

MOLECULAR DYNAMICS INVESTIGATION OF MICROSCOPIC STRUCTURAL MORPHOLOGY OF DEEP EUTECTIC SOLVENTS

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by

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DEPARTMENT OF CHEMISTRY

Submitted

in fulfillment of the requirement of the degree of doctor of philosophy

to the



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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.

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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 सॉल्वेंट्स (डीईएस), नवीन और पर्यावरण के अनुकूल सॉल्वेंट्स 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, इलेक्ट्रोकेमिस्ट्री, बायोट्रांसफॉर्मेशन में हाल के वर्षों में तेजी से वेतन वृद्धि हुई है। इनके सफल कार्यान्वयन के साथ ही इन सॉल्वेंट्स 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 यूक्टेक्टिक सॉल्वेंट्स की विभिन्न श्रेणियों 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 सॉल्वेंट्स 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 जांच 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 + लिथोम साल्ट आधारित डीईएस की सूक्ष्म संरचना के विश्लेषण की ओर निर्देशित है। इनमें से नैनोसंरचना पर पूछ की लंबाई संशोधन और तापमान का प्रभाव का पता सिम्युलेटेड स्कैटरिंग स्ट्रक्चर फंक्शंस और उनके आंशिक उप-घटक की पड़ताल करके किया जाता है। रेडियल डिस्ट्रीब्यूशन फंक्शंस 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-फील्ड 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 रेस्पॉन्सिवेनेस 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 फंक्शंस 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 जांच उसके जलीय मिश्रणों तक भी विस्तारित है। कुल मिलाकर, यह थीसिस विभिन्न डीईएस के सॉल्वेंशन 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

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Contents

Certificate	i
Acknowledgements	iii
Abstract	v
Permissions	vii
Table of Contents	ix
List of Figures	xiii
List of Tables	xxiii
1 Introduction	1
1.1 General Introduction	2
1.2 Computational Details	13
1.2.1 Molecular Dynamics Simulations	13
1.2.1.1 Interaction Potentials and Molecular Models	14
1.2.1.2 Solving the Equations of Motion	15
1.2.1.3 Periodic Boundaries and Minimum Image Convention . .	17
1.2.1.4 Long Range Forces	17
1.2.1.5 Statistical Ensembles	19
1.2.1.6 MD at Constant Temperature and Pressure	20
1.2.2 Estimation of Properties	23
1.2.2.1 Simulated Scattering Structure Functions	23
1.2.2.2 Transport Properties	25
1.2.2.3 Hydrogen Bond Auto-correlation Function	26
1.2.2.4 Radial Angular Distribution Function	26

1.2.2.5 Thermodynamic Properties	27
1.2.2.6 Lateral Pair Correlation Function	28
1.2.2.7 Orientational Order Parameter	29
1.2.2.8 Number Density Profiles	29
1.2.2.9 Electrostatic Properties	30
1.3 Motivation and Organization of the Thesis	32
2A Origin of Nanoscale Spatial Organization in Deep Eutectic Solvents: Effect of Amide Tail Modification	35
2A.1 Introduction	35
2A.2 Molecular Dynamics Simulations	37
2A.3 Results and Discussion	39
2A.3.1 X-ray and Neutron Scattering Structure Functions and their Partial Components	39
2A.3.2 Ion Pairing and Hydrogen Bonding	41
2A.4 Conclusions	45
2B Nanoscale Spatial Organization in Deep Eutectic Solvents: Temperature Dependent Study	47
2B.1 Introduction	47
2B.2 Computational Methodology	48
2B.3 Results and Discussion	51
2B.3.1 X-ray and Neutron Scattering Structure Functions and Partial Components	51
2B.3.2 Real Space Correlations & Hydrogen Bonding	55
2B.4 Conclusion	60
3 Bulk and Interfacial Structure of Reline Deep Eutectic Solvent	62
3.1 Introduction	62
3.2 Molecular Dynamics Simulations	64
3.3 Results and Discussion	66
3.3.1 Bulk phase structure of reline	66
3.3.1.1 Total and partial structure functions	66
3.3.1.2 Radial distribution functions	67

3.3.2 Interfacial structure of reline at graphene surface	69
3.3.2.1 Number density profiles and lateral pair correlation func- tions	69
3.3.2.2 Orientational order parameter	73
3.3.2.3 Electrostatic properties	78
3.4 Conclusions	80
4A Insights Gained from Refined Force-Field for Pure and Aqueous Ethylene Glycol through Molecular Dynamics Simulations	82
4A.1 Introduction	82
4A.2 Force-Field Model and Its Refinement	85
4A.3 Molecular Dynamics Simulations	88
4A.4 Results and Discussion	91
4A.4.1 Accuracy of Refined FF for Pure Ethylene Glycol Liquid	91
4A.4.1.1 X-ray Scattering Structure Function, $S(q)$	91
4A.4.1.2 Real Space Correlation Functions and Hydrogen Bonding	92
4A.4.1.3 Temperature-Dependent Behavior of Structure and Dy- namics of Pure Ethylene Glycol Liquid	93
4A.4.2 Performance of Refined FF for Aqueous Ethylene Glycol	96
4A.5 Concluding Remarks	100
4B Microscopic Structure of Ethaline DES Investigated using Im- proved Force Field Parameters	101
4B.1 Introduction	101
4B.2 Computational Details	103
4B.3 Results and Discussion	104
4B.3.1 Simulated X-ray Scattering Structure Function and its Partial Components	104
4B.3.2 Intra- and Interspecies Pair Correlations	106
4B.3.2.1 Center-of-mass RDFs	106
4B.3.2.2 Ion Pairing and Hydrogen Bonding	107
4B.3.3 Radial Angular Distribution Functions and Hydrogen Bonding Interactions	110

4B.3.4 Spatial Isodensity Surfaces	112
4B.3.4.1 Three-Dimensional Isodensity Surfaces around Choline Cation	112
4B.3.4.2 Three-Dimensional Isodensity surfaces around Ethylene Glycol	112
4B.4 Conclusions	114
5 Effect of hydration on Structure of Ethaline Deep Eutectic Solvent	116
5.1 Introduction	116
5.2 Molecular Dynamics Simulation Details	117
5.3 Results and Discussion	120
5.3.1 Simulated X-ray Scattering Structure Functions and Their Species- wise Deconstruction	120
5.3.2 Prominent Pair Correlations and Spatial Isodensity Surfaces . . .	122
5.4 Conclusions	128
6 Summary and Future Research Perspectives	130
Appendices	134
A Tables for comparison of simulated and experimental physico- chemical properties	134
B Force Field Parameters for different species investigated in this thesis	136
C Tables for nearest neighbor distance and respective coordination num- ber	143
Bibliography	145
Biodata	169

List of Figures

1.1 Schematic representation of solid-liquid phase diagram for eutectic mixture. Here ΔT_f is the depression in the freezing point and the eutectic point refers to the point where the two components melt together to form a single phase.	3
1.2 Molecular structures of typical chemical species used in designing of DESs, (a) hydrogen bond acceptor/salts and (b) hydrogen bond donors. . . .	5
1.3 Chemical structures for the DESs investigated in this thesis (a) alkylamide+LiClO ₄ (81:19), (b) choline chloride+urea (1:2), and (c) choline chloride+ethylene glycol (1:2).	9
2A.1 Chemical structures of (a) the alkylamides (RCONH ₂ with R=CH ₃ and C ₂ H ₅) and (b) the electrolyte (Li ⁺ /ClO ₄ ⁻) constituting the DESs studied.	36
2A.2 Tail length dependence of (a) X-ray scattering and (b) neutron scattering structure functions (S(q)s) for alkylamide+Li ⁺ /ClO ₄ ⁻ systems at temperature 323 K. Acetamide+Li ⁺ /ClO ₄ ⁻ is shown in <i>black</i> and propionamide+Li ⁺ /ClO ₄ ⁻ in <i>red</i>	37
2A.3 Partial X-ray scattering S(q)s for (a) acetamide+Li ⁺ /ClO ₄ ⁻ and (b) propionamide+Li ⁺ /ClO ₄ ⁻	39
2A.4 Equilibrium snapshots of (a) acetamide+Li ⁺ /ClO ₄ ⁻ and (b) propionamide+Li ⁺ /ClO ₄ ⁻ DESs. The Li ⁺ /ClO ₄ ⁻ groups are shown using <i>red</i> isosurfaces in all the systems. The acetamide molecules are shown in <i>green</i> and propionamide in <i>blue</i>	40
2A.5 Radial distribution function (RDF) for (a) Li ⁺ and oxygen (O) atom of ClO ₄ ⁻ (b) Li ⁺ and chlorine (Cl) atom of ClO ₄ ⁻ (c) Li ⁺ -Li ⁺ and (d) Cl-Cl.	42
2A.6 Radial distribution function (RDF) for (a) Li ⁺ and carbonyl oxygen (OR) of the alkylamides, and (b) Li ⁺ and amide nitrogen (N) of the alkylamides.	43

2A.7 Intermolecular RDFs for (a) amide hydrogens (HN) and the carbonyl oxygen (OR) atom of the alkylamides and (b) amide hydrogens (HN) and the oxygen (O) atom of ClO_4^-	43
2A.8 Average three-dimensional density isosurfaces reflecting the nearest solvation shells around (a) ClO_4^- and (b) acetamide for acetamide+ Li^+ / ClO_4^- system. The Li^+ isosurfaces are shown as <i>green</i> , carbonyl oxygen (OR) as <i>transparent red</i> and perchlorate oxygen (O) in <i>red wireframe</i>	44
2B.1 Comparison of simulated (<i>open circles</i>) and experimental (<i>solid circles</i>) densities, ρ at different temperatures. The experimental data has been adopted from that reported by Guchhait et al.[43]	48
2B.2 Temperature dependence of X-ray scattering structure functions (S(q)s) for (a) acetamide+ Li^+ / ClO_4^- and (b) propionamide+ Li^+ / ClO_4^- systems. 49	
2B.3 Temperature dependence of low q peak position (q_{low}) and corresponding characteristic length (D) for (a) acetamide+ Li^+ / ClO_4^- and (b) propionamide+ Li^+ / ClO_4^- systems.	49
2B.4 Temperature dependence of neutron scattering structure functions (S(q)s) for (a) acetamide+ Li^+ / ClO_4^- and (b) propionamide+ Li^+ / ClO_4^- systems.	50
2B.5 Polarity based partial X-ray scattering structure functions for acetamide+ Li^+ / ClO_4^- ((a)-(c)) system at different temperatures. . .	51
2B.6 Electrolyte and alkylamide based partial X-ray scattering structure functions for acetamide+ Li^+ / ClO_4^- ((a)-(c)) system at different temperatures.	52
2B.7 Polarity based partial X-ray scattering structure functions (S(q)s) for propionamide+ Li^+ / ClO_4^- ((a)-(c)) system at different temperatures. .	53
2B.8 Electrolyte and alkylamide based partial X-ray scattering structure functions (S(q)s) for propionamide+ Li^+ / ClO_4^- ((a)-(c)) system at different temperatures.	54
2B.9 Temperature dependent radial distribution functions (RDFs) for (a) Li^+ -Cl, (b) Li^+ - Li^+ and (c) Cl-Cl.	55

2B.10	Temperature dependent radial distribution functions (RDFs) for (a) Li ⁺ -OR, (b) Cl-OR, (c) Li ⁺ -N, (d) HN-O. OR is the acetamide oxygen atom, HN and N are acetamide amide group hydrogen, nitrogen atoms, respectively. O is ClO ₄ ⁻ oxygen.	56
2B.11	Temperature dependent radial distribution functions (RDFs) for (a) HN-OR, (b) N-OR, (c) C-C and (d) CT-CT. HN, OR, C, N, and CT are the amide hydrogen, carbonyl oxygen, carbonyl carbon, nitrogen and methyl carbon atoms, respectively.	57
2B.12	Temperature dependent cumulative coordination numbers for (a) Li ⁺ -Cl, (b) Li ⁺ -Li ⁺ , (c) Cl-Cl, (d) Li ⁺ -OR, (e) Cl-OR, (f) Li ⁺ -N, (g) HN-O, (h) N-OR, (i) C-C and (j) CT-CT for acetamide+Li ⁺ /ClO ₄ ⁻ system.	58
2B.13	Temperature dependent radial distribution functions (RDFs) for (a) Li ⁺ -Cl, (b) Li ⁺ -Li ⁺ , (c) Cl-Cl, (d) Li ⁺ -N, (e) HN-OR, (f) HN-O, (g) Li ⁺ -OR, (h) Cl-OR and (i) C-C. O is ClO ₄ ⁻ oxygen, HN, N, OR and C are propionamide amide group hydrogen, nitrogen, carbonyl oxygen and carbonyl carbon atoms, respectively for propionamide+Li ⁺ /ClO ₄ ⁻ system.	59
3.1	Chemical structures of (a) choline chloride and (b) urea.	64
3.2	(a) Total X-ray and neutron scattering structure functions (S(q)s) for the bulk reline system at 303 K. Note that the ordinate on the left corresponds to the X-ray scattering S(q) and that on right corresponds to the neutron scattering structure function. (b) Partial X-ray scattering structure function for all possible species wise correlations in reline.	67
3.3	Center-of-mass radial distribution functions between (a) [Ch] ⁺ -[Ch] ⁺ , [Ch] ⁺ -[Cl] ⁻ & [Ch] ⁺ -Urea and (b) [Cl] ⁻ -[Cl] ⁻ , [Cl] ⁻ -Urea & Urea-Urea. (c) RDFs for N-[Cl] ⁻ , H-[Cl] ⁻ & HO-[Cl] ⁻ . Here, HO corresponds to hydroxyl hydrogen of [Ch] ⁺ and H & N are the amide hydrogen and nitrogen atoms of urea, respectively.	68

3.4	Number density profiles as a function of distance (z) from the electrode for choline ion ((a) & (b)), chloride ion ((c) & (d)) and urea ((e) & (f)). $\rho_n(z)/\rho_n^o$ is the number density with respect to bulk number density (ρ_n^o) of the corresponding species. Note that these calculations were performed using the center-of-mass of the respective species.	69
3.5	Tangential radial distribution functions (TRDFs) for (a) cation-cation, (b) anion-anion and (c) urea-urea as a function of distance, r	70
3.6	Atomic number density (with respect to bulk number density) profiles as a function of z for (a) oxygen (O) and (b) nitrogen (N) atoms of urea near charged and neutral electrodes.	71
3.7	Equilibrium snapshots representing the arrangement of urea molecules near positive ((a) & (c)) and negative ((b) & (d)) electrodes. The urea oxygen atoms are shown as red spheres whereas nitrogen and carbon atoms are shown in blue and cyan colors, respectively. Note that for the sake of clarity, the hydrogen atoms are not shown here.	72
3.8	Direction vectors for (a) choline cation and (b) urea used for the computation of orientational order parameter.	74
3.9	Orientational order parameter as a function of distance (z) from the electrode for urea ((a) & (b)) and choline ion ((c) & (d)). Note that these calculations were performed for the respective direction vectors (\vec{R}) in urea and choline cation as depicted in Fig. 3.8.	74
3.10	Atomic number density (with respect to bulk number density) profiles as a function of z for (a) oxygen (O) atom and (b) nitrogen (N) atom of choline ion near charged and neutral electrodes, respectively.	75
3.11	Electrostatic potential ($U(z)$ in volts) with respect to the bulk near charged and neutral electrodes as a function of distance (z) from the respective electrodes.	76
3.12	Variation of electric field (E) as a function of distance (z) for reline confined between charged and neutral electrodes. E_0 , E_1 and E_2 are the electric fields corresponding to the liquid confined between the graphene electrodes with surface charge density $ \sigma_s = 0, 16.02$ and $32.04 \mu\text{C}/\text{cm}^2$, respectively.	77

3.13	Differential capacitance (C_d) as a function of electrode potential ($U_{electrode}$) for reline at 303 K. The <i>black</i> circles represent computed C_d and <i>red</i> solid line is the spline fit which is a guide to the eye. The electrode surface charge densities (in $\mu\text{C}/\text{cm}^2$) corresponding to each C_d value are also depicted.	79
3.14	Dependence of surface charge density on the electrode potential ($U_{electrode}$) for reline confined between charged and neutral electrodes.	80
4A.1	The ball and stick model along with labeled atom type notation of ethylene glycol molecule.	84
4A.2	(a) The probability distribution of OG-CG-CG-OG dihedral angle for liquid ethylene glycol using the refined FF at 298 K. The <i>trans</i> and <i>gauche</i> conformations are defined by the range $\pm 180^\circ \leq \phi \leq \pm 145^\circ$ and $-145^\circ \leq \phi \leq 145^\circ$ of OG-CG-CG-OG dihedral angle respectively. (b) Equilibrium simulation box snapshot for pure ethylene glycol liquid at 298 K. Here the blue isosurface represents the <i>gauche</i> conformers. The oxygen, carbon and hydrogen atoms of <i>trans</i> conformers are shown as red, cyan and white spheres respectively.	84
4A.3	Comparison of the probability distribution of OG-CG-CG-OG dihedral angle for liquid ethylene glycol using the (-) refined FF and (-) CGenFF at 298 K. Kindly note that the left and right ordinate give the probability of this dihedral from refined FF and original CGenFF, respectively.	86
4A.4	Comparison of simulated and experimental densities, ρ for (a) pure ethylene glycol at different temperatures and (b) ethylene glycol aqueous mixtures at 298 K.	87
4A.5	Experimental and simulated X-ray scattering structure functions ($S(q)$ s) for pure ethylene glycol at 298 K. The experimental data has been taken from Bakó and coworkers.[201]	88
4A.6	Comparison of simulated X-ray scattering structure functions obtained from refined FF used in present work and original CGenFF with the experimental data.	89

4A.7 Radial distribution function, $g(r)$, for (a) OG-OG, and (b) HO-OG pair. In the HO-OG RDF shown here directly bonded HO and OG pairs are excluded. Radial angular distribution function, $g(r,\theta)$, for (c) \angle HO-OG-OG angle and $r_{\text{OG-OG}}$ distance and (d) \angle HO-OG-OG angle and $r_{\text{HO-OG}}$ distance for the hydrogen bonded HO-OG pair in pure ethylene glycol molecule at 298 K.	90
4A.8 Inter-molecular radial distribution functions, $g(r)$ s for CG-CG and CG-OG pair in pure ethylene glycol at 298 K.	94
4A.9 Dependence of total X-ray scattering structure function, $S(q)$, on temperature. A consecutive offset of 0.1 on ordinate is maintained to clearly show the minor shift in the position of the peaks with temperature. . .	95
4A.10 Distribution of H-bond number ($N_{\text{H-bond}}$) per ethylene glycol molecule for total (intra- and inte-molecular) hydrogen bonded HO-OG pair in pure ethylene glycol at 298, 318 and 338 K.	95
4A.11 Temperature dependence of hydrogen bond autocorrelation function, $C(t)$, for intermolecular hydrogen bonding interaction for HO-OG pair in liquid ethylene glycol. Note that abscissa has been plotted on a logarithmic scale.	96
4A.12 Mean square displacement (MSD) and its first derivative $\beta(t)$ plot for pure ethylene glycol at all temperatures. Note that both abscissa and ordinate of the upper panel have been plotted in logarithmic scale. . . .	97
4A.13 Simulated total X-ray scattering structure functions ($S(q)$ s) for all aqueous mixtures of ethylene glycol at 298 K.	97
4A.14 Inter-molecular radial distribution functions, $g(r)$ s for (a) OG-OG and (b) HO-OG pairs for all the aqueous mixtures of ethylene glycol at 298 K.	98
4A.15 Equilibrium snapshots of the simulation boxes of pure and aqueous ethylene glycol for x_{EG} = (a) 1.0, (b) 0.8, (c) 0.6, (d) 0.4 and (e) 0.2. The <i>gauche</i> and <i>trans</i> conformers of ethylene glycol are shown in blue and white isosurfaces, respectively. The oxygen and hydrogen atoms of water molecule are shown in red and white molecular representations, respectively.	98

4A.16 Composition dependence of (a) MSD and its first derivative $\beta(t)$ and (b) self-diffusion coefficient (D) of ethylene glycol for all aqueous mixtures of ethylene glycol at 298 K.	99
4B.1 Chemical structures of (a) choline chloride ($[\text{Ch}][\text{Cl}]$) and (b) ethylene glycol components of ethaline.	102
4B.2 Equilibrium simulation cell snapshots rendered for (a) ethaline as well as for individual species (b) $[\text{Ch}]^+$ (c) EG and (d) $[\text{Cl}]^-$ present in ethaline. Here blue, red and green color represent the $[\text{Ch}]^+$, EG and $[\text{Cl}]^-$, respectively.	104
4B.3 Comparison of experimental and simulated densities, ρ , of ethaline for temperature range 303–343 K.	104
4B.4 (a) Simulated X-ray scattering structure function, $S(q)$, for bulk ethaline at 303 K. (b) Species-wise partial components of $S(q)$ of ethaline. The corresponding q ranges for the regions I-IV marked here are 0–0.67, 0.67–1.25, 1.25–1.75 and 1.75–3.0 \AA^{-1} , respectively.	105
4B.5 Center-of-mass radial distribution functions for (a) $[\text{Ch}]^+ - [\text{Ch}]^+$, $[\text{Cl}]^- - [\text{Cl}]^-$, and $[\text{Ch}]^+ - [\text{Cl}]^-$ and (b) EG-EG, $[\text{Ch}]^+ - \text{EG}$, and $[\text{Cl}]^- - \text{EG}$ pairs in ethaline at 303 K.	105
4B.6 Radial distribution functions corresponding to (a) $\text{HO}_{[\text{Ch}]^+} - [\text{Cl}]^-$ and $\text{HO}_{\text{EG}} - [\text{Cl}]^-$ (b) $\text{N}_{[\text{Ch}]^+} - [\text{Cl}]^-$ and $\text{N}_{[\text{Ch}]^+} - \text{O}_{\text{EG}}$ (c) $\text{HO}_{[\text{Ch}]^+} - \text{O}_{\text{EG}}$ and $\text{HO}_{\text{EG}} - \text{O}_{[\text{Ch}]^+}$, and (d) $\text{HO}_{\text{EG}} - \text{O}_{\text{EG}}$ and $\text{O}_{\text{EG}} - \text{O}_{\text{EG}}$ atomic pairs in ethaline at 303 K. Here $\text{HO}_{[\text{Ch}]^+}$, $\text{O}_{[\text{Ch}]^+}$, and $\text{N}_{[\text{Ch}]^+}$ are the hydroxyl hydrogen, oxygen, and nitrogen atoms of choline cation, respectively. HO_{EG} and O_{EG} are hydroxyl hydrogen and oxygen atoms of ethylene glycol, respectively.	107
4B.7 Molecular representation of the frequently observed arrangement of $[\text{Ch}]^+$, $[\text{Cl}]^-$, and EG species in bulk ethaline at 303 K. Here, nitrogen, oxygen, carbon, and hydrogen atoms of $[\text{Ch}]^+$ and EG are shown as blue, red, cyan and white spheres, respectively. $[\text{Cl}]^-$ anions are rendered as green spheres. The red dashed lines represent prominent interactions present in the system.	109

4B.8 Radial-angular distribution functions (RADFs) for all the key hydrogen bonding interactions present in ethaline at 303 K. Note that the colors in the panel correspond to different scale for each plots.	110
4B.9 Spatial distribution functions around central [Ch] ⁺ in ethaline at 303 K. Here solid green and transparent pink isosurfaces represent [Cl] ⁻ and oxygen atoms of EG respectively. The isovalues (in nm ⁻³) chosen for rendering these surfaces around central cation for the oxygen of EG and [Cl] ⁻ are 6.2 and 4.6, respectively.	112
4B.11 Spatial distribution functions around central EG having (a) <i>gauche</i> and (b) <i>trans</i> conformations in ethaline at 303 K. Here, solid green isosurface represents [Cl] ⁻ . Solid red and transparent blue isosurfaces represent oxygen and nitrogen atoms of [Ch] ⁺ , respectively. Isovalues (in nm ⁻³) chosen for rendering these isosurfaces for chloride ion, oxygen and nitrogen atoms of the cation around <i>gauche</i> EG are 7.6, 3.15 and 5.26 and those around <i>trans</i> EG are 6.0, 3.02 and 4.05, respectively. . .	113
5.1 Comparison of simulated and experimental densities, ρ , for whole composition range of ethaline-water mixture at 303 K. The deviation in the simulated and experimental densities were found in the range 1.7-2.1 %.	118
5.2 (a) Simulated total X-ray scattering structure function, S(q), for all the ethaline-water mixtures investigated in present work. (b) Variation of reciprocal space length, q, and corresponding real space distance, D (=2 π /q), for the first principal peak observed in total S(q), as a function of increasing hydration level. The data for pure ethaline is taken form Chapter 4A.	118
5.3 Species-wise deconstructed partial X-ray scattering structure functions, S(q)s, for (a) 0.5-w (14 mol%), (b) 1-w (25 mol%), (c) 2-w (40 mol%), and (d) 5-w (62.5 mol%) systems of ethaline-water mixture.	119
5.4 Variation of atomic pair correlation functions, g(r)s, as a function of increasing hydration level between [Cl] ⁻ ion and hydroxyl hydrogen of (a) [Ch] ⁺ (b) EG and (c) water for all ethaline-water mixtures.	121

5.5	Coordination numbers for hydroxyl group of $[\text{Ch}]^+$, hydroxyl group of EG and hydroxyl group of water around $[\text{Cl}]^-$ anion for all the ethaline-water mixtures at 303 K.	121
5.6	Molecular representation of hydration shell of water around $[\text{Cl}]^-$ species of ethaline as a function of increasing hydration level.	122
5.7	Center-of-mass (COM) radial distribution functions, $g(r)$ s, for all self and cross correlation pairs present in ethaline-water mixtures.	123
5.8	Composition dependence of coordination numbers for all the COM RDFs shown in Fig. 5.7.	124
5.9	Isodensity surfaces around central choline cation for ethaline-water mixtures, precisely (a) 0.5-w, (b) 2-w, (c) 10-w and (d) 20-w. Here the transparent red isosurface represents water, transparent orange isosurface represents EG and solid green represents $[\text{Cl}]^-$	124
5.10	Atomic radial distribution function, $g(r)$, between nitrogen atom of $[\text{Ch}]^+$ and (a) oxygen atom of water, (b) oxygen atom of EG, and (c) $[\text{Cl}]^-$, respectively, at different hydration levels.	125
5.11	Variation of radial distribution function, $g(r)$, for atomic pair $\text{HO}_{\text{EG}}-\text{O}_{\text{EG}}$ as a function of increasing hydration level.	126
5.12	Equilibrium simulation cell snapshots of ethaline-water mixtures depicting the segregation of EG species in the (a) 0.5-w, (b) 2-w, (c) 10-w, and (d) 20-w systems. Here the cyan red isosurface represents the SOL and EG species respectively.	126
5.13	Radial Angular Distribution Functions, $g(r, \theta)$, for ethaline-water systems at different water concentrations. Here the angle shown on the ordinate axis corresponds to hydrogen-donor-acceptor, such that the probability below 30° belong to intermolecular interactions and those from $30 - 60^\circ$ are intramolecular.	127
A.1	Molecular structures defining the atom type for (a) acetamide (b) $\text{Li}^+/\text{ClO}_4^-$ and (c) propionamide.	136
A.2	Chemical structures defining the atom type labels for (a) choline, and (b) urea.	139

List of Tables

4A.1	Partial charges (q in $ e $ unit) and non-bonded LJ parameters (σ in nm and ϵ in $kJ mol^{-1}$) for ethylene glycol used in the simulation.	86
4A.2	Parameters defining the bond potential energy functions for ethylene glycol system. The units of r_0 and k_r are in nm and $kJ mol^{-1}nm^{-2}$, respectively. Kindly note that these parameters are taken in its original form from CGenFF.[90–93]	87
4A.3	Parameters defining the angle potential energy functions for ethylene glycol used in the simulation. The units for θ_0 , k_θ , r_{ub0} , and k_{ub} are <i>degrees</i> , $kJ mol^{-1}rad^{-2}$, nm , and $kJ mol^{-1}nm^{-2}$, respectively. Kindly note that these parameters are taken in its original form from CGenFF.[90–93]	87
4A.4	Parameters defining the dihedral potential energy functions for ethylene glycol used in the simulation. The units for δ and k_ϕ are <i>degrees</i> and $kJ mol^{-1}$, respectively.	88
4A.5	Simulated bulk density, isothermal compressibility, thermal expansion coefficient, and self-diffusion coefficient of pure ethylene glycol at 298 K and their comparison with corresponding experimental values.	89
4A.6	Positions (in nm) of first maximum and minimum in total and only inter-molecular RDF pairs in pure ethylene glycol liquid and corresponding coordination number at 298 K.	91
4A.7	Fitting parameters used to fit hydrogen bond autocorrelation function for intermolecular hydrogen bond interaction present in pure ethylene glycol system at all the three temperatures and its respective average lifetime, $\langle\tau\rangle$	96
4A.8	Comparison of simulated and experimental self-diffusion coefficient (D) of ethylene glycol (in $10^{-6} cm^2 s^{-1}$) for pure as well as aqueous mixtures of ethylene glycol.	99

4B.1	Positions of first minimum in different RDF pairs and their corresponding coordination number in ethaline at 303 K.	108
5.1	Compositions of ethaline-water mixtures investigated in the present work.	117
5.2	Nearest neighbour peak position, r_{min} (in nm) and the corresponding coordination number for atomic pairs $N_{[Ch]^+-O_{WAT}}$, $N_{[Ch]^+-O_{EG}}$ and $[Cl]^- - N_{[Ch]^+}$	122
A.1	Comparison of experimental and simulated densities for the alkylamide+ Li^+ / ClO_4^- systems.[43]	134
A.2	Comparison of simulated and experimental densities, ρ in $g\ cm^{-3}$ for pure as well as aqueous mixtures of ethylene glycol. The experimental data has been taken from literature.[210]	134
A.3	Physical properties for pure ethylene glycol at 298 K and 1 bar calculated using various FFs reported in the literature and its comparison with present work.	135
A.4	Comparison of experimental and simulated densities, ρ , of ethaline for temperature range 303–343 K. The experimental data has been taken from Yadav et al.[41]	135
A.5	Parameters used for rigid SPC/E water model.	136
A.6	Partial charges in electron charge unit and Lennard-Jones parameters (σ in nm and ϵ in $kJ\ mol^{-1}$) for acetamide atom types as labeled in Fig. A.1(a).	137
A.7	Partial charges in electron charge unit and Lennard-Jones parameters (σ in nm and ϵ in $kJ\ mol^{-1}$) for propionamide atom types as labeled in Fig. A.1(c).	137
A.8	Partial charges in electron charge unit and Lennard-Jones parameters (σ in nm and ϵ in $kJ\ mol^{-1}$) for lithium perchlorate atom types as labeled in Fig. A.1.	137
A.9	Parameters defining the bond and angle potential energies for acetamide, perchlorate and propionamide. The units for r , k_r , θ , k_θ , r_{ub} , k_{ub} are nm, $kJ\ mol^{-1}\ nm^{-2}$, degrees, $kJ\ mol^{-1}\ rad^{-2}$, nm and $kJ\ mol^{-1}\ nm^{-2}$ respectively.	138

A.10 Parameters defining the dihedral angle potential for acetamide and propionamide.	139
A.11 Partial charges (q) in electron charge unit and non-bonded (Lennard-Jones) force field parameters (σ in nm and ϵ in $kJ mol^{-1}$) for choline cation and chloride anion used in the simulation. The atom type labelling is according to the Fig. A.2(a).	140
A.12 Bonded force field parameters defining the bond and angle potential energies for choline cation used in the simulation. The units for r , k_r , θ , k_θ , r_{ub} , k_{ub} are nm , $kJ mol^{-1} nm^{-2}$, degrees, $kJ mol^{-1} rad^{-2}$, nm and $kJ mol^{-1} nm^{-2}$ respectively.	140
A.13 Parameters defining the dihedral angle potential for choline cation used in the simulation. The units for δ , k_ϕ , ω_0 , and k_ω are degrees, $kJ mol^{-1}$, degrees, and $kJ mol^{-1} rad^{-2}$ respectively.	141
A.14 Partial charges in electron charge unit and Lennard-Jones parameters (σ in nm and ϵ in $kJ mol^{-1}$) for urea as labeled in Fig. A.2(b).	141
A.15 Bonded force field parameters defining the bond and angle potential energies for urea used in the simulation. The units for r , k_r , θ , k_θ , r_{ub} , k_{ub} are nm , $kJ mol^{-1} nm^{-2}$, degrees, $kJ mol^{-1} rad^{-2}$, nm and $kJ mol^{-1} nm^{-2}$ respectively.	141
A.16 Parameters defining the dihedral angle potential for urea used in the simulation. The units for δ , k_ϕ , ω_0 , and k_ω are degrees, $kJ mol^{-1}$, degrees, and $kJ mol^{-1} rad^{-2}$ respectively.	142
A.17 Energy comparison between different residues of acetamide+Li ⁺ /ClO ₄ ⁻ system at various temperatures. Only real-space part of the electrostatic interaction energy is given here. These energies include non-bonded interactions which have been calculated by using the trajectories of final production run.	142
A.18 Temperature dependence of coordination number for different pairs in acetamide+Li ⁺ /ClO ₄ ⁻ system.	143
A.19 Temperature dependence of first maximum and minimum of RDFs corresponding to various pairs of species for both system.	144