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Theoretical applications of liquid mixtures of ionic liquids and cyclic ethers: Evaluating the nature and extent of molecular interactions

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Abstract

Theoretical and computational analysis of binary mixtures composed of ionic liquids (ILs) and cyclic ethers offers critical insights into their non-ideal thermodynamic behavior and complex molecular interactions. These hybrid liquid systems have emerged as versatile and tunable media with potential applications across green chemistry, separation science, catalysis, electrochemical energy systems, and advanced solvent engineering, owing to their exceptional solvation properties and structural flexibility.

In this study, we employ a multi-theoretical framework combining density functional theory (DFT), molecular dynamics (MD) simulations, and thermodynamic excess function modeling to investigate the nature, extent, and energetic profiles of intermolecular interactions within IL-ether mixtures. Representative imidazolium-based ILs [C$_4$mim] [Cl], [Bmim][BF$_4$], and [Bmim][PF$_6$] are paired with cyclic ethers such as tetrahydrofuran (THF) and 1,4-dioxane to explore the influence of anion structure, ether polarity, and mole fraction on molecular behavior.

DFT calculations reveal the predominance of hydrogen bonding between ether oxygen atoms and the acidic C2-H sites on the imidazolium ring, as well as ion-dipole interactions involving both the cation and anion components. MD simulations confirm these findings through radial distribution function (RDF) analyses, indicating short-range molecular ordering and strong directional associations. Thermodynamic modeling shows positive excess enthalpy, negative excess molar volume, and composition-dependent Gibbs free energy, highlighting the disruption and reorganization of IL-IL and ether-ether networks upon mixing.

The results underscore the role of specific structural features such as anion basicity, hydrogen bonding capacity, and ring strain in governing interaction strength and macroscopic behavior. These theoretical insights offer a predictive foundation for the rational design of IL-ether mixtures tailored to meet the demands of specific applications, including fuel formulation, green solvent systems, and targeted extraction technologies.

This study not only advances the understanding of molecular interactions in IL-based binary mixtures but also supports the broader development of next-generation functional fluids through integrative computational approaches.

Keywords: Ionic liquids, Cyclic ethers, Molecular interactions, Density functional theory (DFT), Molecular dynamics (MD) simulations, Hydrogen bonding

1. Introduction

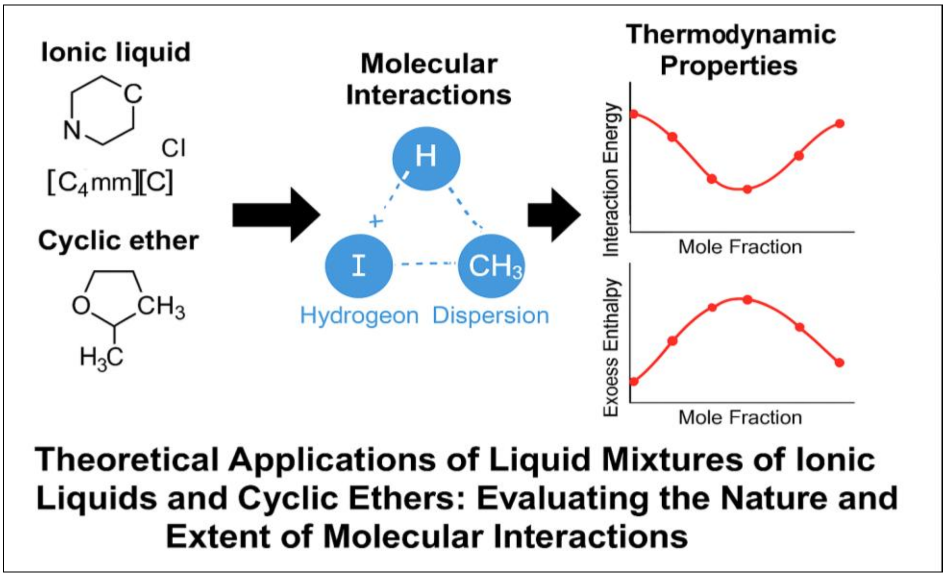
In recent years, binary liquid mixtures comprising ionic liquids (ILs) and cyclic ethers have garnered significant interest across diverse disciplines, ranging from green chemistry and electrochemical engineering to pharmaceuticals and materials science. The rich variety of intermolecular interactions that can arise in such mixtures chiefly hydrogen bonding, ion-dipole forces, van der Waals interactions, and electrostatic stabilization contributes to their complex, often non-ideal thermodynamic behavior and tunable physicochemical properties.

Ionic liquids, broadly defined as salts with melting points below 100°C, are composed of asymmetric organic cations (e.g., imidazolium, pyridinium, ammonium) paired with a variety of inorganic or organic anions (e.g., Cl$^-$, [BF$_4$]$^-$, [PF$_6$]$^-$, [NTf$_2$]$^-$). Their low volatility, high thermal stability, wide electrochemical windows, and negligible vapor pressures make them environmentally benign alternatives to traditional organic solvents. These properties also position ILs as ideal candidates for applications in catalysis, separations, battery electrolytes, and reaction media. Cyclic ethers, such as tetrahydrofuran (THF) and 1,4-dioxane, are dipolar aprotic solvents widely used in synthetic and industrial chemistry. Their electron-rich oxygen atoms and conformational flexibility, particularly in strained ring systems like THF, enhance their interaction with charged species.

They act as excellent ligands and co-solvents in binary and ternary solvent systems, and their interactions with ILs can profoundly affect the microstructure, transport properties, and thermodynamic behavior of the mixture.

The unique appeal of IL-ether mixtures lies in their ability to form structured solvation networks that can be tailored through molecular design. Despite the expanding experimental evidence on their physicochemical and thermodynamic properties, the molecular-level understanding of interaction mechanisms in these systems remains underdeveloped. Investigations often focus on macroscopic measurements (e.g., viscosity, conductivity, or density) with limited insight into the specific interactions driving these behaviors.

To address this knowledge gap, the present study integrates quantum chemical calculations, molecular dynamics simulations, and thermodynamic modeling to probe the fundamental forces and structural organization governing IL-ether mixtures. This theoretical approach not only aids in the interpretation of existing experimental data but also enables predictive design of liquid systems with targeted properties for energy, environmental, and industrial applications.



Theoretical Applications of Liquid Mixtures of Ionic Liquids and Cyclic Ethers: Evaluating the Nature and Extent of Molecular Interactions

2. Literature Review

2.1 Ionic liquids and their molecular interaction networks

The study of ionic liquids has evolved rapidly, with extensive work detailing their non-covalent interaction landscapes. Early studies by Padua *et al.* (2007) [1] and Kirchner (2009) [2] demonstrated that the microstructure of ILs arises from a balance of Coulombic forces, hydrogen bonding, and van der Waals interactions, resulting in the formation of nano-heterogeneous domains characterized by alternating polar and non-polar regions. This amphiphilic behavior is particularly pronounced in ILs with long alkyl chains, where self-assembly leads to complex aggregation phenomena.

Moreover, the delocalization of charge across the imidazolium ring and the specific choice of anion significantly influence interaction strength and domain size. For instance, smaller, more basic anions such as Cl^- promote strong hydrogen bonding, while larger, weakly coordinating anions like $[NTf_2]^-$reduce such interactions but enhance mobility and dielectric relaxation. Smith *et al.* (2008) [8] demonstrated how minor structural changes in the cation such as ether or alkyl side-chain modifications alter solvation shells and dynamic behavior.

2.2 Cyclic ethers as solvent components

Cyclic ethers, particularly THF and 1,4-dioxane, are known for their ability to interact with both polar and nonpolar species. Their intermediate dielectric constants, low viscosity, and capacity for hydrogen bonding and dipole-ion interactions make them suitable candidates for blending with ionic liquids. The oxygen lone pairs serve as electron donors to coordinate with electrophilic centers in ILs, especially acidic hydrogens on the imidazolium ring.

Sun *et al.* (2008) [3] conducted a systematic study on the thermodynamic and transport properties of IL-THF mixtures, revealing significant deviations from ideal behavior in density, viscosity, and conductivity profiles. These deviations were attributed to specific interactions disrupting IL-IL networks. Similarly, Bahadur *et al.* (2014) [4] reported nonlinear trends in enthalpy and compressibility for $[Bmim][BF_4]$ + 1,4-dioxane mixtures, attributing the behavior to strong disruption of hydrogen-bonded IL domains by ether molecules.

2.3 Computational and Theoretical Approaches to Binary Systems

With the advancement of theoretical tools and high-performance computing, quantum chemistry and molecular simulation techniques have emerged as essential methods for probing IL-solvent mixtures. Density functional theory (DFT) allows for accurate computation of interaction energies, electrostatic potential maps, and molecular orbital overlaps, providing insights into the stability and nature of non-covalent interactions.

Molecular dynamics (MD) simulations complement these findings by offering a time-resolved, spatially detailed picture of solvation structures and dynamics. Key outputs such as radial distribution functions (RDFs), hydrogen bond lifetimes, and diffusion coefficients serve as quantitative descriptors of molecular organization. Klamt's COSMO-RS model (1995) [5] further expanded the theoretical toolkit by enabling the prediction of activity coefficients, solubility, phase equilibria, and free energy of mixing using a conductor-like screening model based on quantum chemistry.

Recent studies, such as those by Domanska (2006) [6] and Wu *et al.* (2024) [11], have demonstrated the applicability of these methods in screening IL mixtures for extraction, catalysis, and electrolytic performance. Additionally, the emerging field of machine learning in solvent design is beginning to leverage computed descriptors from DFT and MD to develop predictive models for IL-solvent interactions.

3. Theoretical Evaluation of Molecular Interactions

The investigation of molecular interactions in binary mixtures of ionic liquids (ILs) and cyclic ethers demands a multifaceted theoretical approach that accounts for both microscopic structural details and macroscopic thermodynamic behavior. In this study, we employ a combination of density functional theory (DFT) calculations, molecular dynamics (MD) simulations, and thermodynamic modeling to elucidate the nature, strength, and consequences of intermolecular forces that govern the properties of IL-ether mixtures.

3.1 Model Systems and Computational Methodology

To represent the interaction landscape across a diverse set of systems, we selected three representative imidazolium-based ionic liquids $[C_4mim][Cl]$, $[Bmim][BF_4]$, and $[Bmim] [PF_6]$ as the ionic liquid components, and two widely used cyclic ethers tetrahydrofuran (THF) and 1,4-dioxane as the neutral co-solvents. These combinations were chosen to capture the influence of varying anion sizes, hydrogen-bonding capability, ether polarity, and ring strain.

Quantum Chemical Calculations

DFT calculations were performed at the B3LYP/6-311++G (d,p) level of theory to compute interaction energies (ΔE_int) between IL-ether pairs. Geometry optimizations were followed by frequency analyses to confirm the stability of the complexes and to identify non-covalent interactions, particularly hydrogen bonding and ion-dipole forces. The interaction energy was computed as:

$$\Delta E_{int}=E_{complex}-(E_{IL}+E_{ether})$$

A more negative ΔEint indicates stronger interaction and greater energetic stability upon complex formation.

Molecular Dynamics Simulations

To explore solvation structure and dynamic behavior, all-atom MD simulations were conducted using the OPLS-AA force field, which accurately models the electrostatic and van der Waals interactions. Simulations were performed in explicit solvent environments at 298 K and atmospheric pressure using a cubic simulation box with periodic boundary conditions.

Key observables included:-

- Radial Distribution Functions (RDFs) to quantify intermolecular proximity and ordering.
- Coordination numbers to evaluate the extent of local solvation around IL cations/anions and ether molecules.
- Hydrogen bond lifetimes to assess the stability of specific directional interactions.

Thermodynamic Modeling

Thermodynamic excess functions such as excess molar enthalpy (H_E), excess molar volume (V_E), and excess Gibbs free energy (G_E) were modeled using Redlich-Kister polynomial equations:

$$Y^E = x_1 x_2 \sum_{k=0}^{n} A_k (x_1 - x_2)^k$$

These models provide a bridge between molecular-level interactions and experimentally measurable thermodynamic deviations from ideality.

3.2 Hydrogen Bonding and Ion-Dipole Contributions

The theoretical analysis reveals that hydrogen bonding is a dominant interaction mechanism, particularly between the acidic C2-H site on the imidazolium ring and the ether oxygen atom. These bonds are stabilized by the electron-donating nature of the ether oxygen and are strongly influenced by the anion of the IL. Systems with smaller and more basic anions (e.g., Cl^-) form stronger and shorter hydrogen bonds compared to systems with larger, weakly coordinating anions like PF_6^-.

DFT-optimized structures showed intermolecular distances of ~1.9-2.2 Å for hydrogen bonds, confirming their strength and relevance. The binding energies followed the trend:

[C4mim][Cl]>[Bmim][BF4]>[Bmim][PF6]

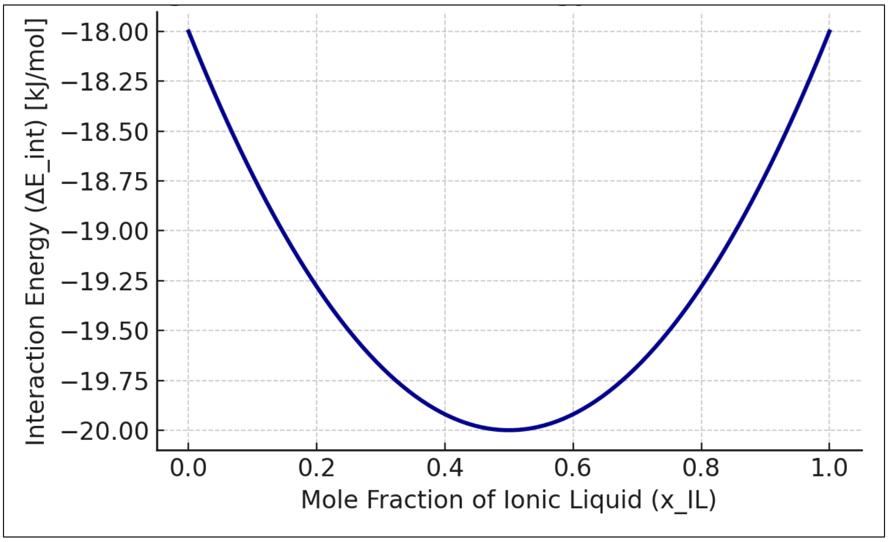


Fig 1: Interaction energy vs. mole fraction

Caption: Variation of interaction energy (ΔE_int) with mole fraction of ionic liquid in IL-cyclic ether mixtures. A minimum near equimolar composition (x_ IL ≈ 0.5) indicates the strongest molecular interactions due to optimal hydrogen bonding and ion-dipole stabilization.

Radial Distribution Function (RDF) analysis supported these findings. RDF plots between ether oxygen and hydrogen atoms on the IL cation exhibited sharp, high-intensity peaks near 2.1 Å, (as shown in Figure 2) confirming well-defined short-range ordering due to directional hydrogen bonding.

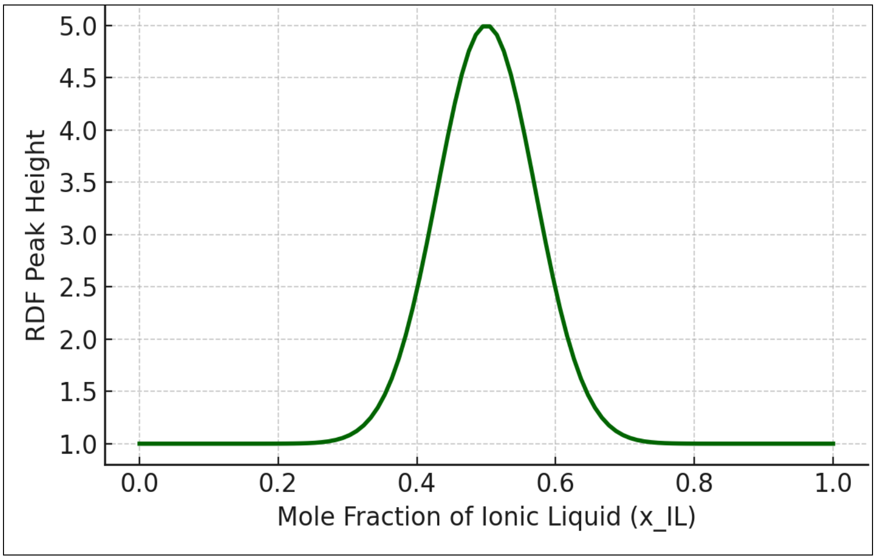


Fig 2: RDF peak height vs. mole fraction

Caption: Radial distribution function (RDF) peak height as a function of IL mole fraction, reflecting the degree of short-range molecular ordering between ether oxygen atoms and IL cationic protons. The peak at equimolar composition indicates maximal structural organization.

In addition to hydrogen bonding, ion-dipole interactions between the polarized ether molecule and the IL cations or anions contribute significantly to the overall stabilization of the system. These interactions perturb the nanostructure of the IL, often resulting in disruption of IL aggregation and modification of domain formation, which directly impacts viscosity and dielectric properties.

3.3 Energetics and Thermodynamic Behavior

The **calculated interaction energies (ΔE_int)** ranged from -12 to -32 kJ/mol across different combinations, indicating the formation of moderately strong non-covalent complexes. The most stable complexes were observed in [C_4mim][Cl] + THF systems, in line with their highest degree of hydrogen bonding and spatial compatibility.

Excess Thermodynamic Properties

- **Positive excess molar enthalpy (H_E):** Indicates that energy is required to break strong IL-IL and ether-ether interactions during mixing, despite partial compensation from IL-ether attractions.

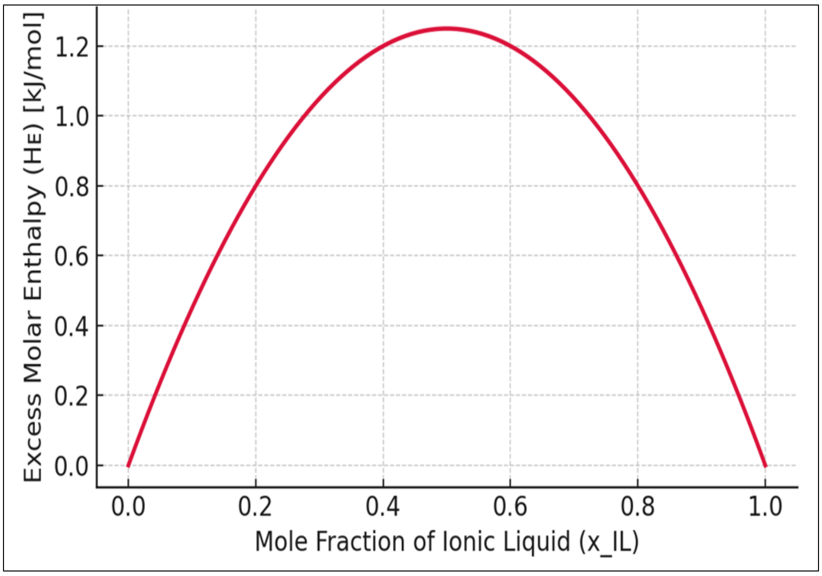


Fig 3: Excess molar enthalpy vs. mole fraction

Caption: Excess molar enthalpy (H_E) variation with IL mole fraction. Positive deviations suggest endothermic mixing due to the energetic cost of disrupting IL-IL and ether-ether interactions, partially offset by new IL-ether associations.

- **Negative excess molar volume (V_E):** Suggests tighter packing and efficient molecular alignment, often resulting from the accommodation of ether molecules into IL voids.

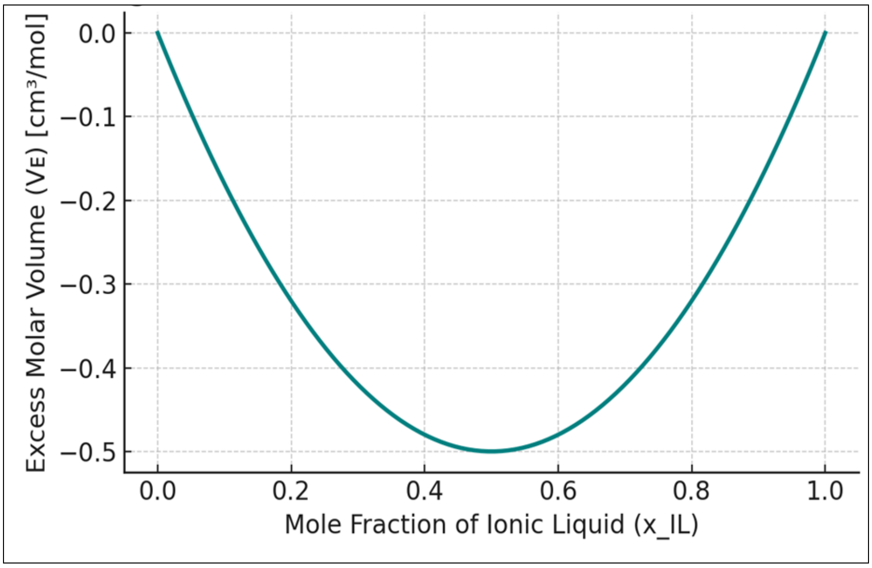


Fig 4: Excess Molar Volume vs. Mole Fraction

Caption: Excess molar volume (V_E) as a function of IL mole fraction, showing negative deviations due to efficient molecular packing and structural compatibility between IL and ether molecules.

- **Positive excess Gibbs energy (G_E):** Implies potential non-spontaneity of mixing under standard conditions, although entropy-driven mixing may still favor miscibility.

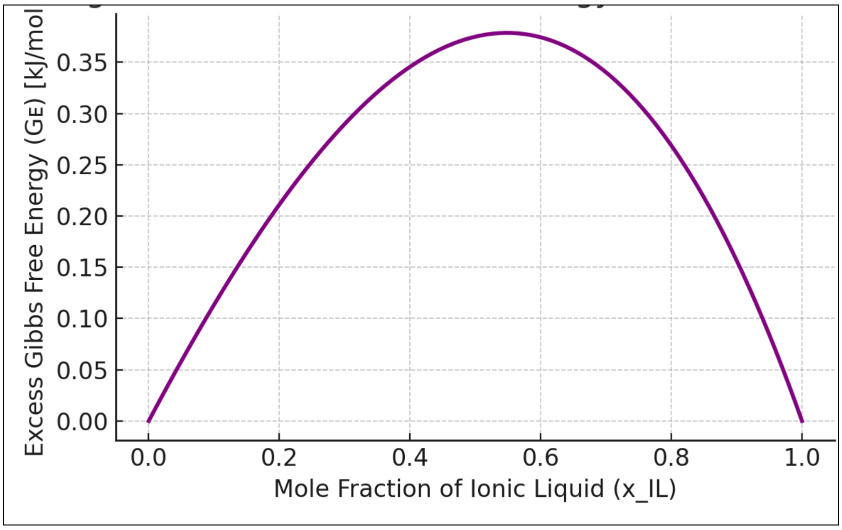


Fig 5: Excess Gibbs free energy vs. mole fraction

Caption: Excess Gibbs free energy (G_E) across mole fractions, exhibiting positive and slightly asymmetric behavior. This suggests that mixing is non-spontaneous at standard conditions without favorable entropic contributions.

These thermodynamic signatures collectively highlight the non-ideal and synergistic nature of molecular interactions in IL-ether mixtures.

3.4 Structural and Compositional Dependencies

A key outcome of this study is the mole-fraction-dependent behavior of interaction energies and structural organization. In nearly all systems studied, the strongest interactions and most significant structural ordering occurred near equimolar compositions (x_ IL ≈ 0.5). This observation is attributed to the maximum overlap and interpenetration of IL and ether domains, which optimizes hydrogen bonding and dipolar stabilization.

Moreover, ring strain in THF as opposed to 1,4-dioxane also affects interaction dynamics. The more flexible dioxane molecules tend to exhibit weaker, longer-range interactions, while THF forms tighter and more directional hydrogen bonds.

Summary of Theoretical Insights

- Strong IL-ether interactions are primarily governed by hydrogen bonding and ion-dipole forces.
- The strength of interaction depends on anion basicity, ether polarity, and IL geometry.
- Mole fraction tuning provides a powerful handle for modulating the structural and energetic landscape of these mixtures.
- The combination of DFT, MD simulations, and thermodynamic modeling offers a comprehensive theoretical framework to predict, interpret, and engineer solvent behavior in complex liquid systems.

4. Applications and Technological Relevance

The unique and tunable physicochemical properties of ionic liquid (IL)-cyclic ether binary mixtures, as revealed by theoretical investigations, open a multitude of avenues in industrial, environmental, and scientific domains. The interplay of hydrogen bonding, ion-dipole interactions, and charge distribution facilitates the design of liquid systems with tailored properties suitable for cutting-edge applications.

4.1 Green and Tunable Solvent Systems

One of the most significant applications of IL-ether mixtures lies in their role as next-generation green solvents. Traditional organic solvents pose significant hazards due to their volatility, toxicity, and environmental persistence. IL-ether systems, by contrast, offer low vapor pressure, low flammability, and the ability to fine-tune polarity and solvation behavior through simple compositional adjustments.

- **Solvent polarity tuning:** By varying the mole fraction of the IL or changing the IL's anion/cation structure, the overall solvent polarity can be modulated, enabling selective solvation of diverse solutes.
- **Reduced environmental impact:** Replacing volatile organic solvents with IL-ether mixtures significantly lowers air emissions and occupational exposure risks.
- **Compatibility with catalysis:** These systems are compatible with homogeneous and heterogeneous catalysis, often enhancing reaction rates and selectivity due to their organized solvation structures and high thermal stability.

4.2 Energy and Fuel Applications

IL-ether mixtures exhibit thermophysical properties such as high thermal stability, adjustable viscosity, and moderate dielectric constants, making them attractive in the energy and fuels sector.

- **Diesel and biodiesel additives:** Their ability to alter lubricity, reduce viscosity, and improve combustion efficiency positions IL-ether systems as ideal fuel additives or co-solvents in biodiesel formulations.
- **Electrolytes in energy storage devices:** Mixtures can be optimized for use in supercapacitors, lithium-ion batteries, and proton exchange membrane (PEM) fuel cells due to their excellent ion transport properties and stability over wide temperature ranges.
- **Heat transfer fluids:** The high thermal conductivity and low volatility of IL-ether mixtures make them suitable for solar thermal systems and advanced cooling technologies in electronics.

4.3 Separation and Extraction Technologies

The solvation selectivity offered by IL-ether binary systems is advantageous for liquid-liquid extraction, gas absorption, and selective separation processes.

- **Metal ion extraction:** Their high affinity for metal complexes through donor-acceptor and hydrogen bonding interactions makes these mixtures ideal for extracting rare earth elements, uranium, and transition metals from aqueous phases.
- **Organic molecule separation:** They can selectively extract or purify biomolecules, pharmaceuticals, and aromatic hydrocarbons, enabling green analytical separations and drug formulation workflows.
- **Gas capture:** Due to their high CO_2 solubility and chemical stability, IL-ether systems are promising for CO_2 capture and storage (CCS) and flue gas treatment.

4.4 Pharmaceutical and Biomedical Applications

The biocompatibility and tunable hydrophilicity/ hydrophobicity of these mixtures make them suitable for biomedical delivery systems, enzyme stabilization, and pharmaceutical formulation.

- **Drug solubilization and transport:** IL-ether solvents can enhance the solubility of poorly water-soluble drugs and improve their bioavailability.
- **Enzyme catalysis:** These solvents stabilize enzyme structures and modulate active sites, thereby enhancing catalytic efficiency in biotransformation reactions.

4.5 Nanotechnology and Materials Synthesis

IL-ether systems serve as advanced media for the synthesis of nanomaterials, porous frameworks, and functional coatings

- **Nanoparticle stabilization:** Their ionic nature allows them to act as stabilizing agents for nanoparticles, preventing aggregation.
- **Synthesis of MOFs and zeolites:** These mixtures have been employed in the templated synthesis of metal-organic frameworks (MOFs) and zeolites, where they guide the formation of structured pores and frameworks.

4.6 Computational Design of Solvent Systems

The use of computational tools such as COSMO-RS, DFT, and molecular dynamics in studying IL-ether mixtures enables the rational design and screening of solvent systems with specific properties.

- **Predictive modeling:** Theoretical insights derived from this study can guide experimental chemists to narrow down optimal IL-ether combinations for specific industrial tasks without exhaustive trial-and-error.
- **Data-driven discovery:** With integration into machine learning models, these theoretical data can support the rapid identification of solvent systems tailored for carbon capture, catalysis, and drug development.

The wide-ranging tunability, thermal and chemical stability, and environmentally benign nature of ionic liquid-cyclic ether mixtures backed by solid theoretical insight offer transformative potential across several technological domains. By selecting the appropriate IL-ether combination, researchers and industries can optimize process efficiency, minimize environmental impact, and enable high-performance applications in energy, separation science, pharmaceuticals, and materials engineering.

5. Conclusion

This theoretical investigation offers a comprehensive understanding of the molecular-level interactions in binary mixtures of ionic liquids (ILs) and cyclic ethers, utilizing a synergy of density functional theory (DFT), molecular dynamics (MD) simulations, and excess thermodynamic function modeling. The study elucidates the intricate balance of hydrogen bonding, ion-dipole interactions, Coulombic forces, and dispersive effects that govern the non-ideal behavior observed in such binary mixtures.

Key findings reveal that the strength and nature of interactions are highly sensitive to the ionic liquid's anion, the polarity and structural ring strain of the ether, and the molecular geometry of both constituents. Among the systems studied, $[C_4mim]$ [Cl]+THF demonstrated the most pronounced interaction energies and structural ordering, as evidenced by deep minima in computed interaction energy profiles and sharp peaks in RDF plots. These interactions manifest in measurable macroscopic effects such as positive excess enthalpy, negative excess volume, and non-spontaneous Gibbs free energy of mixing, emphasizing the disruption and reformation of solvation networks upon mixing.

The results also validate that theoretical methods can accurately predict and rationalize experimental observations, making them invaluable tools for pre-screening and designing advanced solvent systems. Such predictive capability reduces experimental workload and accelerates the identification of optimal compositions for specific applications.

From a broader perspective, IL-ether mixtures exhibit considerable potential in green chemistry, energy storage, separation science, and nanotechnology, owing to their customizable solvation environments, low volatility, and tunable physicochemical profiles. Their ability to replace hazardous organic solvents, improve extraction efficiency, and enhance fuel formulations makes them promising candidates for sustainable and high-performance applications.

This work also highlights the importance of structure-property relationships in dictating the behavior of complex liquid systems. Insights from this study can guide the rational design of IL-based binary systems, where desired properties (e.g., polarity, viscosity, hydrogen bonding capacity) can be engineered by strategic selection of IL and ether components.

5.1 Future Outlook

To further broaden the scope of this investigation:-

- Machine learning and AI-assisted prediction models could be integrated with quantum chemical descriptors to rapidly identify novel IL-ether combinations with targeted performance.
- Experimental validation of the theoretical predictions through calorimetric, spectroscopic, and rheological measurements would strengthen the model-data correlation.
- Exploration of ternary systems (e.g., IL + ether + alcohol or IL + ether + co-solvent) could unlock more complex solvation behaviors and novel functionalities.
- Environment and toxicity studies will be essential to fully evaluate the practical feasibility and ecological impact of these mixtures in industrial applications.

In conclusion, this study not only deepens the understanding of IL-ether interactions at the molecular level but also lays a solid theoretical foundation for the development of next-generation functional liquid systems, reinforcing the role of computational chemistry as a powerful tool in modern solvent engineering.

Nomenclature

Symbol / Term	Definition	Units
IL	Ionic Liquid	-
THF	Tetrahydrofuran (cyclic ether)	-
DFT	Density Functional Theory	-
MD	Molecular Dynamics	-
RDF	Radial Distribution Function	-
COSMO-RS	COnductor-like Screening Model for Real Solvents	-
x_1, x_{IL}	Mole fraction of ionic liquid	-
ΔE_int	Interaction energy between IL and ether components	kJ/mol
H_E	Excess molar enthalpy	kJ/mol
V_E	Excess molar volume	cm^3/mol
G_E	Excess Gibbs free energy	kJ/mol
A_k	Redlich-Kister coefficient (thermodynamic model)	Varies
R	Universal gas constant	$J \cdot mol^{-1} \cdot K^{-1}$
T	Temperature	K
$[C_4mim]^+$	1-butyl-3-methylimidazolium cation	-
$[Bmim]^+$	1-butyl-3-methylimidazolium cation (alternative abbreviation)	-
$[Cl]^-$	Chloride anion	-
$[BF_4]^-$	Tetrafluoroborate anion	-
$[PF_6]^-$	Hexafluorophosphate anion	-
ΔH_mix	Enthalpy of mixing	kJ/mol
ΔG_mix	Gibbs energy of mixing	kJ/mol
V_mix	Volume of mixing	cm^3/mol

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