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Role of Molecular Interactions of Binary Mixtures of Ionic Liquids and Cyclic Ethers in Evaluation of Performance of Diesel Engines

[1]Kuldeep Kumar Solanki, [2]Dr. Arpna, [3]Dr. Sunil Kumar Jangra

[1]Research Scholar, Department of Chemistry, Baba Mastnath University, Rohtak, India
[2]Assistant Professor, Department of Chemistry, Baba Mastnath University, Rohtak, India
[3]Assistant Professor, Department of Chemistry, AIJHM College, Rohtak, India
Author's E-mail: [2]arpnakalonia.bimpat@gmail.com

***Abstract* - Diesel engines have become a vital component of modern transportation, but they are also associated with concerns regarding efficiency, emissions, and fuel consumption. Recent advancements have focused on improving diesel engine performance by exploring alternative fuel formulations and additives. One promising approach involves the use of binary mixtures of ionic liquids (ILs) and cyclic ethers, which have unique physicochemical properties that can influence combustion characteristics, fuel efficiency, and emissions. This paper reviews the role of molecular interactions in binary mixtures of ILs and cyclic ethers, specifically in relation to their effects on diesel engine performance. The interactions between ILs and cyclic ethers—such as ion-dipole interactions, hydrogen bonding, and solvation effects—can alter fuel properties such as viscosity, density, combustion behaviour, and lubricity. Understanding these interactions is crucial for the design of additives that can optimize fuel performance, reduce emissions, and improve engine efficiency. We also discuss how the compatibility of these mixtures with conventional diesel fuels can enhance fuel properties, leading to improved engine operation.**

Keywords: Molecular Interactions, Binary Mixtures, Ionic Liquids, Cyclic Ethers, Diesel Engines.

I. Introduction

The performance of diesel engines has long been a topic of interest in the fields of automotive engineering and fuel science, primarily due to their high fuel efficiency and robustness. However, traditional diesel fuels, while efficient, contribute significantly to environmental pollution, including particulate matter, nitrogen oxides (NOx), and carbon emissions. As a result, there has been growing interest in optimizing diesel engine performance by improving fuel formulations. Among the various avenues explored, the use of alternative fuel additives has gained attention for its potential to reduce emissions, improve combustion efficiency, and increase overall engine performance.

Ionic liquids (ILs), which are salts in the liquid state at ambient temperatures, have shown promise as fuel additives and solvents due to their unique properties, such as low volatility, high thermal stability, and tunability of their chemical structure. On the other hand, cyclic ethers (CEs), such as tetrahydrofuran (THF) and dioxane, are widely used as solvents in fuel formulations because of their high solubility, low toxicity, and good mixing characteristics. Binary mixtures of ILs and CEs offer a unique opportunity to engineer fuel additives that can modify key fuel properties, such as viscosity, lubricity, and combustion characteristics, which are crucial to the performance of diesel engines.

Understanding the molecular interactions between ILs and CEs is critical for predicting how these mixtures will affect the diesel engine's operation. Interactions such as ion-dipole forces, hydrogen bonding, and solvation effects can influence how the additives interact with the fuel and combustion chamber components, ultimately affecting engine performance metrics like power output, fuel efficiency, and emissions. Moreover, the solubility of these mixtures in diesel fuels and their impact on fuel properties, such as density and viscosity, plays a crucial role in determining their effectiveness as additives.

The objective of this research paper is to explore the molecular interactions between ionic liquids and cyclic ethers in binary mixtures, and their subsequent effects on the performance of diesel engines. We aim to provide insights into how these interactions can be leveraged to optimize fuel properties, reduce environmental impact, and enhance engine efficiency. This paper will highlight the current understanding of the role these interactions play in diesel engine operation, focusing on the key aspects of combustion behaviour, emissions, and fuel efficiency.

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II. Molecular Interactions in Binary Mixtures of Ionic Liquids and Cyclic Ethers

A. Ion-Dipole Interactions

Ion-Dipole Interactions in Binary Mixtures of Ionic Liquids and Cyclic Ethers

Ion-dipole interactions are a type of intermolecular force that occurs between an ion and a molecule that has a permanent dipole moment. These interactions play a crucial role in understanding the behaviour of binary mixtures consisting of ionic liquids (ILs) and cyclic ethers (CEs). The presence of both charged species (ions in ILs) and polar molecules (such as cyclic ethers) in the mixture creates a complex network of interactions that influence the mixture's physical and chemical properties, including viscosity, solubility, conductivity, and combustion behaviour in the context of diesel engine performance.

Mechanism of Ion-Dipole Interactions

Ion-dipole interactions arise from the electrostatic attraction between the charged species of an ion and the dipole moment of a polar molecule. In the case of ILs, the ions involved are typically composed of a large organic cation and a smaller inorganic or organic anion. The cation in an IL (e.g., **[C4mim]**$^{+}$ or **[Emim]**$^{+}$) possesses a partial positive charge on the hydrogen or alkyl groups, while the anion (e.g., **[PF$_6$]**$^{-}$, **[BF$_4$]**$^{-}$, or **[Cl]**$^{-}$) carries a negative charge. On the other hand, cyclic ethers, such as **tetrahydrofuran (THF)** or **dioxane**, have an oxygen atom with a lone pair of electrons that induces a dipole moment in the molecule. The oxygen atom, being more electronegative, pulls electron density toward itself, leaving the hydrogen or alkyl groups in the molecule partially positive.

When ILs and CEs are mixed, the cations of the IL are attracted to the oxygen atoms in the cyclic ethers due to the electrostatic interaction between the positive charge of the cation and the partial negative charge on the oxygen atom. Similarly, the anion of the IL can interact with the partial positive sites of the cyclic ether, such as the hydrogen atoms or the alkyl groups.

Factors Influencing Ion-Dipole Interactions in IL-CE Mixtures

The strength and nature of ion-dipole interactions in binary mixtures of ILs and CEs depend on several factors, including:

a) Ion Size and Charge Distribution:

- The size of the ions in the IL significantly influences the strength of ion-dipole interactions. Larger ions with a lower charge density (e.g., **[C4mim]+**) interact more weakly with cyclic ethers than smaller ions with higher charge density (e.g., **[Im]+** or **[EtNH3]+**). Smaller ions tend to produce stronger ion-dipole forces due to the closer proximity of the ion's charge to the dipole of the cyclic ether.
- The charge distribution on the ion also affects the strength of the interaction. Highly charged, symmetrical ions (such as **[PF6]−**) may have different interaction dynamics with cyclic ethers compared to less charged or asymmetric ions (like **[Cl]−**).

b) Dipole Moment of the Cyclic Ether:

- The dipole moment of the cyclic ether plays an important role in determining the strength of the ion-dipole interaction. Cyclic ethers with a higher dipole moment, such as **dioxan**e, tend to have stronger ion-dipole interactions because the oxygen atom in these molecules is more effective at attracting the cation of the IL.
- The presence of substituents on the ether group or changes in the oxygen atom's electronegativity can also modify the dipole moment, influencing how the ether interacts with the IL cation.

c) Polarity and Size of the IL Anion:

- The nature of the anion in the IL also affects ion-dipole interactions. Highly polar or bulky anions (such as **[PF$_6$]**$^{-}$ or **[BF$_4$]**$^{-}$) can influence the ion-dipole interaction by creating competition for interactions between the cation and the cyclic ether. Anions with larger ionic radii may limit the extent of cation-ether interactions due to steric effects, while smaller anions might favor stronger ion-dipole interactions by being more flexible in fitting into the intermolecular space between the IL and the cyclic ether.

d) Concentration and Composition of the Mixture:

- The relative concentrations of the IL and the cyclic ether also influence ion-dipole interactions. At low concentrations of IL in the mixture, the cations and anions may not interact as strongly with the ether molecules, resulting in weaker interactions. As the concentration of IL increases, ion-dipole interactions become more pronounced, which could lead to a more stable mixture and changes in macroscopic properties such as viscosity and solubility.
- Mixtures with higher amounts of cyclic ethers may also lead to greater distribution of ether molecules around the ions, modifying the ion's solvation shell and altering the physicochemical properties of the mixture.

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Impact of Ion-Dipole Interactions on Diesel Engine Performance

The strength and nature of ion-dipole interactions between ILs and CEs in a binary mixture can have significant implications for diesel engine performance, especially in the context of fuel efficiency, combustion behaviour, and emissions.

1. Improved Fuel Atomization and Combustion Efficiency:

- Ion-dipole interactions influence the rheological properties (such as viscosity) of the fuel mixture. A reduced viscosity, caused by the ion-dipole interaction between the IL cation and the cyclic ether, can improve the atomization of the fuel when injected into the combustion chamber. This leads to a finer fuel spray, better mixing with air, and more complete combustion, resulting in higher engine efficiency and lower fuel consumption.
- Additionally, a more homogeneous fuel-air mixture improves combustion characteristics, such as reducing ignition delay and preventing knocking, which can enhance engine performance and reduce harmful emissions (e.g., NO_x and particulate matter).

2. Enhanced Lubricity and Reduced Wear:

- The presence of ionic liquids in the binary mixture can improve the lubricity of the fuel. Ion-dipole interactions between the IL cations and cyclic ether molecules can modify the surface properties of the fuel, leading to reduced friction and wear on engine components, particularly in the fuel injection system. Enhanced lubricity contributes to the longevity of engine parts and the smooth operation of the diesel engine.

3. Reduction in Emissions:

- Strong ion-dipole interactions can promote more efficient combustion by optimizing the fuel-air mixture, thereby reducing incomplete combustion. This reduction in unburned hydrocarbons leads to lower particulate emissions, which is an important factor in improving air quality and meeting environmental regulations.
- The ability of IL-CE mixtures to reduce the formation of soot and NOx emissions, while improving combustion efficiency, makes them a potential candidate for environmentally friendly diesel fuels.

4. Solvency and Fuel Stability:

- The ion-dipole interaction between the IL and cyclic ether also plays a role in the stability and solubility of fuel components. Mixtures with high solvating power can help reduce fuel degradation and minimize the formation of harmful deposits or gum in the engine, ensuring smoother engine operation and longer fuel shelf life.

B. Hydrogen Bonding and Solvation Effects in Binary Mixtures of Ionic Liquids and Cyclic Ethers

Hydrogen bonding and solvation effects are critical factors that govern the molecular interactions in binary mixtures of ionic liquids (ILs) and cyclic ethers (CEs). These intermolecular forces not only influence the physical properties of the mixture, such as viscosity, density, and miscibility, but they also play a significant role in determining how such mixtures perform in practical applications, including their impact on diesel engine operation. Understanding the nature and strength of hydrogen bonding and solvation effects can guide the development of more effective fuel additives, improving combustion efficiency, reducing emissions, and enhancing fuel properties.

1. Hydrogen Bonding: A Key Molecular Interaction

Hydrogen bonding occurs when a hydrogen atom, which is covalently bonded to an electronegative atom (such as oxygen or nitrogen), interacts with a lone pair of electrons on another electronegative atom. In binary mixtures of ionic liquids and cyclic ethers, hydrogen bonding can occur between the cations of the ionic liquid and the oxygen atom of the cyclic ether or between ether molecules themselves.

Hydrogen Bonding Between IL Cations and Cyclic Ethers

Ionic liquids typically contain large organic cations (e.g., **[C4mim]**$^+$, **[Emim]**$^+$) that have a hydrophilic part (often a hydrogen or alkyl group) and a hydrophobic part (often a bulky aromatic or alkyl group). These cations are polar and can form hydrogen bonds with the electronegative oxygen atom of cyclic ethers like tetrahydrofuran (THF), dioxane, or ethylene oxide. The oxygen in these cyclic ethers possesses a lone pair of electrons, making it a good hydrogen bond acceptor.

For example, in a mixture of **[C4mim][PF$_6$]** (1-butyl-3-methylimidazolium hexafluorophosphate) and THF, the lone pair on the oxygen atom of THF can form a hydrogen bond with the hydrogen atoms attached to the imidazolium ring of the cation. This hydrogen bonding interaction strengthens the association between the IL and the cyclic ether, stabilizing the mixture and potentially reducing phase separation.

The presence of such hydrogen bonds can affect the viscosity, solubility, and thermal stability of the binary mixture. When hydrogen bonding is present, it tends to increase the fluidity and decrease the volatility of the mixture, which can be beneficial in applications like fuel additives for

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diesel engines. The enhanced fluidity, for example, may improve fuel atomization, leading to better combustion characteristics.

Hydrogen Bonding Between Cyclic Ether Molecules

Hydrogen bonding is also possible between the oxygen atoms of different cyclic ether molecules. This interaction can create a network of bonds that affects the overall properties of the mixture. In a mixture of ILs and CEs, these intermolecular hydrogen bonds can contribute to the solubility and miscibility of the mixture, as well as influence the thermodynamic properties of the system. For instance, a strong hydrogen bonding network between the ether molecules and the IL cations may reduce the mixture's volatility and prevent the formation of two-phase systems.

Moreover, cyclic ethers like THF and dioxane are known to form self-associated structures in the presence of other polar molecules due to hydrogen bonding. This self-association could modify the solvent characteristics of the mixture, which may be desirable for applications that require high solvent power or selectivity.

2. Solvation Effects: Impact on Ionic Behaviour and Solubility

Solvation refers to the stabilization of ions or molecules by a solvent, which can dramatically affect the solubility, reactivity, and physical properties of the system. In IL-CE mixtures, the solvation effects primarily involve the interaction between the ions in the IL and the molecules of the cyclic ether. The solvation behaviour of ILs can be altered significantly when mixed with cyclic ethers, and this can affect various aspects of diesel engine performance, such as combustion, lubricity, and emissions.

Solvation of IL Ions by Cyclic Ethers

The ionic components of ILs (the cations and anions) are solvated by the cyclic ether molecules in the mixture. In IL-CE binary mixtures, the cyclic ether molecules interact with both the cations and anions in the IL, forming a solvation shell around the ions. The degree of solvation depends on the polarity of the cyclic ether, the size of the ions, and the specific molecular interactions between the ether and the ions.

For example, in a mixture of **[C4mim][PF$_6$]** and THF, the oxygen atom in the THF molecule interacts with the positively charged cation, while the negatively charged **[PF$_6$]$^-$** anion might interact with the hydrophobic regions of the cation or with other ether molecules. This solvation effect helps stabilize the ionic species in solution, which can reduce ion-pairing and increase ionic mobility, potentially improving the conductivity of the mixture. The increased ionic conductivity can, in turn, enhance the electrochemical performance of the fuel and the efficiency of combustion in diesel engines.

Additionally, the solvation effect influences the ability of the mixture to dissolve other components of the fuel, such as hydrocarbon-based compounds, oxygenates, or additives. This enhanced solvation capacity can improve the miscibility of the fuel with other fuel additives, thereby optimizing the overall fuel performance.

Influence of Solvation on Fuel Properties

The solvation of IL ions by cyclic ethers can modify key fuel properties such as viscosity, surface tension, and density. These properties directly affect the behaviour of the fuel within a diesel engine, including how well the fuel atomizes when injected into the combustion chamber and how efficiently it mixes with air for combustion.

- **Viscosity Reduction**: The interaction between ILs and cyclic ethers often results in a reduction in viscosity. This lower viscosity improves fuel atomization, which is crucial for achieving more uniform combustion. More complete combustion leads to higher efficiency and fewer emissions, particularly particulate matter.
- **Surface Tension and Wettability**: Solvation effects can also alter the surface tension of the fuel mixture. A reduction in surface tension can improve the wettability of engine components and fuel injector surfaces, which helps with better lubrication and reduces wear.
- **Density and Specific Heat**: The solvation process can affect the density of the fuel mixture, which in turn influences its energy content and combustion behaviour. A lower density can lead to better fuel atomization and more efficient combustion, while a higher density may help increase energy density.

Solvation and Combustion Behaviour

The solvation of IL ions by cyclic ethers also has implications for the combustion characteristics of the fuel. Solvation can influence the volatility of the fuel, which affects the ignition delay and combustion temperature. For instance, the solvation effect can lead to a reduction in the ignition delay by promoting faster vaporization of the fuel, resulting in more immediate combustion after injection. This can enhance engine performance by optimizing the combustion process and reducing emissions such as NOx and soot.

Furthermore, solvation can also modify the fuel's ability to act as a stabilizer or catalyst in the combustion process. By changing the solubility of certain molecules in the fuel

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mixture, solvation effects can help optimize the fuel's combustion profile, contributing to smoother engine operation and improved fuel efficiency.

3. Influence on Diesel Engine Performance

Both hydrogen bonding and solvation effects play an essential role in determining the overall behaviour of fuel additives in diesel engines, and their influence on various engine performance parameters can be summarized as follows:

- **Improved Combustion Efficiency**: The reduction in viscosity and improved fuel atomization, resulting from hydrogen bonding and solvation effects, leads to better combustion efficiency. This results in higher power output, more complete fuel combustion, and reduced fuel consumption.
- **Lower Emissions**: More complete combustion, achieved through optimized atomization and better mixing of the fuel and air, can significantly reduce emissions, particularly particulate matter (soot) and NOx. The ability of IL-CE mixtures to reduce ignition delays and stabilize combustion temperatures further contributes to lowering harmful emissions.
- **Enhanced Lubricity**: The hydrogen bonding and solvation effects can improve the lubricity of the fuel mixture, reducing wear on engine components, particularly fuel injectors and the combustion chamber. This leads to better engine performance, reduced friction, and extended engine life.
- **Fuel Stability**: Solvation effects ensure the long-term stability of the fuel mixture by preventing phase separation and degradation of the fuel components. This stability is crucial for maintaining the efficiency and performance of the diesel engine over extended periods

4. Effects on Combustion Behaviour

The combustion behaviour of a fuel directly influences diesel engine performance, including factors like power output, fuel efficiency, emissions, and overall engine longevity. The interactions within binary mixtures of ionic liquids (ILs) and cyclic ethers (CEs)—particularly hydrogen bonding and solvation—can significantly impact these combustion characteristics. By altering the fuel's physical properties, such as viscosity, volatility, surface tension, and solubility, these interactions can change how the fuel behaves when injected into the combustion chamber, how it interacts with air, and how it burns. The following sections will explore the specific effects of hydrogen bonding and solvation on combustion behaviour, which can result in enhanced engine efficiency, reduced emissions, and improved operational stability.

a) Hydrogen Bonding and Combustion Behaviour

Hydrogen bonding, a strong intermolecular force, occurs when hydrogen atoms, which are covalently bonded to electronegative atoms like oxygen, nitrogen, or fluorine, interact with lone pairs of electrons on other electronegative atoms. In the case of IL-CE binary mixtures, hydrogen bonding can occur between the cations of ILs (e.g., **[C4mim]+**, **[Emim]+**) and the oxygen atoms of cyclic ethers, such as **tetrahydrofuran (THF)** or **dioxane**, or between ether molecules themselves.

Influence of Hydrogen Bonding on Fuel Volatility

Hydrogen bonding can affect the volatility of a fuel mixture by altering its evaporation characteristics. In a diesel engine, the volatility of the fuel plays a crucial role in determining how quickly and evenly it vaporizes after injection. This directly impacts the fuel-air mixing process and combustion efficiency.

- **Reduced Volatility and Improved Fuel Vaporization**: Hydrogen bonding between the IL cations and cyclic ethers can reduce the overall volatility of the fuel mixture. While lower volatility can be beneficial for minimizing evaporative losses during fuel storage, it can also influence combustion behaviour. If the fuel mixture vaporizes too slowly, it could delay ignition, leading to increased ignition delay and incomplete combustion, especially under cold-start conditions. On the other hand, the presence of hydrogen bonding can also help to control the volatility in a way that improves the rate of vaporization under operating conditions, allowing for a more consistent and efficient combustion process. This can result in improved ignition timing and combustion efficiency, thereby reducing engine knocking and promoting smoother operation.
- **Optimized Combustion Temperature and Ignition Delay**: Hydrogen bonds can impact the ignition delay, which is the time between the injection of the fuel and the start of combustion. The viscosity reduction caused by hydrogen bonding between ILs and CEs can facilitate better fuel atomization and faster vaporization, which reduces the ignition delay. A shorter ignition delay means more efficient combustion at optimal temperatures, reducing the formation of particulate matter and NOx emissions.

Hydrogen Bonding and Fuel Atomization

The ability of a fuel to atomize effectively upon injection is crucial for achieving complete combustion. Hydrogen bonding influences the rheological properties of the fuel

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mixture, particularly viscosity and surface tension, which directly impact atomization.

- **Reduced Viscosity and Improved Atomization**: The hydrogen bonding interaction between ILs and CEs leads to a decrease in viscosity, making the fuel less resistant to flow. This, in turn, facilitates better atomization of the fuel droplets as they enter the combustion chamber. Smaller, more uniform droplets result in more complete mixing with air and more efficient combustion. This leads to a reduction in fuel consumption and improved engine power output. Incomplete atomization, caused by higher viscosity, could result in larger fuel droplets that are less readily vaporized, leading to poor combustion, higher emissions, and engine knocking.
- **Enhanced Combustion Efficiency**: Improved atomization and uniform distribution of the fuel in the combustion chamber result in better fuel-air mixing, which directly contributes to more complete and efficient combustion. As a result, less fuel is wasted, reducing particulate emissions and improving fuel efficiency. Better combustion efficiency is associated with a reduction in both particulate matter (soot) and carbon monoxide (CO) emissions.

b) Solvation Effects and Combustion Behaviour

Solvation refers to the interaction between the fuel components (particularly the ions of the ILs and the molecules of the cyclic ethers), which stabilizes and modifies the properties of the fuel mixture. Solvation effects can significantly influence the combustion behaviour of the fuel by altering factors such as volatility, reactivity, and the solubility of various components within the mixture.

Solvation and Fuel Volatility

Solvation affects the evaporation and volatility of fuel mixtures, which plays a critical role in ignition delay and combustion characteristics. The solvation of IL ions by cyclic ethers can change the fuel's volatility by stabilizing the ions in the mixture and influencing the fuel’s vapor pressure. A more stable mixture promotes better vaporization during the injection process.

- **Optimized Vaporization and Combustion**: Cyclic ethers such as **tetrahydrofuran (THF)** and **dioxane** have a lower boiling point compared to traditional diesel fuels. When combined with ILs, the solvation of the IL cations and anions by the ether molecules can lead to a mixture that vaporizes more efficiently at a lower temperature. This efficient vaporization can lead to better ignition and combustion processes, with a faster and more uniform flame front, thus improving engine performance. More complete combustion reduces harmful emissions such as NOx, particulate matter, and hydrocarbons, which are common pollutants in diesel engines.

Solvation and Reduced Ignition Delay

The solvation effects, particularly the ion-dipole interactions between ILs and cyclic ethers, can reduce the ignition delay by improving the vaporization and mixing of the fuel. A reduced ignition delay allows for faster combustion, which is critical for improving engine performance and reducing the likelihood of engine knocking (premature ignition).

- **Accelerated Ignition and Smoother Combustion**: In a diesel engine, a rapid combustion process is essential for maintaining smooth operation and preventing abnormal combustion events such as knocking or misfiring. Solvation improves fuel properties such as volatility and reduces the energy required to vaporize the fuel, thus accelerating ignition and enhancing combustion efficiency. This results in smoother operation, greater power output, and a reduction in combustion-related emissions.

Solvation and Combustion Temperature Control

Solvation can also influence the temperature at which combustion occurs. A well-solvated mixture, in which IL ions and cyclic ether molecules are tightly bound together, may burn at a more consistent temperature, reducing temperature spikes that contribute to the formation of NOx.

- **Lower Combustion Temperature and NOx Reduction**: The solvation of ILs in cyclic ethers can lead to more controlled combustion temperature profiles, minimizing the formation of NOx, which are produced when the combustion temperature is too high. Lower combustion temperatures also reduce the likelihood of thermal degradation of fuel components, leading to more efficient fuel use and reduced emissions of carbon dioxide (CO_2) and particulate matter (PM).

c) Overall Impact of Hydrogen Bonding and Solvation on Combustion Behaviour

Both hydrogen bonding and solvation effects significantly alter the combustion characteristics of diesel fuel. By modifying properties like fuel volatility, atomization, ignition delay, combustion efficiency, and emission profiles, these intermolecular interactions can provide a variety of benefits for diesel engine performance.

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- **Improved Fuel Atomization**: Reduced viscosity and better atomization of fuel droplets lead to more uniform combustion, which improves fuel efficiency and reduces harmful emissions.
- **Optimized Ignition and Combustion Efficiency**: Faster ignition and better combustion efficiency translate into increased power output and fuel economy, as well as a reduction in unburned hydrocarbons and particulate matter.
- **Emission Reduction**: More efficient combustion processes, enabled by hydrogen bonding and solvation, reduce the formation of soot, CO, NOx, and other pollutants, making the fuel mixture more environmentally friendly.
- **Engine Longevity**: Improved lubrication properties and more efficient combustion reduce engine wear, leading to longer engine life and reduced maintenance costs.

C. Impact of Binary Mixtures of Ionic Liquids and Cyclic Ethers on Fuel Efficiency and Emissions

The quest for improving fuel efficiency and reducing harmful emissions from internal combustion engines, especially diesel engines, has led to increasing interest in the use of alternative fuels and additives. Among these, binary mixtures of ionic liquids (ILs) and cyclic ethers (CEs) have shown great potential in enhancing engine performance while addressing environmental concerns. By modulating the fuel's physical and chemical properties through the interactions between ILs and CEs, these mixtures can optimize various engine characteristics such as combustion behavior, atomization, and lubricity. In turn, these changes lead to improvements in fuel efficiency and a reduction in emissions.

This section will explore how binary mixtures of ILs and CEs influence fuel efficiency and emissions, focusing on the underlying molecular interactions that affect combustion processes, energy consumption, and the production of pollutants like particulate matter (PM), nitrogen oxides (NOx), carbon monoxide (CO), and hydrocarbons (HC).

1. Influence of Binary Mixtures on Fuel Efficiency

Fuel efficiency in diesel engines is typically associated with how effectively the fuel is converted into useful mechanical energy, minimizing waste in the form of unburned fuel or excess heat. The following factors influenced by IL-CE mixtures contribute to improved fuel efficiency:

a) Improved Fuel Atomization and Combustion

One of the critical parameters for achieving high combustion efficiency in diesel engines is fuel atomization—the process of breaking down liquid fuel into fine droplets when injected into the combustion chamber. Binary mixtures of ILs and CEs can significantly improve fuel atomization through their impact on the fuel's viscosity and surface tension.

- **Reduced Viscosity and Enhanced Atomization:** ILs typically have high viscosity due to their large ions, but when mixed with cyclic ethers, the overall viscosity of the mixture can be reduced. This reduction allows for easier injection of fuel into the combustion chamber and better atomization, leading to smaller, more uniform fuel droplets. Better atomization enhances the fuel's contact with air, improving mixing and combustion.
- **More Complete Combustion**: Improved atomization leads to better combustion, as smaller droplets allow for more uniform vaporization and better mixing with air. This results in more complete combustion of the fuel, maximizing energy extraction from the fuel. The efficiency of the combustion process is directly linked to fuel efficiency, as better combustion reduces the need for excess fuel to achieve the desired power output.

b) Enhanced Fuel Vaporization

The rate of vaporization of a fuel is crucial to its combustion characteristics, especially in the context of diesel engines, where fuel must be vaporized rapidly for optimal combustion. Binary mixtures of ILs and CEs can alter the volatility of the mixture, which, in turn, influences vaporization.

- **Faster Vaporization**: The presence of cyclic ethers in the mixture, which are typically more volatile than traditional diesel fuels, can facilitate faster vaporization of the fuel in the combustion chamber. This is especially important at low temperatures or during engine start-up, where quicker vaporization ensures smoother operation, faster ignition, and more complete combustion.
- **Improved Combustion Efficiency**: Faster vaporization means that the fuel reaches the ideal vapor phase more quickly, leading to more consistent ignition and reducing the chances of incomplete combustion. Incomplete combustion can lead to fuel wastage and increased fuel consumption. As a result, optimizing vaporization through IL-CE mixtures can significantly enhance fuel efficiency.

c) Enhanced Lubricity and Reduced Friction

The interaction between ILs and CEs can also improve the lubricity of the fuel mixture, which is beneficial for engine components that come into contact with fuel, such as injectors and fuel pumps.

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- **Improved Lubricity**: ILs are known to exhibit excellent lubricating properties due to their unique molecular structure, which can interact with engine components to form a protective film. By incorporating cyclic ethers into the mixture, the lubricating effect can be enhanced, reducing friction and wear on engine parts. This leads to smoother engine operation, which can enhance overall engine efficiency by reducing the energy lost to friction.
- **Lower Maintenance Costs:** The improved lubricity also contributes to lower maintenance costs, as reduced wear on fuel system components extends the lifespan of injectors and pumps, maintaining optimal performance over time.

d) Optimized Ignition Delay and Combustion Temperature

The ignition delay, which is the time between fuel injection and the start of combustion, plays a significant role in the combustion process. A longer ignition delay can lead to incomplete combustion and reduced efficiency, while a shorter ignition delay promotes more efficient fuel use.

- **Reduction in Ignition Delay:** By modifying the fuel mixture with ILs and CEs, the ignition delay can be optimized. The solvation effects of the mixture, including hydrogen bonding and dipole interactions, can enhance the fuel's ability to vaporize quickly and mix efficiently with air, reducing ignition delay. This ensures that combustion begins at the right time, avoiding issues like knocking and reducing the need for excess fuel to compensate for inefficient combustion.
- **More Consistent Combustion Temperature**: The improved combustion efficiency and better ignition timing result in a more stable and controlled combustion temperature, ensuring that the engine operates within the optimal temperature range. Consistent combustion temperatures help maintain high efficiency and reduce the need for extra fuel to maintain power output.

2. Reduction of Emissions

The emissions produced by diesel engines, including nitrogen oxides (NOx), particulate matter (PM), carbon monoxide (CO), and hydrocarbons (HC), are a significant environmental concern. The use of binary mixtures of ILs and CEs has been shown to reduce these harmful emissions through their impact on combustion efficiency and fuel characteristics.

a) Reduction in Particulate Matter (Soot)

Soot formation is a major concern in diesel engines, primarily caused by incomplete combustion of the fuel. The presence of ILs and CEs in binary mixtures can help reduce soot formation through several mechanisms:

- **Improved Combustion Efficiency:** By enhancing atomization, vaporization, and ignition timing, IL-CE mixtures lead to more complete combustion. When combustion is more complete, fewer carbon-rich particles are formed, resulting in reduced soot emissions.
- **Lower Smoke and Soot Emissions**: As a consequence of improved combustion efficiency, the engine produces less unburned carbon, which directly reduces soot emissions. This is particularly important for meeting regulatory standards for particulate matter, which are becoming increasingly stringent worldwide**.**

b) Nitrogen Oxides (NOx) Emission Reduction

NOx emissions, which are a result of high combustion temperatures, are a significant source of air pollution. High combustion temperatures are typically associated with incomplete combustion, which can be exacerbated by inefficient fuel atomization and delayed ignition. IL-CE mixtures can reduce NOx emissions in several ways:

- **Lower Combustion Temperatures:** The use of ILs and CEs can help maintain more stable and lower combustion temperatures. The enhanced combustion efficiency and improved fuel atomization reduce temperature spikes during the combustion cycle, leading to a reduction in NOx formation.
- **Optimized Ignition and Combustion**: Reduced ignition delay and more controlled combustion prevent the formation of hot spots in the combustion chamber, which are often responsible for high NOx production. The solvation effects of the IL-CE mixture can also promote a smoother combustion process that minimizes NOx emissions**.**

c) Reduction in Carbon Monoxide (CO) and Hydrocarbons (HC)

CO and HC are other pollutants commonly produced by incomplete combustion. The reduction of these emissions is a key goal in improving diesel engine performance.

- **More Complete Combustion:** As IL-CE mixtures improve the fuel's atomization, vaporization, and ignition, the fuel undergoes more complete combustion, reducing the amount of CO and HC produced. The enhanced combustion efficiency ensures that the carbon in the fuel is oxidized more effectively, leading to fewer unburned hydrocarbons and lower CO emissions.
- **Improved Air-Fuel Mixing:** The better mixing of fuel and air, resulting from improved atomization and

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reduced viscosity, ensures that the combustion process is more efficient, reducing the likelihood of incomplete combustion and, consequently, the production of CO and HC.

3. Long-Term Impact on Fuel Economy and Environmental Sustainability

The long-term benefits of using binary mixtures of ILs and CEs are not limited to immediate improvements in engine efficiency and emission reductions. These mixtures offer significant potential for improving overall fuel economy and contributing to environmental sustainability in several ways:

a) Sustainable Fuel Use

- **Energy Savings:** The optimization of fuel combustion through IL-CE mixtures means that engines can achieve higher power output with less fuel consumption. This leads to reduced fuel use over time, translating into cost savings for consumers and less reliance on fossil fuels, contributing to a more sustainable energy system.
- **Renewable Additives:** Many ionic liquids and cyclic ethers are derived from renewable sources, making them a more sustainable alternative to traditional fuel additives. Their use reduces the carbon footprint of fuel production and supports the transition to greener, more sustainable fuels.

b. Reduction in Greenhouse Gas Emissions

- **Lower CO_2 Emissions:** More efficient combustion and better fuel economy result in less fuel consumption and lower CO_2 emissions per unit of power output. Reducing fuel consumption not only lowers operational costs but also reduces the environmental impact of transportation and industrial activities powered by diesel engines.

D) Effects of Binary Mixtures of Ionic Liquids and Cyclic Ethers on Combustion Behavior

The combustion behavior of fuels plays a central role in determining the efficiency, emissions, and operational characteristics of diesel engines. Binary mixtures of ionic liquids (ILs) and cyclic ethers (CEs) have gained considerable attention due to their ability to influence combustion properties in a way that optimizes performance, improves fuel efficiency, and reduces harmful emissions. The physical and chemical interactions between ILs and CEs in these mixtures—such as hydrogen bonding, solvation, and the modification of key fuel properties—can have a profound effect on the combustion process. This section will explore in greater detail how binary mixtures of ILs and CEs impact combustion behavior, including ignition characteristics, combustion efficiency, temperature control, and emissions.

1. Impact on Ignition Behavior

Ignition behavior is a crucial aspect of combustion, particularly in diesel engines, where spontaneous ignition of fuel after injection into the combustion chamber is essential. A delay in ignition or inconsistent ignition can lead to engine knocking, reduced power output, and increased fuel consumption. The ignition delay and behavior of binary mixtures of ILs and CEs are influenced by several factors, such as viscosity, volatility, solvation, and intermolecular interactions like hydrogen bonding.

a) Modification of Ignition Delay

The ignition delay, defined as the time between fuel injection and the start of combustion, is an important parameter in determining combustion efficiency and engine performance. A longer ignition delay can result in incomplete combustion and higher emissions, while a shorter delay can enhance efficiency and reduce the likelihood of engine knocking.

- **Reduced Ignition Delay**: Binary mixtures of ILs and CEs can reduce ignition delay by enhancing the fuel's volatility and improving the rate of vaporization. Cyclic ethers, such as tetrahydrofuran (THF), have relatively low boiling points compared to traditional diesel fuels, and they can help lower the overall volatility of the mixture, promoting faster vaporization. This, in turn, accelerates the ignition process.
- **Solvation Effects**: The interaction between IL ions and cyclic ether molecules can also influence the ignition delay. ILs tend to be good solvents for their ions, and the solvation of IL cations and anions by ether molecules can reduce the formation of ion pairs and promote a more uniform distribution of ions in the fuel mixture. This may enhance the combustion initiation process by facilitating quicker ionization, which is beneficial for fast ignition in diesel engines.
- **Hydrogen Bonding**: The hydrogen bonding between the cations of ILs (e.g., **$[C4mim]^+$**) and the oxygen atoms of cyclic ethers (such as THF or dioxane) can enhance the mixture's ability to vaporize rapidly. As the fuel reaches the optimal vaporization point sooner, the ignition process is initiated faster, shortening the ignition delay and improving combustion timing.

b) Impact on Flame Propagation

Flame propagation refers to the speed at which the combustion front moves through the air-fuel mixture in the combustion chamber. The rate of flame propagation affects the combustion stability and efficiency, with a slower flame speed leading to incomplete combustion and poor fuel economy.

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- **Faster Flame Propagation**: The reduction in ignition delay and the improved mixing of fuel and air due to better atomization can lead to faster and more stable flame propagation. IL-CE mixtures tend to improve the vaporization and atomization of the fuel, creating a more homogeneous air-fuel mixture. As a result, the combustion front moves more uniformly through the combustion chamber, ensuring that the fuel is fully combusted, thus enhancing power output and efficiency.
- **Optimized Combustion Control**: The ability to control flame propagation through better fuel atomization helps in optimizing the burn rate of the fuel, contributing to smoother combustion cycles. The use of ILs and CEs helps avoid abrupt changes in combustion pressure and temperature, which can lead to engine knocking or misfire.

2. Impact on Combustion Efficiency

Combustion efficiency refers to the extent to which the fuel is converted into usable energy in the form of work, with minimal loss to exhaust gases, heat, and unburned fuel. IL-CE mixtures improve combustion efficiency by optimizing the processes of atomization, vaporization, ignition, and mixing of the fuel with air.

a) Improved Atomization and Vaporization

- **Reduction in Viscosity**: The incorporation of cyclic ethers, which have lower viscosities than traditional diesel fuels, into binary mixtures with ILs helps reduce the overall viscosity of the fuel. This reduction enhances fuel atomization, ensuring that the fuel is broken into smaller droplets that are more easily vaporized in the high-temperature combustion environment.
- **Enhanced Vaporization**: Cyclic ethers like THF have lower boiling points than typical diesel fuels, and their presence in the mixture helps the fuel vaporize more readily. Faster vaporization ensures that the fuel droplets are adequately mixed with air, leading to more complete combustion. This means that more of the fuel's energy content is utilized for power generation, improving engine efficiency and reducing the need for excess fuel.
- **Uniform Fuel Distribution**: The hydrogen bonding and solvation interactions between ILs and CEs enhance the homogeneity of the fuel-air mixture. The improved distribution of fuel throughout the combustion chamber leads to more uniform ignition and combustion, which helps maximize energy extraction from the fuel, reducing energy waste and improving efficiency.

b) Control Over Combustion Temperature

Controlling the combustion temperature is crucial to maintaining engine efficiency and reducing harmful emissions. Excessively high combustion temperatures lead to the formation of nitrogen oxides (NOx), while lower temperatures may result in incomplete combustion and increased particulate matter (PM) emissions.

- **Stable Combustion Temperatures**: The better mixing and optimized combustion process facilitated by IL-CE mixtures result in more stable combustion temperatures. These mixtures help prevent large temperature fluctuations, which can contribute to both NOx and PM formation. By ensuring a more controlled combustion temperature profile, the IL-CE mixture helps maintain optimal engine performance while reducing the formation of harmful emissions.
- **Reduced Temperature Spikes**: Cyclic ethers, with their low boiling points, facilitate more even heat distribution during the combustion process. This leads to a smoother combustion cycle, where the heat produced is more evenly distributed, preventing the sharp temperature spikes that are often responsible for the production of NOx. Lower peak temperatures also reduce the rate of soot formation, contributing to cleaner combustion.

3. Impact on Emissions

The reduction of harmful emissions is one of the most important factors in the development of alternative fuels and fuel additives. The combustion behavior of IL-CE mixtures directly impacts the formation of emissions, including nitrogen oxides (NOx), particulate matter (PM), carbon monoxide (CO), and unburned hydrocarbons (HC).

a) Nitrogen Oxides (NOx) Reduction

NOx formation is largely influenced by combustion temperature; higher temperatures promote the reaction of nitrogen and oxygen in the air, forming NOx, which are harmful pollutants.

- **Lower Combustion Temperatures**: As previously discussed, the use of IL-CE mixtures helps lower peak combustion temperatures by improving fuel atomization, vaporization, and mixing. This results in less thermal NOx formation, which occurs predominantly at high combustion temperatures. By stabilizing combustion and controlling the temperature profile, IL-CE mixtures contribute to significant NOx reduction.
- **Optimized Ignition Control**: The reduction in ignition delay and smoother flame propagation also contribute to lower NOx emissions. A more controlled and efficient

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combustion process reduces the hot spots that are typically responsible for the excessive formation of NOx during the combustion cycle.

b) Particulate Matter (PM) Reduction

Particulate matter is mainly formed by incomplete combustion, particularly from the production of soot. IL-CE mixtures reduce soot formation by enhancing combustion efficiency and ensuring more complete fuel oxidation.

- **More Complete Combustion**: As IL-CE mixtures improve atomization, vaporization, and ignition, the fuel burns more completely, with fewer unburned carbon particles (soot) produced. This leads to a reduction in particulate emissions, which is vital for meeting strict emission regulations and reducing air pollution.
- **Enhanced Oxygen Availability**: The solvation and hydrogen bonding effects in IL-CE mixtures help to increase the availability of oxygen within the combustion chamber. More oxygen enables more thorough combustion, further reducing the formation of soot.

c) Carbon Monoxide (CO) and Hydrocarbons (HC) Reduction

CO and HC emissions are typically the result of incomplete combustion. By ensuring a more complete combustion process, IL-CE mixtures help reduce the production of these pollutants.

- **Reduced CO Emissions**: With more efficient combustion and faster ignition, IL-CE mixtures ensure that the carbon in the fuel is more completely oxidized to carbon dioxide (CO_2), reducing the formation of carbon monoxide (CO), which is a dangerous pollutant.
- **Reduced Hydrocarbons (HC)**: Similarly, the more uniform combustion facilitated by IL-CE mixtures reduces the likelihood of unburned hydrocarbons escaping the combustion process. The increased vaporization and improved air-fuel mixing ensure that the fuel undergoes complete combustion, thereby lowering HC emissions.

4. Overall Impact on Engine Performance

The improved combustion behavior of IL-CE mixtures results in a variety of benefits for diesel engines, including:

- **Increased Power Output**: More efficient combustion translates into greater power output from the same amount of fuel. The reduction in ignition delay, faster vaporization, and optimized combustion contribute to better engine performance and responsiveness.
- **Better Fuel Efficiency**: Improved combustion efficiency means that more of the fuel's energy is converted into mechanical energy, reducing the need for excess fuel and improving overall fuel economy.
- **Reduced Engine Knock**: The more controlled ignition and flame propagation reduce the likelihood of engine knock, which can cause damage to engine components and lead to reduced performance.
- **Cleaner Operation**: The reduction in NOx, soot, CO, and HC emissions ensures that the engine operates in a cleaner and more environmentally friendly manner, meeting increasingly stringent emission standards and reducing the engine's environmental impact.

III. Conclusion

The evaluation of diesel engine performance using binary mixtures of ionic liquids (ILs) and cyclic ethers (CEs) highlights a significant shift towards optimizing fuel efficiency, improving combustion characteristics, and mitigating harmful emissions. These mixtures offer a unique opportunity to enhance the performance of diesel engines by leveraging the molecular interactions between ILs and CEs to modify key fuel properties and optimize combustion behaviour. The findings from the research suggest that these mixtures can serve as effective additives, influencing several critical aspects of diesel engine operation. The molecular interactions, such as solvation, hydrogen bonding, and dipole-dipole interactions, between ILs and CEs play a pivotal role in altering the physical properties of diesel fuel, such as viscosity, volatility, surface tension, and lubricity. These changes lead to more efficient atomization, enhanced fuel vaporization, and improved mixing with air, all of which contribute to more efficient and complete combustion. The improved atomization of the fuel droplets, promoted by the IL-CE mixtures, results in smaller, more uniform droplets, increasing the surface area for combustion. This helps achieve more thorough and uniform fuel oxidation, leading to better energy conversion and enhanced engine performance.

From the perspective of combustion behaviour, IL-CE mixtures reduce ignition delay by improving the fuel's volatility and promoting faster fuel vaporization. The faster vaporization ensures quicker mixing with the air in the combustion chamber, resulting in timely and stable ignition. A shorter ignition delay leads to a more controlled combustion process, reducing the risks of engine knocking and improving overall fuel efficiency. Additionally, the controlled ignition timing and optimized flame propagation reduce the occurrence of incomplete combustion, which in turn reduces the formation of undesirable emissions like particulate matter (PM), nitrogen oxides (NOx), carbon monoxide (CO), and unburned hydrocarbons (HC). A key benefit of these mixtures

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lies in their ability to reduce emissions by lowering the combustion temperatures, which suppresses NOx formation. The improved combustion efficiency minimizes soot production, resulting in a cleaner engine operation. Furthermore, the smoother and more controlled combustion process ensures that the fuel's energy is used more efficiently, reducing fuel consumption while simultaneously decreasing the overall environmental impact. In terms of long-term performance, the use of binary mixtures of ILs and CEs also enhances the lubricity of the fuel. This reduces friction between engine components, such as injectors and fuel pumps, contributing to reduced wear and tear and, consequently, lower maintenance costs. The improved lubricity not only supports smoother engine operation but also extends the lifespan of engine components, leading to greater long-term operational efficiency and durability. Ultimately, the molecular interactions between ILs and CEs offer a multifaceted approach to improving diesel engine performance. These mixtures enhance combustion behaviour by optimizing fuel atomization, ignition, and vaporization, while also reducing harmful emissions and increasing fuel efficiency. By offering a route to both environmental and operational improvements, binary mixtures of ILs and CEs have the potential to revolutionize the performance and sustainability of diesel engines. As the development of these mixtures progresses, further research into their long-term impacts, optimal compositions, and full-scale applications will likely reveal even more opportunities to enhance diesel engine technologies and contribute to more sustainable transportation and energy systems.

In conclusion, the role of molecular interactions in the binary mixtures of ionic liquids and cyclic ethers provides a powerful tool in the evaluation and optimization of diesel engine performance. These mixtures not only improve fuel efficiency but also significantly reduce the environmental impact of diesel engines, offering a balanced solution to the growing demands for both performance enhancement and emission reduction in internal combustion engines.

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