () में एक नगण्य परिवर्तन κ का अर्थ है कि डीए ने डीए-आधारित डीईएस, विशेष रूप से इसकी कार्बोक्जिलिक एसिड कार्यक्षमता में सूक्ष्म संरचनात्मक परिवर्तन लाने में महत्वपूर्ण भूमिका निभाई। इसे यूवी-वीआईएस और एफटीआईआर अवशोषण, और डीएससी अध्ययनों द्वारा समर्थित किया गया था, जो सभी उन्नत आयनिक इंटरैक्शन और विस्तारित एच-बॉन्डिंग नेटवर्क का संकेत देते हैं। प्रतिदीप्ति माइक्रोफ्लुइडिटी जांच के साइबोटैक्टिक क्षेत्रों [बीपीपी - एक इंटरमोल्यूलर एक्साइमर बनाने की जांच के साथ-साथ पेरिलीन और डीपीएच - अच्छी तरह से स्थापित अनिसोट्रॉपी जांच] ने भी η ईटीए के अलावा डीए-आधारित डीईएस प्रणाली में अभूतपूर्व वृद्धि को प्रकट किया, यह दर्शाता है कि देखे गए संरचनात्मक परिवर्तन आणविक इंटरैक्शन-संचालित हैं। सॉल्वैटोक्रोमिक जांच विश्लेषण (डीईएनए, एनआर और एनए जांच के माध्यम से) ने ईटीए के अलावा माइक्रोस्ट्रक्चरल ट्रांजिशन को आगे दिखाया। कुल मिलाकर, अध्ययन से पता चला है कि डीए की कार्बोक्जिलिक एसिड कार्यक्षमता ने ईटीए जोड़ पर माइक्रोस्ट्रक्चरल संक्रमण लाने में महत्वपूर्ण भूमिका निभाई, जो उन्नत आयनिक इंटरैक्शन और विस्तारित एच-बॉन्डिंग के संयोजन से प्रेरित है। जबकि गैर-डीए डीईएस में, विस्तारित एच-बॉन्डिंग नेटवर्क हावी रहे और सहक्रियात्मक चिपचिपाहट व्यवहार को प्राप्त किया।

अध्याय 7 शीर्षक 'परफ्लोरिनेटेड सर्फैक्टेंट-असिस्टेड पोलर-इन-फ्लोरोस नॉन-एक्रियस माइक्रोइमल्शन: फॉर्मेशन एंड सोल्यूट सॉल्वेशन' पीएचएमसी को थोक माध्यम के रूप में उपयोग करके एक फ्लोरोस निरंतर चरण के भीतर ध्रुवीय गैर-जलीय सॉल्वेंट्स को फैलाकर गठित एमई का पहला प्रयोगात्मक साक्ष्य प्रदान करने पर केंद्रित है। अध्ययन में गैर-जलीय घटकों के रूप में ईटीओएच, ईजी,

फॉर्मामाइड और डीएमएफ और पीएफएचए को एक पायसीकारक के रूप में शामिल किया गया। एमई को स्थिर-राज्य अवशोषण और प्रतिदीप्ति स्पेक्ट्रोस्कोपी, समय-हल प्रतिदीप्ति अनिसोट्रॉपी, प्रतिदीप्ति सहसंबंध स्पेक्ट्रोस्कोपी (एफसीएस), डीएलएस, और छोटे-कोण एक्स-रे बिखरने (एसएएक्सएस) का उपयोग करके विशेषता थी, जो ध्रुवीय-विलायक-समृद्ध गैर-जलीय डोमेन के गठन की पुष्टि करती है। एमई की संरचनात्मक अखंडता ध्रुवीयता, हाइड्रोजन-बंधन क्षमता और ध्रुवीय विलायक के कार्यात्मक समूहों पर दृढ़ता से निर्भर करती है। कौमारिन रंगों (**C102** और **C153**) का उपयोग करके एक दोहरी-डाई तुलना ने थोक और इंटरफेसियल संरचनाओं दोनों में अंतर्दृष्टि प्रदान की। **C153** ने मुख्य रूप से सर्फैक्टेंट संगठन द्वारा शासित इंटरफेसियल माइक्रोएन्वायरमेंट में भिन्नता का जवाब दिया, जबकि **C102** ने थोक फ्लोरस चरण में परिवर्तन को प्रतिबिंबित किया। इस दोहरे डाई दृष्टिकोण ने इन उपन्यास फ्लोरस विलायक-आधारित एमई के भीतर इंटरफेसियल संरचना और थोक-चरण गतिशीलता दोनों में पूरक अंतर्दृष्टि प्रदान की।

अध्याय 8 शीर्षक 'निष्कर्ष और भविष्य के परिप्रेक्ष्य' समग्र जांच और काम के भविष्य के दायरे से निकाले गए निष्कर्षों को नीचे रखता है। यह अध्याय अध्ययन के प्रमुख निष्कर्षों को सारांशित करता है और भविष्य के शोध के लिए आशाजनक दिशाओं की रूपरेखा तैयार करता है। इस अध्ययन ने सर्फैक्टेंट स्व-संयोजन के लिए अपरंपरागत सॉल्वैंट्स - आईएल, डीईएस और एफएल - की खोज की। IL $[C_2C_{1im}][EtSO_4]$ और हाइड्रेटेड धातु लवण ने मिश्रित-सर्फैक्टेंट एकत्रीकरण का प्रभावी ढंग से समर्थन किया। इथेनॉलमाइन-आधारित डीईएस जहरीले सर्फैक्टेंट के लिए पर्यावरण के अनुकूल विकल्प प्रदान कर सकते हैं। डीईएस में सर्फैक्टेंट-मुक्त एमई टिकाऊ फॉर्मूलेशन रणनीतियों का प्रदर्शन कर सकते हैं। फ्लोरस-चरण एमई उन्नत फैलाव चरण इंजीनियरिंग के लिए पानी मुक्त प्रणाली प्रदान करते हैं, संभावित रूप से फ्लोरोस-चरण रसायन विज्ञान में एक नई दिशा खोलते हैं।

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LIST OF ABBREVIATIONS

Abbreviation	Full form
DES	Deep Eutectic Solvent
IL	Ionic Liquid
PFS	Perfluorinated Solvents
FLs	Fluorous Solvents
PFC	Perfluorocarbons
VOC	Volatile Organic Compounds
CAC	Critical Aggregate Concentration
ChCl	Choline Chloride
NADES	Natural Deep Eutectic Solvent
DLS	Dynamic Light Scattering
HBA	Hydrogen Bond Acceptor
HBD	Hydrogen Bond Donor
VFT	Vogel-Fulcher-Tammann
EG	Ethylene Glycol
Py	Pyrene
PyCHO	Pyrene-1-Carboxyaldehyde
SDS	Sodium Dodecyl Sulfate
TCSPC	Time-Correlated Single Photon Counting
TX-100	Triton X-100
UV	Ultraviolet
Vis	Visible
DMF	<i>N,N</i> -Dimethylformamide
FA	Formamide

EtOH	Ethanol
SAXS	Small-Angle X-Ray Scattering
FCS	Fluorescence Correlation Spectroscopy
DTAB	Dodecyltrimethylammonium Bromide
SBME	Surfactant-Based Microemulsion
SFME	Surfactant-Free Microemulsion
ME	Microemulsion
O/W	Oil in Water
W/O	Water in Oil
RM	Reverse Micelle
MHC	Minimum Hydrotrope Concentration
ETA	Ethanolamine
PFMC	Perfluoromethylcyclohexane
[C ₂ C ₁ im][EtSO ₄]	1-Ethyl-3-Methylimidazolium Ethylsulfate
BPP	1,3- <i>Bis</i> -(1-pyrenyl)propane
DENA	<i>N,N</i> -Diethyl-4-Nitroaniline
NA	4-Nitroaniline
NR	Nile Red
PFHA	Perfluoroheptanoic Acid
DMA	9,10-Dimethylanthracene