MOLECULAR DYNAMICS INVESTIGATION OF MICROSCOPIC STRUCTURAL MORPHOLOGY OF DEEP EUTECTIC SOLVENTS

SUPREET KAUR

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
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by

SUPREET KAUR
DEPARTMENT OF CHEMISTRY

Submitted
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Dedicated to

My Family

Certificate

This is to certify that the thesis titled "**MOLECULAR DYNAMICS INVESTIGATION OF MICROSCOPIC STRUCTURAL MORPHOLOGY OF DEEP EUTECTIC SOLVENTS**" is being submitted by **Ms. Supreet Kaur** 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 her 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.

Dr. Hemant K. Kashyap
Associate Professor
Department of Chemistry
Indian Institute of Technology Delhi
New Delhi-110016, India

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Abstract

Deep eutectic solvents (DESs) have emerged as an exclusive class of novel and green solvents in the beginning of this century. DESs render low toxicity, lower vapor pressure, better biodegradability, and sustainability than traditional solvent media. These liquids are moderate conductors, possess good solvation tendency and optimum electrochemical potential window. The studies reporting the applications of these solvent in interdisciplinary fields such as synthesis, electrochemistry, biotransformations, have grown exponentially in recent years. Furthermore, the successful implementation as well as development of these solvents requires a strong fundamental understanding of these solvents, which unfortunately is in its infancy stage. In this thesis, we report the molecular dynamics simulation investigation to explore the structure of different classes of deep eutectic solvents in bulk and near confinement. The choice of constituents of these solvents is not limited to only ionic species and various combinations of molecular components and/or ions can be adopted. Hence the changes in the structural morphology of DESs by varying the constituent species of DESs is also included in our investigation.

Here we describe a thorough structure study of two major classes of DESs, namely, Li^+ salt-based and choline chloride ([Ch][Cl])-based. First part of this thesis is directed towards the analysis of microscopic structure of alkylamide+Li^+/ClO_4^- based DESs. The effect of tail length modification and temperature on the nanostructure of these DESs is explored by investigating the simulated scattering structure functions and their partial sub-components. Real space correlations and isodensity surfaces further provided the quantification of intermolecular correlations existing in the DESs. The second part comprises of bulk and confinement studies of choline chloride based DES, namely reline (molar mixture of [Ch][Cl] and urea in ratio 1:2). The comparison of bulk phase arrangement of reline components with the existing literature studies validates the force field model utilized for carrying out the classical simulations. Number density profiles, lateral pair correlation functions along with orientational order parameter were computed to gain insights on the responsiveness of reline when confined between uncharged and charged carbon electrodes. In the last domain, we have used a different hydrogen bond donor along with [Ch][Cl] salt (ethaline) and explored the structural

features thoroughly. Simulated X-ray scattering structure functions and its partial components, radial, radial angular, and spatial distribution functions collectively provide insights over short and long-range arrangement present in this eutectic mixture and further this investigation is extended to its aqueous mixtures as well. Overall, this thesis is a coherent body of systematic investigations to explore the solvation structure of different DESs.

सार

इस सदी की शुरुआत में डीप यूक्टेक्टिक सॉल्वैंट्स (डीईएस), नवीन और पर्यावरण के अनुकूल सॉल्वैंट्स के एक विशेष वर्ग के रूप में उभरा है। डीईएस कम विषाक्तता, कम वाष्प दबाव प्रदान करते हैं तथा पारंपरिक विलायक मीडिया की तुलना में बेहतर जैवअवक्रमण और स्थिर है । ये द्रव पदार्थ मध्यम संवाहक होते हैं, और इनमें अच्छी उत्कीर्णन प्रवृत्ति और विद्युत स्थिरता मौजूद हैं। इन विलायक के अनुप्रयोगों की रिपोर्ट करने वाले अध्ययन अंतःविषय क्षेत्रों जैसे कि संश्लेषण, इलेक्ट्रोकैमिस्ट्री, बायोट्रांसफॉर्मेशन में हाल के वर्षों में तेजी से वेतन वृद्धि हुई है। इनके सफल कार्यान्वयन के साथ ही इन सॉल्वैंट्स के विकास के लिए एक मजबूत मूलभूत समझ की आवश्यकता होती है, जो दुर्भाग्य से अपने प्रारंभिक अवस्था में है। इस थीसिस में हम इन यूटैक्टिक सॉल्वैंट्स की विभिन्न श्रेणियाँ की बल्क फेज में और कॉन्फिनमेंट के पास गहरी संरचना को आणविक गतिशीलता सिमुलेशन जांच के माध्यम से रिपोर्ट करते हैं । घटक की पसंद इन सॉल्वैंट्स केवल आयनिक प्रजातियों और विभिन्न संयोजनों तक सीमित नहीं हैं आणविक घटकों और / या आयनों को अपनाया जा सकता है। इसलिए डीईएस के अलग-अलग घटक प्रजातियों का उपयोग करते हुए संरचनात्मक में परिवर्तन और इनके आकृति विज्ञान जाँच भी शामिल है।

यहां हम डीईएस के दो प्रमुख वर्गों के गहन संरचना अध्ययन का वर्णन करते हैं, जो हैं, लिथियम साल्ट-आधारित और कोलीन क्लोराइड आधारित। इस थीसिस का पहला भाग एल्केलामाइड + लिथौम साल्ट आधारित डीईएस की सूक्ष्म संरचना के विश्लेषण की ओर निर्देशित है। इनमें से नैनोसंरचना पर पूंछ की लंबाई संशोधन और तापमान का प्रभाव का पता सिम्युलेटेड स्कैटरिंग स्ट्रक्चर फ़ंक्शंस और उनके आंशिक उप-घटक की पड़ताल करके किया जाता है । रेडियल डिस्ट्रीब्यूशन फ़ंक्शंस और आइसोडेंसिटी सतहें डीईएस में आगे विद्यमान अंतर-आणविक सहसंबंधों का परिमाण प्रदान करता है। दूसरे भाग में कोलीन क्लोराइड आधारित डीईएस के बल्क फेज और कॉन्फिनमेंट के पास के अध्ययन शामिल हैं, अर्थात् रीलाइन (मोलर मिश्रण कोलीन क्लोराइड और यूरिया १:२ अनुपात में) । रीलाइन घटकों की बल्क फेज स्ट्रक्चर की तुलना मौजूदा साहित्य अध्ययनों के साथ करके रीलाइन की फोर्स-फ़ील्ड मॉडल का उपयोग आणविक सिमुलेशन के लिए किया है । संख्या घनत्व प्रोफाइल, पार्श्व जोड़ी सहसंबंध फंक्शन के साथ-साथ ओरिएंटेशनल ऑर्डर पैरामीटर की बिना चार्ज और चार्ज कार्बन इलेक्ट्रोड के बीच रेस्पोंसिवेनेस्स पर अंतर्दृष्टि प्राप्त करने के लिए गणना की गई थी । अंतिम डोमेन में हमने एक अलग हाइड्रोजन बॉन्ड डोनर का प्रयोग कोलीन क्लोराइड साल्ट के साथ किया है और संरचनात्मक विशेषताओं को अच्छी तरह से पता लगाया । सिम्युलेटेड स्कैटरिंग स्ट्रक्चर फ़ंक्शंस और उनके आंशिक उप-घटक रेडियल, रेडियल कोणीय, और स्थानिक वितरण कार्य सामूहिक रूप से इस युक्टेक्टिक मिश्रण में मौजूद छोटी और लंबी दूरी की व्यवस्था की अंतर्दृष्टि प्रदान करते हैं और आगे यह जाँच उसके जलीय मिश्रणों तक भी विस्तारित है । कुल मिलाकर, यह थीसिस विभिन्न डीईएस के सॉल्वैंशन संरचना का पता लगाने के लिए व्यवस्थित जांच का एक सुसंगत निकाय है।

Permissions

Permissions have been taken for the following publications from the respective Journals.

List of Publications Related to Work Presented in this Thesis as on Thesis Submission Date

1. **Supreet Kaur**, Aditya Gupta and Hemant K. Kashyap, Nanoscale spatial heterogeneity in deep eutectic solvents, *J. Phys. Chem. B*, **120**, 6712 (2016).

2. **Supreet Kaur**, Shobha Sharma and Hemant K. Kashyap, Bulk and interfacial structure of reline deep eutectic solvent: A molecular dynamics study, *J. Chem. Phys.*, **147**, 194507 (2017).

3. **Supreet Kaur** and Hemant K. Kashyap, Unusual temperature dependence of nanoscale structural organization in deep eutectic solvents, *J. Phys. Chem. B*, **122**, 5242 (2018).

4. **Supreet Kaur**, Shobhna and Hemant K. Kashyap, Insights gained from refined force field for pure and aqueous ethylene glycol through molecular dynamics simulations, *J. Phys. Chem. B*, **123**, 6543 (2019).

5. **Supreet Kaur**, Akshay Malik and Hemant K. Kashyap, Anatomy of microscopic structure of ethaline deep eutectic solvent decoded through molecular dynamics simulations, *J. Phys. Chem. B*, **123**, 6543 (2019).

6. **Supreet Kaur**, Aditya Gupta and Hemant K. Kashyap, How Hydration Affects the Microscopic Structural Morphology in a Deep Eutectic Solvent, *J. Phys. Chem. B*, **124**, 2230 (2020).

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