MOLECULAR DYNAMICS STUDIES OF BULK AND INTERFACIAL STRUCTURE OF IONIC LIQUIDS

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by

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Dedicated to

My Family

Certificate

This is to certify that the thesis titled "**MOLECULAR DYNAMICS STUDIES OF BULK AND INTERFACIAL STRUCTURE OF IONIC LIQUIDS**" is being submitted by **Ms. Shobha Sharma** 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.

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Shobha Sharma

Abstract

In this thesis, we report the responsiveness of the bulk and interfacial structure of ionic liquids towards external stimuli using molecular dynamics simulations. Owing to their peculiar and notable properties at ambient as well as extreme conditions, ionic liquids are now utilized as promising alternative material in progressive energy storage devices such as super-capacitors, Li- and Na-ion batteries, and dye-sensitized solar cells along with tribological applications. Here, we have mainly focused on the effect of high pressure and various confinements on the structure of ionic liquids. The ionic liquids chosen for this purposes belong to the broader class of phosphonium, pyrrolidinium, and quaternary ammonium cation-based ionic liquids. In most of the work presented here, these cations are paired with bis(trifluoromethylsulfonyl)imide anion. As ionic liquids can be tailored according to the requirements, these are known as designer solvents, and understanding the effect of changing structural architecture and molecular compositions is the driving motivation of this thesis. At ambient conditions, ionic liquids consisting ions with longer alkyl tails are known to possess nanoscale heterogeneity along with charge ordering. Herein, we have systematically studied how these orderings respond to external stimuli. These stimuli can be broadly classified as high pressure, confinement, temperature.

In the first domain, we report the pressure responsiveness of the microscopic structure of the $P_{666,14}{}^{+}$ and $Pyrr_{1,n}{}^{+}$ based ionic liquids under high pressure. For this purpose, real space correlation functions along with total X–ray structure functions are examined. To further understand the heterogeneity in the structure and contribution of ionic moieties and their structural design, we used several methodologies to split the total X-ray structure function into partial structure functions based on the polarity and charge distribution on the ions. Conformational flexibility of the cationic tails and anion is expressed in the microscopic structure of these ionic liquids with change in pressure and is quantified in this thesis by exploring the dihedral distribution in the ionic components.

In the next domain, we have extended our studies for exploring the effect of confinement on the ionic arrangement in the interfacial region and electrostatic properties of the ionic liquids. Interfacial layering of the ions is investigated by looking at the

average number and charge (ionic and subionic) densities along the reference (z) axis. For orientational details at the molecular level, we examined the average atomic number density profiles along with the orientational order parameter profiles. Insights gained for interfacial structural orientation were properly employed to examine the electrostatic properties such as electric field, electrostatic potential, and differential capacitance. Bin-wise charge density is utilized to interpret the screening and over–screening tendencies of the ions.

सार

इस थीसिस में, हम आणविक गतिकी सिमुलेशन का उपयोग करके बाहरी उत्तेजनाओं की ओर आयनिक तरल पदार्थ के थोक की प्रतिक्रियाशीलता और अंतर संरचना की सूचना दे रहे हैं । परिवेश के साथ-साथ चरम स्थितियों में उनके अजीब और उल्लेखनीय गुणों के कारण, आयनिक तरल पदार्थ अब सुपर-कैपेसिटर, लिथियम- और सोडियम-आयन बैटरी, और डाई-संवेदीकृत जैसे प्रगतिशील ऊर्जा भंडारण उपकरणों के साथ साथ स्नेहन अनुप्रयोगों तथा सौर सेल में वैकल्पिक सामग्री के रूप में उपयोग किए जाते हैं। यहां, हमने मुख्य रूप से आयनिक तरल पदार्थों की संरचना पर उच्च दबाव और विभिन्न कारावासों के प्रभाव पर ध्यान केंद्रित किया है। इस उद्देश्य के लिए चुने गए आयनिक तरल पदार्थ फॉस्फोनियम, पाइरोलिडिनियम और चतुर्धातुक अमोनियम धनायन आधारित आयनिक तरल पदार्थों के व्यापक वर्ग के हैं। यहां प्रस्तुत अधिकांश कार्यों में, इन धनायनों को बीस (ट्राइफ्लूरोमेथाइलसुल्फोनील) आयनों के साथ जोड़ा जाता है। जैसा कि आयनिक तरल पदार्थ आवश्यकताओं के अनुसार अनुकूलित किया जा सकता है, इन्हें डिजाइनर सॉल्वैंट्स के रूप में जाना जाता है, और बदलते संरचनात्मक वास्तुकला और आणविक रचनाओं के प्रभाव को समझना इस थीसिस की प्रेरणा है। परिवेशी स्थितियों में, आयनिक तरल पदार्थ जिसमें एल्काइल पूंछ होते हैं, को चार्ज व्यवस्था के साथ नैनोस्केल विषमता के अधिकारी के रूप में जाना जाता है। इसमें, हमने व्यवस्थित रूप से अध्ययन किया है कि ये व्यवस्था बाहरी उत्तेजनाओं पर कैसे प्रतिक्रिया देते हैं। इन उत्तेजनाओं को मोटे तौर पर उच्च दबाव, परिरोध, तापमान के रूप में वर्गीकृत किया जा सकता है।

पहले डोमेन में, हम उच्च दबाव में $P_{666,14}^{+}$और $Pyrr_{1,n}^{+}$ आयन आधारित तरल पदार्थसूक्ष्म की संरचना की जवाबदेही की रिपोर्ट करते हैं। इस प्रयोजन के लिए, कुल एक्स-रे संरचना कार्यों के साथ वास्तविक अंतरिक्ष सहसंबंध कार्यों की जांच की जाती है। आयनिक मौजों की संरचना और योगदान और उनके संरचनात्मक डिजाइन में विविधता को समझने के लिए, हमने कुल कार्यप्रणाली का इस्तेमाल किया, जो कि कुल एक्स-रे संरचना कार्य को आंशिक संरचना के कार्यों में विभाजित करने के लिए ध्रुवीयता और आयनों पर आवेश वितरण के आधार पर किया गया। धनायन पूंछों और आयनों के संवहन लचीलेपन को दबाव में परिवर्तन के साथ इन आयनिक तरल पदार्थों की सूक्ष्म संरचना में व्यक्त किया जाता है और आयनिक घटकों में डायहेड्रल वितरण की खोज करके इस थीसिस में प्रस्तुत किया गया है।

अगले डोमेन में, हमने आयनिक तरल पदार्थ के इलेक्ट्रोस्टैटिक गुणों के परस्पर क्षेत्र में आयनिक व्यवस्था पर प्रभाव की खोज के लिए अपनी पढ़ाई का विस्तार किया है। आयनों की इंटरफैसिअल लेयरिंग की जांच आवेश (आयनिक और सबियनिक) घनत्व की संदर्भ (z) अक्ष के साथ औसत संख्या को देखकर किया जाता है। आणविक स्तर पर ओरिएंटेशनल विवरण के लिए, हमने ओरिएंटल ऑर्डर पैरामीटर प्रोफाइल के साथ औसत परमाणु संख्या घनत्व प्रोफाइल की जांच की। इंटरफैसिअल संरचनात्मक अभिविन्यास के लिए प्राप्त अंतर्दृष्टि को विद्युत क्षेत्र, इलेक्ट्रोस्टैटिक क्षमता और विभेदक समाई जैसे इलेक्ट्रोस्टैटिक गुणों की जांच करने के लिए ठीक से नियोजित किया गया था। बिन-वार चार्ज घनत्व का उपयोग आयनों की स्क्रीनिंग और स्क्रीनिंग की प्रवृत्ति की व्याख्या करने के लिए किया जाता है।

Permissions

Permissions have been taken from the respective journals to reprint the publications related to the work presented in this thesis.

List of Publications Related to Work Presented in this Thesis

1. **Shobha Sharma** and Hemant K. Kashyap, "Structure of Quaternary Ammonium Ionic Liquids at Interfaces: Effects of Cation Tail Modification with Isoelectronic Groups", *J. Phys. Chem. C*, **119**, 23955 (2015).

2. **Shobha Sharma**, Aditya Gupta and Hemant K. Kashyap, "How the Structure of Pyrrolidinium Ionic Liquids is Susceptible to High Pressure", *J. Phys. Chem. B*, **120**, 3206 (2016).

3. **Shobha Sharma**, Aditya Gupta, Debdas Dhabal and Hemant K. Kashyap, "Pressure-dependent Morphology of Trihexyl(tetradecyl) phosphonium Ionic Liquids: A Molecular Dynamics Study", *J. Chem. Phys.*, **145**, 134506 (2016).

4. **Shobha Sharma** and Hemant K. Kashyap, "Interfacial Structure of Pyrrolidinium Cation Based Ionic Liquids at Charged Carbon Electrodes: The Role of Linear and Non-linear Alkyl Tails", *J. Phys. Chem. C*, **121**, 13202 (2017).

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