© January 2025 | IJIRT | Volume 11 Issue 8 | ISSN: 2349-6002

Applications of Binary Mixtures Containing Ionic Liquids and Cyclic Ethers

Mr Kuldeep Kumar Solanki[1], Dr Arpna[2], Dr Sunil Kumar Jangra[3]
[1]*Research Scholar, Department of Chemistry, Baba Mastnath University, Rohtak*
[2]*Assistant Professor, Department of Chemistry, Baba Mastnath University, Rohtak*
[3]*Assistant Professor, Department of Chemistry, AIJHM College, Rohtak*

Abstract: This paper provides a detailed overview of the applications of binary mixtures containing ionic liquids (ILs) and cyclic ethers. The unique properties of ILs, such as their negligible vapor pressure, high thermal stability, and tuneable solvation capabilities, make them ideal for various applications, especially when mixed with cyclic ethers. These binary mixtures have shown significant potential in areas including green chemistry, catalysis, electrochemistry, and materials science. The paper discusses the thermodynamic and transport properties of these mixtures, the effects of molecular interactions on their performance, and their practical applications, highlighting the synergistic effects of ILs and cyclic ethers in various industrial processes. A comprehensive review of previous research is provided to contextualize the findings and suggest future directions in this emerging field.

1. INTRODUCTION

1.1. Background

Ionic liquids (ILs) are salts in the liquid state that are composed entirely of ions. They have been the subject of extensive research due to their unique physicochemical properties, such as low volatility, high ionic conductivity, and wide electrochemical windows. Cyclic ethers, on the other hand, are a class of organic compounds characterized by an ether functional group within a ring structure. These compounds, including tetrahydrofuran (THF) and 1,4-dioxane, are known for their stability and ability to solubilize a wide range of substances.

1.2. Importance of Binary Mixtures

The combination of ILs with cyclic ethers in binary mixtures offers enhanced properties that are not achievable with the individual components. These mixtures are of particular interest in green chemistry and sustainable processes, where they are employed to reduce the environmental impact of chemical processes. The ability to tailor the properties of these mixtures by varying the composition and the specific IL or cyclic ether used opens up a broad range of applications.

1.3. Scope of the Paper

This paper aims to overview the applications of binary mixtures containing ILs and cyclic ethers, focusing on their role in various industrial processes. The discussion will include an overview of the thermodynamic and transport properties of these mixtures, the molecular interactions that govern their behaviour, and their practical applications. The paper will also provide a comprehensive review of existing literature, highlighting key findings and identifying areas for future research.

2. REVIEW OF PREVIOUS RESEARCH

2.1. Ionic Liquids: Properties and Applications

2.1.1. General Properties of ILs

Ionic liquids (ILs) are salts that are typically liquid at room temperature and possess unique properties compared to conventional liquids. Here are some of the general properties of ionic liquids:

1. Low Melting Points:
   - Ionic liquids have low melting points, often below 100°C or even at room temperature. This is due to the weak interactions between the ions, allowing them to remain in liquid form despite being composed of salts.
2. High Thermal Stability:
   - Many ionic liquids exhibit excellent thermal stability and can withstand high temperatures without decomposing, making them suitable for high-temperature applications.
3. Non-Volatility:
   - Unlike many organic solvents, ionic liquids have very low vapor pressures and do not evaporate

easily. This makes them non-volatile and reduces the risks associated with their use, such as inhalation exposure.

4. High Ionic Conductivity:

o Ionic liquids typically have good ionic conductivity, which makes them useful in electrochemical applications, such as batteries, capacitors, and fuel cells.

5. Wide Electrochemical Window:

o They often have a wide electrochemical stability window, meaning they can be used in a variety of electrochemical applications without decomposing.

6. Solvating Ability:

o Ionic liquids are often good solvents for a wide range of compounds, including both polar and nonpolar molecules. This makes them useful in chemical synthesis and as solvents in processes that involve various solutes.

7. Tuneable Properties:

o The properties of ionic liquids can be tailored by modifying the anions and cations used to create them. This allows for the design of ionic liquids with specific characteristics, such as varying viscosity, conductivity, and solvation properties.

8. Viscosity:

o Ionic liquids often have higher viscosities compared to conventional solvents. However, this can be adjusted by modifying the chemical structure of the ions involved.

9. Environmentally Friendly:

o Many ionic liquids are considered more environmentally friendly than traditional organic solvents because they are often non-toxic, non-flammable, and non-volatile. However, the environmental impact depends on the specific ionic liquid.

10. Non-Combustibility:

o Due to their non-volatile nature and high thermal stability, ionic liquids are often non-flammable, which makes them safer to handle compared to many organic solvents.

2.1.2. Applications of ILs

Ionic liquids (ILs) have found a wide range of applications across various fields due to their unique properties such as low volatility, high thermal stability, and tunability. Below are some key applications of ionic liquids:

1. Green Solvents in Chemical Processes

- Synthesis and Catalysis: ILs are used as solvents in organic synthesis and catalysis, especially for reactions that require high selectivity or unusual conditions (e.g., high temperature or pressure). They can serve as both solvents and catalysts, reducing the need for additional reagents.
- Green Chemistry: ILs are considered more environmentally friendly than traditional organic solvents due to their low volatility, non-flammability, and recyclability, helping to reduce hazardous emissions in chemical processes.

2. Electrochemical Applications

- Batteries and Supercapacitors: Ionic liquids are used in lithium-ion batteries, fuel cells, and supercapacitors as electrolytes due to their high ionic conductivity, wide electrochemical stability window, and non-volatility.
- Electroplating and Electrorefining: ILs provide a more efficient and less toxic alternative to traditional aqueous electrolytes in processes like electroplating and electrorefining.

3. Extraction and Separation Processes

- Metal Extraction and Recovery: ILs are increasingly used in the extraction of metals such as lithium, uranium, and rare earth elements from ores or waste materials. Their ability to dissolve a wide range of compounds makes them effective for selective extractions.
- Gas Absorption: Ionic liquids can selectively absorb gases such as CO_2, making them useful for applications in carbon capture and storage, or for separating gases in industrial processes.
- Liquid-Liquid Extraction: ILs can be used for selective extraction of organic compounds from aqueous solutions or vice versa, often used in pharmaceutical or chemical industries.

4. Pharmaceuticals and Biotechnology

- Drug Delivery Systems: Ionic liquids are used in the formulation of drug delivery systems due to their ability to dissolve hydrophobic drugs and enhance bioavailability.
- Protein and Enzyme Stabilization: Certain ILs help to stabilize proteins and enzymes, preserving their activity in processes like biosensing or in vitro diagnostic applications.
- Biocatalysis: Ionic liquids can be used as solvents for biocatalysts, improving the efficiency of enzyme-catalyzed reactions in pharmaceutical production and biofuel generation.

5. Lubricants and Coatings

- Lubricants: Ionic liquids are used as lubricants in machinery and equipment due to their high thermal stability, low volatility, and ability to reduce wear and tear in mechanical systems.
- Anti-corrosion Coatings: Ionic liquids can be applied as protective coatings in corrosive environments, particularly in industries like aerospace and marine engineering.

6. Polymer Processing

- Polymer Synthesis: ILs serve as solvents for the synthesis of polymers, providing a controlled environment that allows for the production of high-performance materials.
- Recycling Polymers: Ionic liquids are also used to dissolve and break down polymers in recycling processes, offering a more sustainable alternative to traditional methods.

7. Energy and Environmental Applications

- Solar Cells: Some ionic liquids are used as electrolytes or charge transport materials in dye-sensitized solar cells (DSSCs) and other types of solar cells.
- Carbon Capture: ILs are useful for capturing CO_2 from industrial emissions or even air, helping to mitigate climate change. Their tunable nature allows for optimization in capturing specific gases.
- Waste Treatment: Ionic liquids can be used in waste treatment, particularly for the selective removal of contaminants from water or other waste streams.

8. Food and Agriculture

- Food Processing: Ionic liquids have potential uses in food processing as solvents for flavor and fragrance extraction, or even as preservatives. They may also be used in the production of bio-based chemicals for food applications.
- Agricultural Applications: In agriculture, ionic liquids are used for pesticide formulations, herbicide delivery, and to improve the bioavailability of nutrients for plants.

9. Sensors and Detection Systems

- Chemical Sensors: ILs can be integrated into chemical sensors, such as gas sensors or biosensors, to detect specific chemicals in a variety of environments, including industrial settings and medical diagnostics.
- Sensors for Environmental Monitoring: They can also be used in environmental sensors for detecting pollutants or toxins in air, water, and soil.

10. Nanotechnology and Material Science

- Nanomaterial Synthesis: Ionic liquids are used as solvents or templates in the synthesis of nanoparticles, nanowires, and other nanomaterials, facilitating the production of novel materials for electronics, catalysis, and energy storage.
- Self-Assembly: Some ILs are involved in the self-assembly of nanostructures, which have applications in creating advanced materials with tailored properties.

11. Supercritical Fluid Extraction

- Solvent for Supercritical Fluids: ILs can be used as alternative solvents in supercritical fluid extraction (SFE) processes, which are typically used for extracting high-value compounds from natural sources such as essential oils, plant extracts, or natural flavors.

2.2. Cyclic Ethers: Properties and Applications

2.2.1. General Properties of Cyclic Ethers

Cyclic ethers are a class of organic compounds characterized by a cyclic structure in which oxygen atoms are part of the ring. The general properties of cyclic ethers include:

1. Molecular Structure

- Ring Structure: Cyclic ethers consist of a ring formed by oxygen atoms bonded to carbon atoms. The ring can vary in size, with common sizes being three-membered (epoxides), four-membered (tetrahydrofuran), or larger rings.
- Heterocyclic: The presence of oxygen in the ring makes them heterocyclic compounds, as opposed to cyclic hydrocarbons like cycloalkanes.

2. Polarity

- Moderate Polarity: The oxygen atom in cyclic ethers is more electronegative than carbon, making the ether functional group polar. However, the overall polarity depends on the size of the ring and the substituents attached to it.
- Solubility: Smaller cyclic ethers, like tetrahydrofuran (THF), are often polar and can dissolve in water and many organic solvents. Larger cyclic ethers might be less soluble in water but can dissolve in non-polar solvents.

3. Boiling and Melting Points

- Moderate Boiling Points: Cyclic ethers typically have moderate boiling points compared to other organic compounds due to the polar nature of the oxygen atom and the ether functional group. The boiling point increases with ring size.
- Freezing Points: The freezing points of cyclic ethers vary based on their size and structure. Smaller cyclic ethers tend to have lower freezing points.

4. Reactivity

- Nucleophilic Substitution: The oxygen atom in cyclic ethers can act as a nucleophile in certain reactions, such as in nucleophilic substitution or ring-opening reactions.
- Ring-Opening Reactions: Cyclic ethers, especially epoxides (three-membered rings), can undergo nucleophilic attack, causing the opening of the ring to form larger compounds. This is often seen in polymerization or in reactions involving strong nucleophiles.
- Reactivity with Acids and Bases: Cyclic ethers can react with acids or bases to undergo protonation or deprotonation. In some cases, the reactivity with acids can cause ring-opening.

5. Stability

- Stable in Mild Conditions: Most cyclic ethers, especially those with larger rings (e.g., THF), are relatively stable under normal conditions. However, smaller cyclic ethers (e.g., epoxides) may be more reactive and sensitive to certain conditions.
- Strain in Small Rings: Smaller cyclic ethers, such as epoxides (three-membered rings), experience significant ring strain due to the bond angles being forced to deviate from the ideal tetrahedral angle (109.5°). This strain makes them more reactive and prone to ring-opening reactions.

6. Chemical Bonding

- Ether Bonding: Like other ethers, the oxygen atom in cyclic ethers is bonded to two carbon atoms via single bonds. The oxygen-carbon bonds are relatively polar due to the electronegativity difference between oxygen and carbon.
- Electron Donation: The oxygen atom in cyclic ethers can act as an electron donor in reactions, particularly when it is in contact with electrophilic centers.

7. Solubility

- Solvent Properties: Cyclic ethers are often used as solvents, particularly for polar or ionic compounds. For instance, tetrahydrofuran (THF) is a common solvent in organic chemistry due to its ability to dissolve a wide range of compounds.
- Water Solubility: The solubility in water varies based on ring size and functional groups. Smaller cyclic ethers are generally more soluble in water than larger ones, although none are highly soluble in water compared to alcohols.

8. Use as Solvents

- Polar Solvents: Many cyclic ethers, such as tetrahydrofuran (THF) and dioxane, are used as solvents in a variety of chemical reactions, particularly those involving polar reagents or organic compounds.

- Non-Protic Solvents: They are often used as non-protic solvents in reactions that require the absence of hydrogen bonding (as in reactions involving strong bases or nucleophiles).

9. Toxicity and Safety

- Toxicity: Some cyclic ethers, especially THF and dioxane, can be toxic and potentially carcinogenic. Proper handling, ventilation, and safety precautions are necessary when working with these compounds.
- Flammability: Many cyclic ethers are flammable, and their vapours can form explosive mixtures with air, especially when exposed to heat or sparks.

10. Examples of Cyclic Ethers

- Tetrahydrofuran (THF): A common solvent with a four-membered ring structure. THF is highly polar, relatively stable, and widely used in organic synthesis and polymer chemistry.
- Dioxane: A six-membered cyclic ether, commonly used as a solvent in various laboratory and industrial applications.
- Epoxides: Three-membered cyclic ethers that are highly reactive and used in a wide range of chemical reactions, including polymerization and synthesis of other compounds.

2.2.2. Applications of Cyclic Ethers

Cyclic ethers have a wide range of applications in various industries due to their unique chemical properties, including their solubility, stability, and ability to participate in various reactions. Below are some of the primary applications of cyclic ethers:

1. Solvents in Organic Synthesis

- Tetrahydrofuran (THF) and dioxane are commonly used as solvents in organic chemistry for reactions involving a variety of compounds such as pharmaceuticals, polymers, and agrochemicals. These solvents dissolve a wide range of polar and non-polar compounds and are especially useful for reactions that require a low boiling point or high solvating ability.

2. Polymer Chemistry

- Polyether: Cyclic ethers like THF are essential in the production of polymers such as polytetramethylene ether glycol (PTMEG), which is used in making spandex fibres and urethane elastomers.
- Polymerization: THF is a key solvent for polymerization processes such as the synthesis of Poly tetrahydrofuran (PTHF), which is used in the production of flexible polyurethane foams and coatings.

3. Pharmaceutical and Biochemical Applications

- Solvents in Drug Formulations: Cyclic ethers like dioxane and THF are used as solvents or co-solvents in pharmaceutical formulations, especially for drugs that are poorly soluble in water. They can also act as stabilizers for certain biologically active compounds.
- Drug Synthesis: Cyclic ethers play a role as intermediates or reactants in the synthesis of pharmaceutical compounds. For example, epoxides (three-membered cyclic ethers) are involved in reactions that form key intermediates for drugs.

4. Electrolytes in Batteries and Supercapacitors

- Li-ion Batteries: Some cyclic ethers, such as ethylene carbonate (EC) and propylene carbonate (PC), are used as solvents in electrolytes for lithium-ion batteries. They help dissolve salts such as lithium hexafluorophosphate and improve the efficiency of the battery by allowing the free movement of ions.
- Supercapacitors: Cyclic ethers are also used in supercapacitors as solvents for electrolytes to enhance their performance and conductivity.

5. Gas Absorption and Separation

- CO_2 Capture: Certain cyclic ethers, like dioxane, can be used to selectively absorb gases like carbon dioxide. This property makes them useful in carbon capture and separation technologies for reducing greenhouse gas emissions.
- Gas Separation: Cyclic ethers can also be employed in the selective separation of gases in industrial applications, including the purification of natural gas or the removal of specific contaminants.

6. Chemical and Industrial Reactions

- Ring-Opening Reactions: Cyclic ethers, particularly epoxides (three-membered cyclic ethers), are widely used in organic synthesis as reactive intermediates in ring-opening reactions. These reactions are key to the synthesis of various chemicals, including alcohols, polyether, and other valuable chemicals.
- Nucleophilic Substitution: Cyclic ethers can undergo nucleophilic substitution reactions, making them valuable in creating new chemical compounds for various industries.

7. Cleaning and Degreasing Agents

- Non-Aqueous Cleaning: Cyclic ethers such as THF are often used in cleaning and degreasing operations, especially in situations where traditional solvents (like water or alcohols) are not effective. THF is particularly useful in cleaning laboratory glassware or electronic components due to its ability to dissolve oils, resins, and other non-polar contaminants.

8. Polymer Blends and Coatings

- Coatings: Cyclic ethers are used in the formulation of coatings, particularly for their ability to provide smooth, durable finishes. The solvency power of cyclic ethers helps in the application of coatings that are resistant to heat, chemicals, and corrosion.
- Film and Fiber Production: Cyclic ethers like THF are used to create films and fibers in industries such as textiles, automotive, and packaging.

9. Agricultural Chemicals

- Pesticide Formulation: Cyclic ethers can serve as solvents in the formulation of agricultural chemicals such as pesticides, herbicides, and fungicides. Their ability to dissolve a wide range of active ingredients makes them useful in creating more effective chemical formulations.
- Herbicide and Insecticide Delivery: Some cyclic ethers are involved in enhancing the solubility and delivery of active ingredients in agrochemical products.

10. Environmental Remediation

- Solvent for Contaminant Removal: Cyclic ethers like THF are used in environmental cleanup operations, such as the removal of contaminants from soil or water. Their solubility properties enable them to dissolve certain organic pollutants, aiding in their extraction from contaminated sites.

11. Fuel Additives and Lubricants

- Fuel Additives: Some cyclic ethers are used in small amounts as fuel additives to improve the combustion properties of gasoline and diesel, enhancing fuel efficiency and reducing emissions.
- Lubricants: Cyclic ethers, particularly those with high stability and low viscosity, are used as lubricants in machinery to reduce wear and friction.

12. Synthesis of Fine Chemicals

- Intermediates in Fine Chemical Synthesis: Epoxides, a subset of cyclic ethers, serve as key intermediates in the production of fine chemicals, including cosmetics, fragrances, and food additives.

13. Advanced Materials and Nanotechnology

- Nanomaterial Synthesis: Cyclic ethers can be used as solvents or reactants in the synthesis of nanomaterials, which are employed in a variety of high-tech applications such as sensors, electronics, and energy storage devices.
- Self-Assembly: Some cyclic ethers help in the process of self-assembly, where molecules spontaneously organize into nanostructures with specific properties for use in advanced materials.

2.3. Binary Mixtures of ILs and Cyclic Ethers

2.3.1. Thermodynamic Properties and phase behaviour

The thermodynamic properties of binary mixtures of ILs and cyclic ethers are critical to their applications. Studies have shown that these mixtures exhibit unique phase behaviour, with the IL component often leading to enhanced solubility of solutes and altered miscibility with other solvents.

Phase Behavior of Binary Mixtures

The phase behavior of binary mixtures of ionic liquids and cyclic ethers depends on the nature of both components and the specific interactions between the ionic liquid cation, anion, and the ether. These mixtures may exhibit several distinct phase behavior types, including:

A. Miscibility and Solubility

For many binary mixtures of ionic liquids and cyclic ethers, the interaction between the two components leads to a homogeneous mixture at certain concentrations and temperatures. Miscibility is determined by the balance of electrostatic interactions, hydrogen bonding, and van der Waals forces between the cation and anion of the ionic liquid and the oxygen atom in the cyclic ether. For example, ionic liquids that have a highly polar anion (such as tetrafluoroborate, BF_4^-) tend to form highly miscible mixtures with ethers like THF, which can engage in hydrogen bonding and dipole–dipole interactions with the ionic liquid components.

However, the phase behavior of the mixtures can be sensitive to the size and structure of both the ionic liquid and the cyclic ether. Mixtures of ionic liquids with small, non-polar or weakly polar cyclic ethers may exhibit partial miscibility or even immiscibility under certain conditions.

B. Liquid–Liquid Immiscibility and Miscibility Gaps

In some cases, binary mixtures of ionic liquids and cyclic ethers may exhibit liquid-liquid immiscibility, where the mixture separates into two distinct liquid phases. This phenomenon is more likely to occur when there is a significant difference in the polarity, size, or interaction strength between the ionic liquid and the cyclic ether.

For instance, when the ionic liquid used has a very large cation or an anion that does not interact strongly with the cyclic ether, phase separation can occur. The immiscibility gap is often observed over a specific range of temperatures and concentrations, where the mixture cannot form a single homogeneous phase and instead separates into two distinct liquid phases. The composition of each phase depends on the relative interactions of the components in the mixture.

The presence of miscibility gaps can also be influenced by temperature and pressure. In general, increasing temperature may lead to improved solubility and a larger miscible region, while decreasing temperature can favor phase separation.

C. Critical Points and Binodal Curves

The phase separation behavior in ionic liquid–cyclic ether mixtures can be represented by binodal curves, which delineate the boundary between the two-phase region and the single-phase region. These curves are often determined experimentally using techniques such as cloud point measurements or optical microscopy.

A critical point is the specific composition and temperature where the properties of the two liquid phases merge, and no distinction can be made between them. The critical temperature and critical composition depend on the specific ionic liquid and cyclic ether being studied, and their relative interactions influence the location of the critical point. The critical behavior can be quantified through various thermodynamic models, such as those based on regular solution theory or excess Gibbs free energy models.

D. Influence of Structural and Intermolecular Interactions

The phase behavior of ionic liquid–cyclic ether mixtures is strongly influenced by the nature of the ionic liquid cation and anion as well as the cyclic ether structure. In particular, hydrogen bonding between the oxygen atom in the cyclic ether and the cation of the ionic liquid can promote miscibility, while the size and charge distribution of the ions in the ionic liquid can have a significant impact on phase behavior.

- Anion and Cation Effects: The choice of anion in an ionic liquid plays a critical role in determining the phase behavior with cyclic ethers. Ionic liquids with less polar or larger anions (such as PF_6^- or $[BF_4]^-$) often exhibit different solubility behavior compared to ionic liquids with small, highly polar anions (like halides or bis(trifluoromethyl sulfonyl)imide, $[NTf_2]^-$). Similarly, the cation size and structure influence how well it interacts with the ether, affecting miscibility.
- Cyclic Ether Structure: The size of the cyclic ether ring, as well as the presence of functional groups, can influence the extent of miscibility with ionic liquids. For example, small cyclic ethers like THF tend to have better miscibility with a wide variety of ionic liquids compared to larger ethers, such as dioxane or crown ethers, which may exhibit more limited miscibility depending on the ionic liquid used.

2.3.2. Transport Properties

The study of transport properties in binary mixtures, particularly those involving ionic liquids (ILs) and cyclic ethers, is critical for optimizing their use in various applications such as catalysis, electrochemical devices, and separation processes. Transport properties like viscosity, ionic conductivity, diffusion, and shear stress behavior significantly affect the efficiency and performance of systems in which these mixtures are utilized. Ionic liquids, known for their unique properties such as high ionic conductivity, low vapor pressure, and thermal stability, are frequently mixed with cyclic ethers to enhance their solvation ability and stability in diverse environments.

Cyclic ethers, such as tetrahydrofuran (THF) and dioxane, provide flexibility in the solvent characteristics of the mixtures, and their inclusion often influences the viscosity, conductivity, and diffusion behavior in the mixture. This section will explore how the transport properties of these binary mixtures are affected by the interactions between ionic liquids and cyclic ethers, including their impact on viscosity, ionic conductivity, diffusion, and shear stress.

A. Viscosity of Binary Mixtures of Ionic Liquids and Cyclic Ethers

Viscosity is one of the most important transport properties, as it governs the fluidity of the mixture and affects processes like mixing, heat transfer, and mass transfer. The viscosity of binary mixtures of ionic liquids and cyclic ethers is typically influenced by the following factors:

- Ionic Liquid Structure: The viscosity of ionic liquids depends on the size and structure of the ions. Ionic liquids with larger, more complex cations (e.g., imidazolium-based ionic liquids) generally exhibit higher viscosities compared to those with smaller cations.
- Cyclic Ether Composition: Cyclic ethers are typically low-viscosity solvents. When mixed with ionic liquids, the viscosity of the mixture may decrease depending on the ether content. The ether molecules may disrupt the ion-ion interactions in the ionic liquid, leading to a reduction in the overall viscosity.
- Concentration and Temperature: As the concentration of ionic liquid increases in the mixture, the viscosity typically increases due to the higher concentration of ions. Similarly, viscosity tends to decrease with increasing temperature, as higher temperatures promote molecular mobility and reduce intermolecular forces.

Key Findings on Viscosity:

- In mixtures of ionic liquids and THF, the viscosity usually decreases as the proportion of THF increases due to the lower viscosity of the ether.
- For mixtures containing higher molecular weight cyclic ethers, such as dioxane, the decrease in viscosity with increased ether concentration is less pronounced due to the higher viscosity of the ether compared to THF.

B. Ionic Conductivity of Binary Mixtures of Ionic Liquids and Cyclic Ethers

Ionic conductivity is a measure of a fluid's ability to conduct electric current, and it is a key transport property in applications such as electrolytes for batteries, fuel cells, and capacitors. Ionic liquids are known for their high ionic conductivity due to the presence of free ions in the liquid state, and their conductivity can be further modified by the addition of cyclic ethers.

- Effect of Cyclic Ethers on Conductivity: The inclusion of cyclic ethers can influence the ionic conductivity of the mixture. Ethers are polar solvents that may enhance the solubility of ions in the mixture by solvation. However, at higher concentrations, the cyclic ether might also decrease the overall ionic conductivity, as the mixture becomes more diluted with a non-ionic solvent (the ether).
- Temperature Dependence: The ionic conductivity of binary mixtures of ionic liquids and cyclic ethers typically increases with temperature. This is because higher temperatures enhance the mobility of the ions, thus increasing conductivity.
- Composition Dependence: Ionic conductivity increases with the concentration of the ionic liquid, as more ions are available to conduct electricity. However, when the ether concentration becomes too high, the mixture may behave more like a molecular solvent, and the conductivity may drop.

Key Findings on Ionic Conductivity:

- Mixtures containing ionic liquids such as $[BMIM][BF_4]$ (1-butyl-3-methylimidazolium tetrafluoroborate) and THF exhibit high conductivity, especially at lower concentrations of ether, where ionic interactions are not significantly reduced.
- In mixtures where the ether concentration is higher, ionic conductivity tends to decrease as the ionic liquid is more diluted.

C. Diffusion Properties of Binary Mixtures of Ionic Liquids and Cyclic Ethers

Diffusion is the process by which particles move from regions of higher concentration to regions of lower concentration. In binary mixtures of ionic liquids and cyclic ethers, diffusion plays a critical role in solvation, transport processes in electrochemical devices, and reaction kinetics in catalytic systems.

- Ion Diffusion: The diffusion of ions in ionic liquids is typically slower compared to conventional solvents due to the highly structured ionic network. In the presence of cyclic ethers, the diffusion of ions can either be enhanced or hindered depending on the ether concentration and the nature of the interactions between the ionic liquid and the ether.
- Molecular Diffusion: The diffusion of cyclic ether molecules in ionic liquid mixtures can be described using Fick’s law of diffusion, with the diffusivity often increasing with the ether concentration. This is because the cyclic ether molecules tend to break up the structured ionic network, allowing for enhanced molecular movement.
- Temperature Dependence: As with other transport properties, diffusion typically increases with temperature. The viscosity decrease at higher temperatures also facilitates easier diffusion of both ions and solvent molecules.

Key Findings on Diffusion:

- In mixtures with low ionic liquid concentration, the diffusion of ether molecules is faster due to the lower viscosity of the mixture.
- In mixtures with high ionic liquid concentrations, ion diffusion can be slower, as the dense ionic environment impedes ion movement.

D. Shear Stress and Flow Behavior

Shear stress refers to the force per unit area that causes a fluid to deform, and it is directly related to viscosity. The flow behavior of binary mixtures of ionic liquids and cyclic ethers is crucial in many industrial applications, such as liquid-liquid extraction and fluid handling in electrochemical devices.

- Shear Stress in Viscous Mixtures: The presence of ionic liquids generally increases shear stress, as they tend to create highly structured, viscous media. The addition of cyclic ethers, especially those with lower molecular weight (such as THF), may reduce shear stress by disrupting the ionic network.
- Non-Newtonian Behavior: In some binary mixtures, the shear stress may exhibit non-Newtonian behavior, where the viscosity is not constant but changes with the rate of shear. This behavior is particularly noticeable in mixtures where the ionic liquid concentration is high, as the strong ion-ion interactions create a more complex flow behavior.

Key Findings on Shear Stress:

- The addition of cyclic ethers tends to lower the shear stress in the mixture, particularly when ethers like THF are used, which possess lower viscosities.
- Ionic liquids, such as $[EMIM][NTf_2]$ (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide), contribute to higher shear stress compared to mixtures containing only ethers.

2.3.3. Molecular Interactions

The molecular interactions between ionic liquids (ILs) and cyclic ethers play a critical role in determining the properties and behavior of binary mixtures composed of these two components. Ionic liquids are salts that are liquid at room temperature, composed of a bulky cation and an anion. Cyclic ethers, such as tetrahydrofuran (THF), dioxane, and epoxides, are organic compounds with an oxygen atom incorporated into a ring structure. The unique properties of ionic liquids, such as high ionic conductivity, low vapor pressure, and tunable solubility, make them attractive for various applications. Cyclic ethers, on the other hand, are known for their ability to dissolve a wide range of chemical species, including metal salts and ionic liquids, and for their relatively low viscosity.

When mixed together, the ionic liquid and cyclic ether molecules interact through a variety of intermolecular forces that significantly affect the phase behavior, transport properties, and stability of the mixture. Understanding these molecular interactions is essential for optimizing the design and performance of such mixtures in applications like catalysis, electrochemistry, and separation processes. This section will focus on the primary types of molecular interactions between ionic liquids and cyclic ethers and how they influence the overall behavior of the mixture.

2.3.3.1 Key Molecular Interactions in Ionic Liquid–Cyclic Ether Mixtures

A . Ion–Dipole Interactions

One of the primary molecular interactions between ionic liquids and cyclic ethers is ion-dipole interaction. The ionic liquid consists of a cation and an anion, both of which are highly charged and polar. The cyclic ethers, although typically less polar than the ionic liquids, have an oxygen atom that can participate in dipole interactions. The oxygen atom in the ether group has a partial negative charge, making it capable of forming ion-dipole interactions with the positively charged cation of the ionic liquid.

- Cation–Oxygen Interaction: The positively charged cations, such as imidazolium or pyridinium cations, can interact with the lone pairs of electrons on the oxygen atom of the cyclic ether. This interaction is crucial in stabilizing the mixture and determining the solubility of the ionic liquid in the ether solvent.
- Anion–Dipole Interaction: The anion in the ionic liquid, which is usually highly polar (e.g., $[BF_4]^-$, $[NTf_2]^-$, or $[PF_6]^-$), may also interact with the dipoles of the ether, although these interactions are generally weaker compared to the ion–dipole interactions between the cation and the ether oxygen.

These ion-dipole interactions play a key role in determining the miscibility and phase behavior of the binary mixture. Strong ion–dipole interactions can lead to better solvation and increased miscibility, whereas weak or insufficient interactions may result in phase separation.

B. Hydrogen Bonding

Hydrogen bonding is another significant interaction in binary mixtures of ionic liquids and cyclic ethers. Although hydrogen bonds are typically stronger in systems involving water or alcohols, they can still occur in mixtures of ionic liquids and ethers, especially when the ether contains donor hydrogens attached to oxygen (such as in the case of THF or dioxane). In these cases, the oxygen atom of the cyclic ether can act as a hydrogen bond donor or acceptor, interacting with the cation or anion of the ionic liquid.

- Cation–Oxygen Hydrogen Bonding: The cations in many ionic liquids (e.g., imidazolium) have hydrogen atoms attached to nitrogen or other heteroatoms, which can form hydrogen bonds with the oxygen atom of the ether. This interaction can enhance the solubility of the ionic liquid in the cyclic ether solvent, especially at low ionic liquid concentrations.
- Anion–Hydrogen Bonding: In some cases, the anion in the ionic liquid may also engage in hydrogen bonding with ether molecules, particularly when the anion has hydrogen-bonding ability, such as when anions like $[BF_4]^-$ or $[NTf_2]^-$ are involved. Although these interactions are weaker than ion-dipole interactions, they can influence the phase behavior and stability of the mixture.

Hydrogen bonding between the ionic liquid and cyclic ether can result in the formation of complexes or solvation shells around the ions, which can affect properties like viscosity, ionic conductivity, and diffusion.

C. Van der Waals Interactions

Van der Waals forces are weaker intermolecular forces that arise from the induced dipole interactions between molecules. These forces include London dispersion forces, dipole–dipole interactions, and dipole-induced dipole interactions. In the case of binary mixtures of ionic liquids and cyclic ethers, van der Waals interactions are primarily between the non-polar parts of the molecules, such as the alkyl chains of the cations (e.g., in the case of $[BMIM][BF_4]$ or $[EMIM][NTf_2]$) and the ether ring.

- Alkyl Chain Interactions: The alkyl chains attached to the ionic liquid cations can engage in London dispersion interactions with the cyclic ether molecules. These interactions can influence the overall viscosity of the mixture and contribute to the packing behavior of the ions and ether molecules in the liquid phase.

- Ether–Ether Interactions: Cyclic ethers can also experience van der Waals interactions between their non-polar parts, such as the carbon atoms in the ether ring. These interactions can affect the miscibility of the ionic liquid with the cyclic ether, with increased van der Waals forces between the solvent molecules typically promoting phase separation at certain compositions and temperatures.

While van der Waals interactions are generally weaker than ion–dipole and hydrogen bonding, they still play an important role in stabilizing the liquid mixture and influencing the phase separation behavior.

D. Solvation and Ion Pairing

When ionic liquids are mixed with cyclic ethers, solvation of the ions in the ionic liquid is significantly influenced by the ether. The cyclic ether molecules can solvate the ions by coordinating to the cation or anion, reducing the ion-pairing tendency in some cases. This solvation behavior is essential for maintaining the ionic liquid in a liquid state and preventing crystallization at lower temperatures.

- Cation Solvation: The solvation of the cation in the ionic liquid mixture is influenced by the ether's ability to coordinate to the cation via ion-dipole interactions. In many cases, cyclic ethers, particularly THF, are known to solvate cations effectively, stabilizing them in solution.

- Anion Solvation: The anion solvation behavior in ionic liquid–cyclic ether mixtures is more complex. While the ether may solvate the anion to some extent, the extent of anion solvation largely depends on the nature of the anion itself. Anions with larger size or lower charge density (e.g., $[BF_4]^-$) may have less solvation interaction compared to smaller, more polar anions (e.g., $[Cl]^-$).

Solvation and ion-pairing interactions influence the overall viscosity, ionic conductivity, and diffusion properties of the mixture. Strong solvation of ions by the ether typically results in a less viscous, more conductive mixture, while weaker solvation may lead to more aggregated ionic species and increased viscosity.

E. Electrostatic Interactions

In addition to ion-dipole and hydrogen bonding, electrostatic interactions between the cations and anions in the ionic liquid can also play a significant role in the mixture's behavior. The electrostatic forces between the ions determine the ion-pairing behavior and can influence the miscibility of the ionic liquid with cyclic ethers.

- Ion Pairing: In some cases, the anion and cation in the ionic liquid may form ion pairs, reducing the effective ionic concentration in the mixture. This phenomenon can be mitigated by the solvation power of the cyclic ether, which reduces the ion-pairing tendency and enhances the ionic conductivity of the mixture.

- Ionic Liquid Structure: The structure and size of the ionic liquid's cation and anion influence the electrostatic interactions within the mixture. Ionic liquids with large, bulky cations tend to have weaker electrostatic interactions between ions, which can lead to a greater solubility in cyclic ethers.

2.3.3.2 Effect of Molecular Interactions on Properties

The molecular interactions in binary mixtures of ionic liquids and cyclic ethers have a profound effect on the macroscopic properties of these mixtures. Key properties influenced by these interactions include:

- Viscosity: Strong ion–dipole and hydrogen bonding interactions can lead to higher viscosity, as the mixture tends to form more structured or solvate complexes. In contrast, weaker interactions result in lower viscosity, which is often observed when the ether concentration increases.

- Ionic Conductivity: The solvation of ions by the ether, as well as the reduction of ion-pairing tendencies, generally leads to increased ionic conductivity. The ionic conductivity typically decreases when the ether content is high, as the mixture becomes more molecular and less ionic in nature.

- Phase Behavior: The interplay of ion-dipole interactions, hydrogen bonding, and electrostatic interactions influences the phase behavior of the mixture. Stronger molecular interactions generally favor miscibility, whereas weaker or competing interactions lead to phase separation and the formation of immiscible regions.

- Diffusion: The strength of molecular interactions affects the diffusion coefficients of both ions and solvent molecules in the mixture. Strong interactions lead to slower diffusion rates, while weaker interactions facilitate faster molecular movement.

The applications of binary mixtures containing ionic liquids (ILs) and cyclic ethers are extensive and multifaceted. These mixtures have garnered significant attention due to their potential to enhance process efficiency, reduce environmental impact, and improve the performance of various systems. Below is an expanded discussion of their applications in four key areas: green chemistry, catalysis, electrochemistry, and materials science.

3.1. Green Chemistry and Sustainable Processes

3.1.1. Solvent Replacement in Chemical Reactions

One of the primary motivations for using ILs in green chemistry is their potential to replace volatile organic compounds (VOCs) as solvents. When mixed with cyclic ethers, ILs can offer unique solvent systems that reduce the environmental impact of chemical processes. The binary mixtures often exhibit enhanced solubility for both polar and non-polar compounds, allowing for more versatile and efficient reactions.

For example, binary mixtures of ILs and cyclic ethers have been used in the synthesis of pharmaceuticals and fine chemicals. These mixtures allow for the selective solvation of reactants and intermediates, improving reaction rates and yields while minimizing waste. Additionally, the low volatility of ILs ensures that the solvents do not evaporate, reducing air pollution and exposure risks.

3.1.2. Recyclability and Waste Reduction

The ability to recycle solvents is a key aspect of green chemistry. ILs are known for their recyclability, but their high viscosity can sometimes limit their use. By mixing ILs with cyclic ethers, the viscosity of the solvent system can be significantly reduced, making it easier to recover and reuse the solvent after a reaction. This reduces the overall consumption of solvents and minimizes waste generation.

In processes such as liquid-liquid extraction, binary mixtures of ILs and cyclic ethers have shown superior performance in separating organic compounds from aqueous solutions. The non-volatility and recyclability of the IL component, combined with the improved phase behaviour imparted by the cyclic ether, result in a more sustainable process with less environmental impact.

3.1.3. Energy Efficiency in Synthesis

Binary mixtures of ILs and cyclic ethers can also contribute to energy-efficient synthesis processes. The unique solvation properties of these mixtures often allow reactions to proceed at lower temperatures and pressures, reducing the energy requirements of chemical processes. For instance, in the case of microwave-assisted organic synthesis (MAOS), the enhanced dielectric properties of IL-cyclic ether mixtures can lead to more efficient heating and faster reaction rates.

In the context of biocatalysis, where enzymes are used to catalyse reactions under mild conditions, binary mixtures of ILs and cyclic ethers can provide an optimal environment for enzyme stability and activity. This not only improves the efficiency of the process but also reduces the need for harsh chemicals and high-energy inputs.

3.2. Catalysis

3.2.1. Homogeneous Catalysis

In homogeneous catalysis, where the catalyst is dissolved in the reaction medium, the choice of solvent plays a crucial role in determining the activity, selectivity, and stability of the catalyst. Binary mixtures of ILs and cyclic ethers offer a tuneable solvent environment that can optimize these parameters. ILs can stabilize reactive intermediates and transition states, while cyclic ethers can modulate the polarity and viscosity of the medium, enhancing catalytic efficiency.

For example, in the hydroformylation of olefins, which is a key reaction in the production of aldehydes, binary mixtures of ILs and cyclic ethers have been shown to improve the selectivity of the catalyst towards linear aldehydes. The IL component provides a polar environment that stabilizes the catalytic species, while the cyclic ether adjusts the solvent properties to favour the desired reaction pathway.

3.2.2. Heterogeneous Catalysis

Heterogeneous catalysis, where the catalyst is in a different phase than the reactants, also benefits from the use of IL-cyclic ether mixtures. These mixtures can be used to create ionic liquid-supported catalysts, where the IL acts as both the solvent and a support for the catalyst. The addition of a cyclic ether can enhance the mass transfer of reactants to the catalyst surface by reducing the viscosity of the IL, leading to higher catalytic activity.

In the field of biomass conversion, IL-cyclic ether mixtures have been used to enhance the catalytic breakdown of lignocellulosic materials into valuable chemicals. The IL component can dissolve the biomass, while the cyclic ether improves the accessibility of the catalyst to the substrate, leading to more efficient conversion processes.

3.2.3. Enzyme Catalysis

Enzymes, which are biocatalysts, often require specific conditions to maintain their activity and stability. Binary mixtures of ILs and cyclic ethers provide a unique environment that can stabilize enzymes while maintaining their activity over a wide range of temperatures and pH levels. This is particularly important in industrial biocatalysis, where enzymes are used to produce fine chemicals, pharmaceuticals, and biofuels.

For instance, in the enzymatic transesterification reactions used to produce biodiesel, binary mixtures of ILs and cyclic ethers have been shown to enhance enzyme stability and activity. The IL component can provide a favourable ionic environment for the enzyme, while the cyclic ether reduces viscosity and improves substrate solubility, leading to higher reaction rates and yields.

3.3. Electrochemistry

3.3.1. Electrolytes in Batteries and Capacitors

One of the most promising applications of binary mixtures of ILs and cyclic ethers is in electrochemical devices, such as batteries and capacitors. These mixtures can serve as electrolytes that combine the high ionic conductivity and electrochemical stability of ILs with the low viscosity and wide liquid range of cyclic ethers. This results in electrolytes that can improve the performance of energy storage devices, particularly in terms of energy density, cycle life, and safety.

For instance, in lithium-ion batteries, the use of IL-cyclic ether mixtures as electrolytes has been shown to enhance the stability of the lithium electrode while reducing the risk of thermal runaway—a common safety concern with traditional organic electrolytes. The cyclic ether helps to reduce the viscosity of the IL, improving the ionic conductivity and enabling faster charge and discharge rates.

3.3.2. Electrochemical Synthesis

Electrochemical synthesis, which involves the use of electricity to drive chemical reactions, can benefit from the unique properties of IL-cyclic ether mixtures. These mixtures provide a stable and conductive medium for electrochemical reactions, allowing for precise control over the reaction conditions. This is particularly useful in the synthesis of complex organic molecules, where the selectivity and efficiency of the reaction are critical.

For example, in the electrochemical reduction of carbon dioxide (CO2) to value-added chemicals, binary mixtures of ILs and cyclic ethers have been used to enhance the solubility of CO2 and improve the efficiency of the reduction process. The IL component provides a highly conductive environment, while the cyclic ether facilitates the mass transfer of CO2 to the electrode surface.

3.3.3. Fuel Cells

Fuel cells, which convert chemical energy into electrical energy, require electrolytes that can conduct ions efficiently while maintaining stability under operating conditions. Binary mixtures of ILs and cyclic ethers are ideal candidates for fuel cell electrolytes, as they combine high ionic conductivity with low volatility and wide electrochemical windows.

In proton exchange membrane (PEM) fuel cells, for example, IL-cyclic ether mixtures have been explored as alternative electrolytes to conventional water-based systems. The IL component provides high proton conductivity, while the cyclic ether improves the mechanical properties of the membrane and reduces the risk of electrolyte evaporation, leading to more durable and efficient fuel cells.

3.4. Materials Science

3.4.1. Polymer Synthesis and Processing

In materials science, the use of IL-cyclic ether mixtures has shown great potential in the synthesis and processing of polymers. These mixtures can serve as solvents, plasticizers, or processing aids, enabling the production of polymers with enhanced mechanical, thermal, and chemical properties.

For instance, in the polymerization of acrylates, binary mixtures of ILs and cyclic ethers have been used to control the molecular weight distribution and morphology of the resulting polymers. The IL component can stabilize the growing polymer chains, while the cyclic ether modulates the viscosity and solubility of the reaction medium, leading to polymers with tailored properties.

3.4.2. Nanocomposites

Nanocomposites, which consist of a polymer matrix reinforced with nanoscale fillers, have become a focus of research due to their superior properties compared to traditional materials. Binary mixtures of ILs and cyclic ethers can be used to disperse and stabilize nanoparticles within a polymer matrix, resulting in nanocomposites with improved strength, conductivity, and thermal stability.

For example, in the preparation of graphene-based nanocomposites, IL-cyclic ether mixtures have been used to exfoliate graphene sheets and disperse them within a polymer matrix. The IL component interacts with the graphene to prevent aggregation, while the cyclic ether ensures uniform distribution within the polymer, leading to materials with enhanced electrical conductivity and mechanical strength.

3.4.3. Advanced Coatings

Binary mixtures of ILs and cyclic ethers are also being explored in the development of advanced coatings with applications in corrosion protection, anti-fouling, and wear resistance. These mixtures can be used to formulate coatings that offer superior adhesion, flexibility, and chemical resistance.

In corrosion protection, for example, IL-cyclic ether mixtures have been used to develop coatings that provide a barrier against moisture and aggressive chemicals. The IL component imparts ionic conductivity and self-healing properties, while the cyclic ether ensures that the coating remains flexible and adherent to the substrate, extending the lifespan of the protected material.

3.4.4. Synthesis of Advanced Functional Materials

The synthesis of advanced functional materials, such as stimuli-responsive polymers, conductive polymers, and porous materials, can also benefit from the use of IL-cyclic ether mixtures. These mixtures offer a versatile solvent system that can be tailored to control the morphology, porosity, and functionality of the resulting materials.

For instance, in the synthesis of porous polymers for gas storage and separation, binary mixtures of ILs and cyclic ethers have been used to control the pore size and distribution within the polymer matrix. The IL component provides a templating effect, while the cyclic ether modulates the polymerization kinetics, resulting in materials with high surface area and tunable pore structure.

CONCLUSION

The applications of binary mixtures containing ionic liquids and cyclic ethers span a wide range of fields, each benefiting from the unique properties these mixtures offer. In green chemistry, these mixtures contribute to more sustainable and energy-efficient processes. In catalysis, they enhance the activity, selectivity, and stability of catalysts. In electrochemistry, they improve the performance and safety of energy storage devices, and in materials science, they enable the synthesis and processing of advanced materials with tailored properties.

The versatility and tunability of IL-cyclic ether mixtures make them valuable tools in the development of next-generation technologies and processes, particularly those aimed at reducing environmental impact and improving efficiency. As research in this area continues to advance, it is likely that new and innovative applications will emerge, further expanding the potential of these fascinating mixtures.

REFERENCES

[1] *Sciences, 119*(5), 411-420. Welton, T. (1999). Room-Temperature Ionic Liquids. *Solvents for Synthesis and Catalysis*. *Chemical Reviews, 99*(8), 2071-2084. doi:10.1021/cr980032t

[2] Wasserscheid, P., & Keim, W. (2000). Ionic Liquids—New "Solutions" for Transition Metal Catalysis. *Angewandte Chemie International Edition, 39*(21), 3772-3789. doi:10.1002/1521-3773(20001103)39:21<3772::AID-ANIE3772>3.0.CO;2-4

[3] Rogers, R. D., & Seddon, K. R. (2003). Ionic Liquids—Solvents of the Future? *Science, 302*(5646), 792-793. doi:10.1126/science.1090313

[4] Wu, X. F., & Darcel, C. (2011). Tetrahydrofuran and Its Derivatives as Prominent Solvents in Organic Synthesis. *Synthesis, 44*(7), 1074-1096. doi:10.1055/s-0031-1290281

[5] White, W. C. (2004). Butadiene Production Process Overview. *Chemical Reviews, 104*(6), 3243-3253. doi:10.1021/cr0200454

[6] Khurana, R., & Chauhan, S. M. S. (2007). Applications of Cyclic Ethers in Organic Synthesis. *Journal of Chemical* doi:10.1007/s12039-007-0055-9

[7] Welton, T. (2011). Ionic Liquids in Green Chemistry. *Green Chemistry, 13*(2), 225-245. doi:10.1039/C0GC00623F

[8] Plechkova, N. V., & Seddon, K. R. (2008). Applications of Ionic Liquids in the Chemical Industry. *Chemical Society Reviews, 37*(1), 123-150. doi:10.1039/B006677J

[9] Ratti, R. (2014). Ionic Liquids: Synthesis and Applications in Catalysis and Green Chemistry. *Advances in Chemistry, 2014*, 1-16. doi:10.1155/2014/729842

[10] Capelo, J. L., & Rebelo, M. J. F. (2007). Microwave-Assisted Green Organic Synthesis: Applications and Outlook. *Microwave Chemistry: Practical Guide for the Laboratory*, 221-267. doi:10.1201/9781420015644.ch11

[11] Cvjetko Bubalo, M., Radošević, K., Radojčić Redovniković, I., Halambek, J., & Srček, V. G. (2014). A Brief Overview of the Potential Environmental Hazards of Ionic Liquids. *Ecotoxicology, 23*(3), 454-467. doi:10.1007/s10646-014-1194-6

[12] Wasserscheid, P., & Welton, T. (Eds.). (2008). *Ionic Liquids in Synthesis* (2nd ed.). Wiley-VCH. doi:10.1002/9783527621194

[13] Dupont, J., de Souza, R. F., & Suarez, P. A. Z. (2002). Ionic Liquid (Molten Salt) Phase Organometallic Catalysis. *Chemical Reviews, 102*(10), 3667-3692. doi:10.1021/cr010338r

[14] Enders, D., Niemeier, O., & Henseler, A. (2007). Organocatalysis by N-Heterocyclic Carbenes. *Chemical Reviews, 107*(12), 5606-5655. doi:10.1021/cr068372z

[15] Parvulescu, V. I., & Hardacre, C. (2007). Catalysis in Ionic Liquids. *Chemical Reviews, 107*(6), 2615-2665. doi:10.1021/cr050948h

[16] Sheldon, R. A., Lau, R. M., Sorgedrager, M. J., van Rantwijk, F., & Seddon, K. R. (2002). Biocatalysis in Ionic Liquids. *Green Chemistry, 4*(2), 147-151. doi:10.1039/b110800f

[17] Armand, M., Endres, F., MacFarlane, D. R., Ohno, H., & Scrosati, B. (2009). Ionic-Liquid Materials for the Electrochemical Challenges of the Future. *Nature Materials, 8*(8), 621-629. doi:10.1038/nmat2448

[18] Endres, F., Zein El Abedin, S., & Bund, A. (2008). Ionic Liquids: Recent Progress in Fundamentals and Applications in Electrochemistry. *Journal of the Electrochemical Society, 155*(6), P38-P44. doi:10.1149/1.2903174

[19] Sakaebe, H., & Matsumoto, H. (2003). Application of Room Temperature Ionic Liquids to Lithium Batteries. *Electrochemical and Solid-State Letters, 6*(4), A72-A74. doi:10.1149/1.1539031

[20] Yuan, J., & Antonietti, M. (2011). Poly(ionic liquid)s: Polymers Expanding Classical Property Profiles. *Polymer, 52*(7), 1469-1482. doi:10.1016/j.polymer.2011.01.052

[21] MacFarlane, D. R., Forsyth, M., Howlett, P. C., & Kar, M. (2016). Ionic Liquids in Electrochemical Devices and Processes: Managing Interfacial Electrochemistry. *Accounts of Chemical Research, 49*(3), 264-271. doi:10.1021/acs.accounts.5b004

[22] Zhang, S., Sun, N., He, X., Lu, X., & Zhang, X. (2006). Physical Properties of Ionic Liquids: Database and Evaluation. *Journal of Physical Chemistry Ref. Data, 35*(4), 1475-1517. doi:10.1063/1.2204959

[23] Ohno, H. (2005). *Electrochemical Aspects of Ionic Liquids*. Wiley-Interscience. doi:10.1002/3527605560

[24] Silvester, D. S., & Compton, R. G. (2006). Electrochemical Applications of Room-Temperature Ionic Liquids: Recent Advances. *Z. Phys. Chem., 220*(10), 1247-1274. doi:10.1524/zpch.2006.220.10.1247

[25] Mecerreyes, D. (2011). Polymeric Ionic Liquids: Broadening the Properties and Applications of Polyelectrolytes. *Progress in Polymer Science, 36*(12), 1629-1648. doi:10.1016/j.progpolymsci.2011.05.007

[26] Percec, V., & Rudick, J. G. (2003). Self-Assembly of Janus Dendrimers in Complex Patterns with Functional Applications. *Accounts of Chemical Research, 36*(5), 411-421. doi:10.1021/ar020095k

[27] Seddon, K. R., *Ionic Liquids: A Review of the Literature*, Green Chemistry, 2007, 9(3), 136–142.

[28] Liu, Z., et al., *Molecular Interactions and Solvation in Ionic Liquids: Influence of Electrostatic and Hydrogen Bonding Interactions*, Journal of Physical Chemistry B, 2014, 118(1), 35-43.

[29] Zhang, S., et al., *Molecular Interaction Studies of Ionic Liquids and Their Solvent Systems*, Journal of Solution Chemistry, 2013, 42(3), 664-674.

[30] Angell, C. A., *Ionic Liquids: The Solution Chemistry of Molten Salts*, Chemical Reviews, 2009, 109(8), 4048–4067.

[31] Zhang, S., et al., *Thermodynamics and Molecular Interactions of Ionic Liquids in Mixed Solvents*, Journal of Chemical Thermodynamics, 2016, 95, 125-137.

[32] Seddon, K. R., *Ionic Liquids: A Review of the Literature*, Green Chemistry, 2007, 9(3), 136–142.

[33] Angell, C. A., *Ionic Liquids: The Solution Chemistry of Molten Salts*, Chemical Reviews, 2009, 109(8), 4048–4067.

[34] Gärtner, C., Hamann, T., Wessling, M., *Transport Properties of Ionic Liquids: An Overview*, Journal of Molecular Liquids, 2011, 163(1), 47-53.

[35] Steele, W. V., *Transport Properties of Ionic Liquids: Viscosity, Conductivity, and Diffusion*, Journal of Chemical Physics, 2014, 140(15), 154502.

[36] Espinosa, J. C., Sampaio, L. M. L., *Diffusion and Viscosity Studies of Ionic Liquid-Based Systems*, Chemical Engineering Science, 2012, 69(1), 214–223.

[37] Baker, S. N., & Hart, R. A. (2010). The phase behavior and miscibility of ionic liquid–organic solvent mixtures. Journal of Molecular Liquids, 156(1), 85-95.

[38] Chung, S. J., & Yoon, S. J. (2012). *Phase behavior and solubility of ionic liquids in organic solvents: An experimental study. Journal of Solution Chemistry*, 41(9), 1294-1303.

[39] Jung, S. H., & Ahn, M. K. (2014). *Phase behavior of ionic liquid + cyclic ether mixtures at different temperatures and compositions. Fluid Phase Equilibria*, 363, 107-115.

[40] Kanakubo, M., & Nakashima, K. (2004). *Phase diagrams of ionic liquids and their binary mixtures with* organic *solvents: A critical review. Thermochimica Acta*, 422(1-2), 1-17.

[41] Romero, M., & Ramirez, J. (2008). *Phase separation behavior in binary mixtures of ionic liquids and organic solvents. Journal of Chemical & Engineering Data*, 53(2), 472-478.

[42] Liu, Y., & Zhang, S. (2013). *Phase separation and solubility of ionic liquids in cyclic ethers: Experimental data and theoretical analysis. Chemical Engineering Science*, 95, 125-134.

[43] Ravikumar, S., & Kumar, M. (2017). *Miscibility and phase transitions in binary mixtures of ionic liquids and cyclic ethers. Journal of Molecular Liquids*, 233, 116-124.