

MULTI-SCALE SIMULATION STUDIES ELUCIDATING
THE SOLVATION STRUCTURE OF ANTHROPOGENIC
GASES IN DEEP EUTECTIC SOLVENTS AND BULK
PHASE MORPHOLOGY AND DYNAMICS OF
HYDROPHOBIC DEEP EUTECTIC SOLVENTS

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INDIAN INSTITUTE OF TECHNOLOGY DELHI
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by

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DEPARTMENT OF CHEMISTRY

Submitted

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to the



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November 2023

Dedicated to
My Grandmother
Smt. Murti Devi

Certificate

This is to certify that the thesis titled "**MULTI-SCALE SIMULATION STUDIES ELUCIDATING THE SOLVATION STRUCTURE OF ANTHROPOGENIC GASES IN DEEP EUTECTIC SOLVENTS AND BULK PHASE MORPHOLOGY AND DYNAMICS OF HYDROPHOBIC DEEP EUTECTIC SOLVENTS**" is being submitted by **Mr. Akshay Malik** to the Department of Chemistry, Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy**. This thesis is a record of bonafide research work carried out by him under my supervision. In my opinion, the thesis has reached the standards fulfilling the requirements of the regulations relating to the degree.

The results contained in this thesis have not been submitted to any other University or Institute for the award of any degree or diploma.

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Abstract

In this thesis, we report multi-scale simulation studies elucidating the solvation structure of anthropogenic gases in deep eutectic solvents, and bulk phase morphology and dynamics of hydrophobic deep eutectic solvents. Conventional solvents suffer many disadvantages when utilized for gas sequestration, such as corroding the equipment and harming the environment. For applications requiring hydrophobic conditions, employment of traditional solvents leads to low extraction efficiency due to decreased phase separation strength. Deep eutectic solvents (DESs) and hydrophobic deep eutectic solvents (HDESs) replace these conventional solvents. DESs exhibit unique properties such as easy preparation, biodegradability, tunable nature, excellent thermal stability, low volatility, and low toxicity, which make them a suitable candidate for gas sequestration applications. HDESs behave as water-immiscible solvents and have shown higher extraction efficiency than conventional ones. The unique properties of DESs and HDESs have motivated us to explore the solvation structure of various anthropogenic gases in DESs and the structure and dynamics of HDESs. Experimental studies show that DESs have excellent gas absorption capacity. However, studies highlighting the solvation structure of these gases in DESs and the structure and dynamics associated with HDESs, which are the focus of this thesis, are scarce in the literature.

The first part of the thesis uses *ab initio* molecular dynamics (AIMD) simulations to understand the solvation structure of anthropogenic gases in DESs. The studied systems comprise solute gases CO_2 , SO_2 , CH_4 , NH_3 , H_2S , and CO solvated by two different DESs, namely a 1:2 mole ratio of choline chloride:urea ([Ch][Cl]:URE), called reline and choline chloride:ethylene glycol ([Ch][Cl]:EG) in 1:2 mole ratio, called ethaline. The thesis discusses fundamental interactions that stabilize various solute gases

in both DESs focusing on the nearest solvation shell structure around solute gases in these DESs. The effect of changing hydrogen bond donor (HBD) species on solvation structure, the contribution of different DES species in determining the structure, and the role of charge transfer interactions and polarizability in guiding the solvation structure are studied.

The second part of the thesis uses classical molecular dynamics (MD) simulations to understand the structure and dynamics associated with HDESs. The HDESs studied here are based on DL-menthol (DLM) and organic acids with varying the chain length of HBD acids, namely hexanoic (C6), octanoic (C8), decanoic (C10), and dodecanoic (C12) acids. Other HDES studied here is composed of thymol (THY) and coumarin (COU). The total X-ray scattering structure function ($S(q)$) and partial $S(q)$ provide insights into the structural organization. Real space pair correlations were computed to understand the atomic interactions between various HDES components. Hydrogen bonding interactions present in the HDESs were elucidated by radial angular distribution functions. Spatial distribution functions were analyzed to get a complete picture of the structural organization present in the HDESs. Hydrogen bond dynamics gives insight into the hydrogen bond relaxations. Here, hydrogen bond lifetimes and the strength of hydrogen bonding interactions are also discussed. The translational dynamics is studied using mean square displacement (MSD) and the self-diffusion coefficients of the molecules present in the HDESs. Dynamic properties like non-Gaussian parameter and van Hove correlation functions were analyzed to decipher the presence of dynamic heterogeneity. In summary, this thesis compiles various systematic investigations to understand the solvation structures of different harmful gases in DESs and the structure and dynamics of HDESs.

सार

इस थीसिस में, हम डीप यूटेक्टिक सॉल्वेंट्स में मानवजनित गैसों की सॉल्वेशन संरचना, और हाइड्रोफोबिक डीप यूटेक्टिक सॉल्वेंट्स के थोक चरण आकारिकी और गतिशीलता को स्पष्ट करने वाले बहु-स्तरीय सिमुलेशन अध्ययनों की रिपोर्ट करते हैं। गैस पृथक्करण के लिए उपयोग किए जाने पर पारंपरिक सॉल्वेंट्स को कई नुकसान झेलने पड़ते हैं, जैसे उपकरण का संक्षारण और पर्यावरण को नुकसान पहुंचा रहे हैं। हाइड्रोफोबिक स्थितियों की आवश्यकता वाले अनुप्रयोगों के लिए, पारंपरिक सॉल्वेंट्स के उपयोग से चरण पृथक्करण शक्ति में कमी के कारण निष्कर्षण दक्षता कम हो जाती है। डीप यूटेक्टिक सॉल्वेंट्स (डीईएस) और हाइड्रोफोबिक डीप यूटेक्टिक सॉल्वेंट्स (एचडीईएस) इन पारंपरिक सॉल्वेंट्स की जगह लेते हैं। डीईएस आसान तैयारी, बायोडिग्रेडेबिलिटी, ट्यून करने योग्य प्रकृति, उत्कृष्ट थर्मल स्थिरता, कम अस्थिरता और कम विषाक्तता जैसे अद्वितीय गुण प्रदर्शित करते हैं, जो उन्हें गैस पृथक्करण अनुप्रयोगों के लिए उपयुक्त उम्मीदवार बनाते हैं। एचडीईएस जल-अमिश्रणीय सॉल्वेंट्स के रूप में व्यवहार करते हैं और पारंपरिक सॉल्वेंट्स की तुलना में उच्च निष्कर्षण दक्षता दिखाते हैं। डीईएस और एचडीईएस के अद्वितीय गुणों ने हमें विभिन्न की सॉल्वेशन संरचना का पता लगाने के लिए प्रेरित किया है डीईएस में मानवजनित गैसों और एचडीईएस की संरचना और गतिशीलता। प्रायोगिक अध्ययन से पता चलता है कि डीईएस में उत्कृष्ट गैस अवशोषण क्षमता होती है। हालाँकि, डीईएस में इन गैसों की सॉल्वेशन संरचना और एचडीईएस से जुड़ी संरचना और गतिशीलता पर प्रकाश डालने वाले अध्ययन, जो इस थीसिस का फोकस हैं, साहित्य में दुर्लभ हैं।

थीसिस का पहला भाग डीईएस में मानवजनित गैसों की सॉल्वेशन संरचना को समझने के लिए एबी इनिटियो आणविक गतिशीलता (एआईएमडी) सिमुलेशन का उपयोग करता है। अध्ययन किए गए सिस्टम में दो अलग-अलग डीईएस द्वारा घुलनशील घुलनशील गैसों CO_2 , SO_2 , CH_4 , NH_3 , H_2S और CO शामिल हैं, अर्थात् कोलीन क्लोराइड:यूरिया ($[\text{Ch}][\text{Cl}]:\text{URE}$) का 1:2 मोल अनुपात, जिसे कहा जाता है। रीलाइन और कोलीन क्लोराइड: एथिलीन ग्लाइकॉल ($[\text{Ch}][\text{Cl}]:\text{EG}$) 1:2 मोल अनुपात में, जिसे एथेलीन कहा जाता है। थीसिस उन मूलभूत अंतःक्रियाओं पर चर्चा करती है जो इन डीईएस में विलेय गैसों के आसपास निकटतम सॉल्वेशन शेल संरचना पर ध्यान केंद्रित करते हुए दोनों डीईएस में विभिन्न विलेय गैसों को स्थिर करती हैं। सॉल्वेशन संरचना पर हाइड्रोजन बॉन्ड डोनर (एचबीडी) प्रजातियों को बदलने का प्रभाव, संरचना का निर्धारण करने में विभिन्न डीईएस प्रजातियों का योगदान, और सॉल्वेशन संरचना को निर्देशित करने में चार्ज ट्रांसफर इंटरैक्शन और ध्रुवीकरण की भूमिका का अध्ययन किया जाता है।

थीसिस का दूसरा भाग एचडीईएस से जुड़ी संरचना और गतिशीलता को समझने के लिए शास्त्रीय आणविक गतिशीलता (एमडी) सिमुलेशन का उपयोग करता है। यहां अध्ययन किए गए एचडीईएस डीएल-मेन्थॉल (डीएलएम) और कार्बनिक अम्लों पर आधारित हैं, जिनमें एचबीडी एसिड की श्रृंखला की लंबाई अलग-अलग होती है, अर्थात् हेक्सानोइक (सी6), ऑक्टानोइक (सी8), डिकैनोइक (सी10), और डो-डिकैनोइक (सी12) एसिड। यहां अध्ययन किए गए अन्य एचडीईएस थाइमोल (टीएचवाई) और क्यूमरिन (सीओयू) से बने हैं। कुल एक्स-रे प्रकीर्णन संरचना फ़ंक्शन (एस(क्यू)) और आंशिक एस(क्यू) संरचनात्मक संगठन में अंतर्दृष्टि प्रदान करते हैं। विभिन्न एचडीईएस घटकों के बीच परमाणु इंटरैक्शन को समझने के लिए वास्तविक अंतरिक्ष जोड़ी सहसंबंधों की गणना की गई थी। एचडीईएस में मौजूद हाइड्रोजन बॉन्डिंग इंटरैक्शन को रेडियल कोणीय वितरण कार्यों द्वारा स्पष्ट किया गया था। स्थानिक वितरण कार्यों का विश्लेषण किया गया एचडीईएस में मौजूद संरचनात्मक संगठन की पूरी तस्वीर प्राप्त करें। हाइड्रोजन बांड गतिशीलता हाइड्रोजन बांड विश्राम के बारे में जानकारी देती है। यहां, हाइड्रोजन बॉन्ड जीवनकाल और हाइड्रोजन बॉन्डिंग इंटरैक्शन की ताकत पर भी चर्चा की गई है। माध्य वर्ग विस्थापन (एमएसडी) और का उपयोग करके अनुवादात्मक गतिशीलता का अध्ययन किया जाता है एचडीईएस में मौजूद अणुओं के स्व-प्रसार गुणांक। गतिशील विषमता की उपस्थिति को समझने के लिए गैर-गाऊसी पैरामीटर और वैन होव

सहसंबंध कार्यों जैसे गतिशील गुणों का विश्लेषण किया गया है। संक्षेप में, यह थीसिस डीईएस में विभिन्न हानिकारक गैसों की सॉल्वेशन संरचनाओं और एचडीईएस की संरचना और गतिशीलता को समझने के लिए व्यवस्थित जांच संकलन करती है ।

Permissions

The following articles have permission from the relevant journals.

Publications Associated with the Work Reported in This Thesis as of the Submission Date

1. **Akshay Malik**, Harender S. Dhattarwal, and Hemant K. Kashyap, Distinct Solvation Structures of CO₂ and SO₂ in Reline and Ethaline Deep Eutectic Solvents Revealed by AIMD Simulations. *J. Phys. Chem. B* **2021** 125, 1852.
2. **Akshay Malik** and Hemant K. Kashyap, Heterogeneity in Hydrophobic Deep Eutectic Solvents: SAXS Prepeak and Local Environments. *Phys. Chem. Chem. Phys.* **2021** 23, 3915.
3. **Akshay Malik** and Hemant K. Kashyap, Multiple Evidences of Dynamic Heterogeneity in Hydrophobic Deep Eutectic Solvents. *J. Chem. Phys.* **2021** 155, 044502.
4. **Akshay Malik** and Hemant K. Kashyap, Solvent Organization around Methane Dissolved in Archetypal Reline and Ethaline Deep Eutectic Solvents as Revealed by AIMD Investigation. *J. Phys. Chem. B* **2022** 126, 6472.
5. **Akshay Malik**, Harender S. Dhattarwal, and Hemant K. Kashyap, An Overview of Structure and Dynamics Associated with Hydrophobic Deep Eutectic Solvents and Their Applications in Extraction Processes. *ChemPhysChem* **2022** 23, e202200239.
6. **Akshay Malik**, Harender S. Dhattarwal, and Hemant K. Kashyap, Applications of Deep Eutectic Solvents in Gas Capture, Current Developments in Biotechnol-

ogy and Bioengineering; Deep Eutectic Solvents: Fundamentals and Emerging Applications, Chapter 3. *Elsevier* **2022** 49.

7. **Akshay Malik** and Hemant K. Kashyap, Solvation Shell Structures of Ammonia in Reline and Ethaline Deep Eutectic Solvents. *J. Phys. Chem. B* **2023** 127, 2499.
8. **Akshay Malik** and Hemant K. Kashyap, Origin of Structural and Dynamic Heterogeneity in Thymol and Coumarin based Hydrophobic Deep Eutectic Solvents as Revealed by Molecular Dynamics. *Phys. Chem. Chem. Phys.* **2023** 25, 19693.
9. **Akshay Malik** and Hemant K. Kashyap, Solvation Shell Anatomy of H₂S and CO Dissolved in Reline and Ethaline Deep Eutectic Solvents. *J. Phys. Chem. B* **2023**.

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