TRIBOLOGICAL AND THERMAL PROPERTIES OF IONIC LIQUIDS

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Increasing the efficiency of existing refrigeration systems is possible if a new alternative refrigerant can be selected. An ideal refrigerant would be CO\(_2\) because it is a natural refrigerant with an extremely high efficiency. In an effort to use CO\(_2\) as a refrigerant, ionic liquid lubricants were considered to carry the CO\(_2\) and act as the working fluid. The thermal conductivity, viscosity, and pressure-viscosity coefficient were measured for several ionic liquids using a Unitherm Thermal Conductivity Measurement System, a viscometer, and an Elastohydrodynamic Lubrication (EHL) rig, respectively. The ionic liquids tested are 1-butyl-3-methylimidazolium-trifluoromethanesulfonate, tributyl(dodecyl)phosphonium 1,2,3-triazolide and trihexyl(tetradecyl)phosphonium 1,2,3-triazolide. Tests were also performed on paraffin, hexadecane, and dodecane for comparison. Results show that ionic liquids have the potential to be suitable lubricants.
## TABLE OF CONTENTS

Figures................................................................................................................................................... iv

Tables........................................................................................................................................................ vii

Acknowledgements................................................................................................................................... viii

Chapter 1: Introduction and Motivation ................................................................................................. 1
  1.1 Evolution of Refrigerants .................................................................................................................. 1
  1.2 Carbon Dioxide as a Refrigerant ..................................................................................................... 1
  1.3 Ionic Liquids as Co-fluids and Lubricants ....................................................................................... 2
  1.4 Project Overview .............................................................................................................................. 3

Chapter 2: Previous Research .................................................................................................................. 4
  2.1 Regimes of Lubrication ...................................................................................................................... 4
  2.2 Elastohydrodynamic Lubrication ....................................................................................................... 7
  2.3 Hertz Contact Theory ...................................................................................................................... 10
  2.4 Hamrock Dowson Theory ................................................................................................................. 12
    2.4.1 Hamrock Dowson for Hard EHL ............................................................................................. 13
    2.4.2 Hamrock Dowson for Soft EHL ............................................................................................. 14
  2.5 Lubricating Properties of Ionic Fluids ............................................................................................... 14
  2.6 Friction and Wear Performance of Ionic Fluids .............................................................................. 19
  2.7 Ionic Liquids as Co-fluids .................................................................................................................. 22
    2.7.1 Ionic Liquid Design and Modification ..................................................................................... 23
    2.7.2 CO₂ as a an Alternative to Current Refrigerants .................................................................... 24
    2.7.3 Viscosity of Ionic Liquid Mixtures ........................................................................................... 25

Chapter 3: Fundamental Liquid Properties .............................................................................................. 34
  3.1 Viscosity .......................................................................................................................................... 34
    3.1.1 Viscometer ............................................................................................................................... 34
    3.1.2 Results .................................................................................................................................... 35
  3.2 Thermal Conductivity ....................................................................................................................... 36
    3.2.1 Unitherm Thermal Conductivity Measurement System ....................................................... 36
    3.2.2 Results .................................................................................................................................... 38

Chapter 4: Tribological Properties of Ionic Fluids ................................................................................... 40
  4.1 EHL Ultra Thin Film Measurement System ..................................................................................... 40
FIGURES

Figure 2.1: A Stribeck curve shows the regimes of lubrication based on Hersey number and coefficient of friction [17]. ................................................................. 5

Figure 2.2: Regimes of lubrication. a) A full film, b) Mixed, and c) Boundary lubrication [17] ................................................................. 6

Figure 2.3: Comparison of film thickness profiles for piezoviscous and isoviscous liquids. Due to the increase in viscosity, film thickness is greater for piezoviscous liquids [17] ....................................................................................... 8

Figure 2.4: Comparison pressure profiles for piezoviscous and isoviscous liquids. A pressure spike occurs for the piezoviscous while the isoviscous liquid behaves according to Hertz contact theory [17] ........................................................................................................ 9

Figure 2.5: Mapper image of a lubricated contact ................................................................. 9

Figure 2.6: Inverse of film thickness profile as predicted using the code presented in Venner and Lubrecht, where film thickness is in nanometers .................................................................................. 10

Figure 2.7: Thermal conductivity values of CO₂ at 9 MPa [43] .............................................. 23

Figure 2.8: Predicted viscosity of a mixture of the ionic liquid (n-C₇H₁₅)(C₂H₅)(i-C₃H₇)₂N’N’(SO₂CF₃)₂ and tetraglyme, which decreases as the mole fraction of tetraglyme increases based on the Grunberg-Nissan equation using data from Sun [37] .............................................................................................................. 28

Figure 2.9: Viscosity predicted using the Grunberg-Nissan equation for a mixture of P66614 and tetraglyme with increasing mole fraction of tetraglyme for a range of G values, since the actual G value is unknown .............................................................................................................. 28

Figure 2.10: Bingham equation plotted using the viscosities of P66614 and tetraglyme ........................................... 29

Figure 2.11: Change in viscosity based on mole fraction for mixtures of ionic liquids mixed with water [35] .................................................................................................................. 30

Figure 2.12: Comparison of change in viscosity for an ionic liquid mixed with ethanol and water [45] .................................................................................................................. 30

Figure 2.13: Change in viscosity of an ionic liquid mixed with several other liquids [6] 31
Figure 2.14: Change in viscosity with mole fraction compared with the Bingham equation for a mixture of 2 ionic liquids [23].

Figure 2.15: Grunberg-Nissan equation plotted with experimental data for a mixture of P66614 and tetraglyme. Source: Data courtesy of Joseph Fillon, Chemical Engineering Department.

Figure 3.1: Ubbelohde viscometer used to measure viscosity [19].

Figure 3.2: Unitherm Thermal Conductivity Measurement System used for thermal conductivity measurements.

Figure 3.3: Schematic of Model 2022 Unitherm Thermal Conductivity System used to measure thermal conductivity of ionic liquids [41].

Figure 3.4: Schematic of the test section of the Model 2022 Unitherm Thermal Conductivity System [40].

Figure 3.5: Experimental thermal conductivity data for the ionic liquids Bmim, P66614, and P44412.

Figure 4.1: EHL Ultra Thin Film Measurement System from PCS Instruments, used to measure film thickness in a ball on disc geometry.

Figure 4.2: Schematic of EHL rig test area during a center film thickness test [13].

Figure 4.3: Ball carriage assembly used for all tests on the EHL rig. The ball rests on this assembly and rotates with the disc in the Center Film Thickness and Mapper tests and is driven independently for the Traction and Stribeck tests.

Figure 4.4: EHL rig set up for a film thickness measurement with the green spacer layer disc.

Figure 4.5: Schematic of optical interference technique used on the EHL rig. White light shines through a glass disk so part of the of the light is reflected back from the chromium layer on the disk while the rest goes through the layer and lubricant to be reflected off the steel ball. The light paths are recombined to form an interference image that passes through a spectrometer and high resolution CCD black and white camera. The image goes through a spectrometer and central film thickness is measured using software [10].

Figure 4.6: Images of the mapper test as rolling speed is increased from 0 mm/s to 1000.2 mm/s. As the speed increases, the constriction that develops at the trailing edge demonstrates the piezoviscous behavior of the liquid.

Figure 4.7: Traction and Stribeck tests use a ball driven by a motor and a highly polished steel disc.
Figure 4.8: Coefficient of friction measured by a Stribeck test, demonstrating that the coefficient of friction remains sufficiently low as the rolling speed is increased for a constant slide-to-roll ratio of 0.5. ..........................................................................................50

Figure 4.9: Traction test demonstrating the initial increase in friction coefficient as the slide to roll ratio is increased. ..........................................................................................51
### TABLES

Table 2.1 Lubricating properties of two polyalphaolefins as controls compared with two ionic liquids, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMI Im) and 1-butyl-3-methylimidazolium hexafluorophosphate (BMI PF₆) [34] 18

Table 2.2 Results of four-ball tests comparing the ionic liquids 1-ethyl-3-hexylimidiazolium tetrafluoroborate (L206) and 1-ethyl-3-octylimidazolium tetrafluoroborate (L208) to liquid paraffin containing 1% zinc dialkyldithiophosphate (LP+1%ZDDP) [24] .......................................................... 20

Table 2.3 Coefficient of friction for sliding pairs comparing an ionic liquid to 2 synthetic lubricants [47] ........................................................................................................... 21

Table 2.4 Comparison of GWP and ODP for common refrigerants and CO₂ [3] .......... 25

Table 2.5 Viscosity data for tetraglyme and the ionic liquid (n-C₇H₁₅)(C₂H₅)(i-C₃H₇)₂N⁺N⁻(SO₂CF₃)₂ [37] ........................................................... 27

Table 2.6 Viscosity values for P66614 and Tetraglyme used to generate Figure 2.8 using the Grunberg-Nissan equation ................................................................. 29

Table 3.1 Experimental viscosity data ...................................................................... 36

Table 4.1 Lubricating characteristics of the liquids tested ........................................... 46
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CHAPTER 1:
INTRODUCTION AND MOTIVATION

1.1 Evolution of Refrigerants

Some of the first successful refrigerants were \((\text{CH}_3\text{CH}_2)_2\text{O}\) and \(\text{NH}_3\) because of their low efficiencies. However, they are also both flammable, \((\text{CH}_3\text{CH}_2)_2\text{O}\) is explosive, and \(\text{NH}_3\) is poisonous [43]. In the 1930s, chlorofluorocarbons (CFCs), commercially known as Freon [8], became prevalent because they are non-toxic, non-combustible and chemically stable. However, the environmental effects of CFCs resulted in significant ozone depletion and the Montreal Protocol required that they be phased out [43]. Hydrochlorofluorocarbons (HCFCs) were considered next, but because of their high GWP, the Kyoto agreement determined that they were also not sustainable and needed to be replaced [29], creating the need for a new refrigerant that is both efficient and environmentally friendly.

1.2 Carbon Dioxide as a Refrigerant

Carbon dioxide \((\text{CO}_2)\) is an ideal refrigerant because it has a much higher coefficient of performance than previously considered refrigerants. While its high efficiency is what initially led to its consideration as a refrigerant, it is also natural, nontoxic, and non-flammable. Compared to existing refrigerants, the environmental effects of \(\text{CO}_2\) are not significant. \(\text{CO}_2\) is a greenhouse gas, but it has a GWP of 1, which
is thousands of times lower than that of R134a [3, 29]. Additionally, CO₂ released from many industrial processes can be recycled for use as a refrigerant [29]. However, the extremely high operating pressure required for CO₂, on the order of 1000 psi, eliminates it as a viable working fluid [29]. To use CO₂ as the working fluid, a new refrigeration system that operates at much higher pressures would need to be developed. However, if a viable liquid can be developed to carry the CO₂ and act as the working fluid for the refrigeration system, higher operating pressures would not be necessary. Dissolving CO₂ in a co-fluid could potentially result in an increased efficiency without requiring an increase in operating pressures.

1.3 Ionic Liquids as Co-fluids and Lubricants

Ionic liquids, which already have desirable characteristics including high thermal stability, nonvolatility, and low melting point, can be designed to have other characteristics, such as CO₂ solubility. For an ionic liquid to function as the working fluid in a refrigeration system, it must also be a suitable lubricant so that existing equipment can be used. Refrigerants are used as lubricants for machine elements, so it is important that the ionic liquid developed can serve as a lubricant so that current equipment will not require modification.

To determine which ionic liquid is most suitable for use as the co-fluid, lubricating properties of several ionic liquids were evaluated. The viscosities were measured and the pressure-viscosity coefficient of each was calculated using the Hamrock Dowson Equation [16] from the results of film thickness tests on an elastohydrodynamic lubrication (EHL) rig. Thermal conductivity tests were also performed on each of the ionic liquids considered.
1.4 Project Overview

In collaboration with the Chemical Engineering Department, the goal of this project was to determine a suitable ionic liquid to act as a co-fluid for CO$_2$. Viscosity, pressure-viscosity coefficient, and thermal conductivity of several ionic liquids were determined. The ionic liquids tested so far are 1-butyl-3-methylimidazolium-trifluoromethanesulfonate (Bmim), tributyl(dodecyl)phosphonium 1,2,3-triazolide (P44412) and trihexyl(tetradecyl)phosphonium 1,2,3-triazolide (P66614). Tests were also performed on paraffin, hexadecane, and dodecane for comparison, as they are more thoroughly understood liquids.
2.1 Regimes of Lubrication

The regimes of lubrication characterize load transfer between lubricated surfaces. The load can be supported entirely by asperities, by a combination of asperities and the lubricant, or entirely by the lubricant [17]. These regimes are called boundary lubrication, partial or mixed lubrication, and full film lubrication, respectively. Full film lubrication is sometimes further divided into thin-film and thick-film regimes [17].

The regimes of lubrication are demonstrated graphically by a Stribeck curve, showing the variation in friction coefficient as a function of Hersey number, shown in Figure 2.1. The Hersey number is

\[
\text{Hersey number} = \frac{\eta \omega}{p} \tag{2.1}
\]

where \(\eta\) is the viscosity, \(\omega\) is the rotational velocity, and \(p\) is the pressure [17].
Figure 2.1: A Stribeck curve shows the regimes of lubrication based on Hersey number and coefficient of friction [17].

Figure 2.2 also demonstrates the regimes of lubrication by showing the load support in each regime. In boundary lubrication, the load is supported entirely by the asperities in the contact and a boundary film on the surfaces acts as the lubricant. The rate of wear is very high in boundary lubrication, and the lubricant is a thin film on the surfaces of the contact with film thicknesses in the range of 1 to 10 nm [17]. The lubrication effectiveness is determined by the properties of the surfaces in contact that create the boundary film. Boundary lubrication occurs in a starved contact, when the load increases, speed decreases, or viscosity of the lubricant decreases. A starved contact occurs when the inlet is not fully flooded with lubricant and the minimum film thickness is affected [17]. Decreases in viscosity can result from rising temperature due to friction. In these conditions, the surfaces are sufficiently close to cause the monomolecular or
multimolecular films on each surface to come into contact [4]. These films act as the lubricant and protect the surfaces. Failure in this regime is caused by chemical, adhesive, and abrasive wear.

Figure 2.2: Regimes of lubrication. a) A full film, b) Mixed, and c) Boundary lubrication [17].

Lubrication is also quantified by the dimensionless film thickness parameter,

\[ \Lambda = \frac{h_{\text{avg}}}{\sqrt{R_{qu}^2 + R_{qb}^2}} \]  

(2.2)

where \( h_{\text{avg}} \) is the average film thickness, and \( R_{qu} \) and \( R_{qb} \) are the RMS surface roughnesses for the surfaces in contact. In boundary lubrication, the film thickness parameter is between 0 and 1. For mixed lubrication, it is between 1 and 3. In mixed lubrication, the lubricant and asperities each support part of the load and film thicknesses are typically between 0.01 and 1 µm.

Full film lubrication, also referred to as hydrodynamic lubrication, occurs when the lubricant supports the entire load, with a minimum film thickness greater than 1 µm for typical ground surfaces. The film thickness parameter is typically greater than 3. The load is fully supported by the lubricant and asperities rarely come into contact. In this regime, a layer of lubricant is pulled into the contact area where the pressure is sufficiently high to support the load. This is most common with highly viscous fluids or
under high operating speeds. In this lubrication regime, asperities do not come into contact, decreasing wear.

2.2 Elastohydrodynamic Lubrication

Elastohydrodynamic lubrication (EHL) occurs in non-conformal contacts when surface deformations become significant. This regime is found when a large load acts over a small contact between gear teeth or a bearing and its race, for example. In EHL, the high pressure in the contact elastically deforms the surfaces and can increase the viscosity of the lubricant [36]. This increase in viscosity is known as a piezoviscous. Two forms of EHL are commonly encountered, hard and soft, depending on both the materials in contact and the properties of the lubricant [17].

Hard EHL occurs for materials with a high elastic modulus, such as metals, and with piezoviscous lubricants. The maximum pressures in the contact typically reach 1 to 3 GPa [13], and the viscosity of the lubricant can vary up to 10 orders of magnitude [17]. Under these high pressures, the surface deformation can be several orders of magnitude larger than the minimum film thickness. The load does not significantly affect the film thickness in this regime, since deformation of the surfaces increases the contact area, spreading the load support.

In soft EHL with polymer or rubber materials, the deformations are much larger and the maximum pressures are much lower than in hard EHL [17]. Soft EHL occurs in materials with low elastic modulus, such as rubber, and occurs in seals and soft liners of bearings. Soft EHL can also occur in harder materials with isoviscous liquids when contact pressure is sufficiently high [7].
Because of the surface deformation in the elastohydrodynamic regime, the film thickness is greater in the center of the contact than at the trailing edge, as shown in Figure 2.3. The pressure spike, shown in Figure 2.4, is a result of piezoviscous flow and occurs only in hard EHL. The pressure spike occurs at a restriction in flow at the back side of the bearing; this is necessary to maintain the flow gradient throughout the bearing. This pressure spike is visible in an image of a contact between a ball and disc, shown in Figure 2.5. The lubricant gathers in the center of the contact, and the constriction and pressure spike are visible on the trailing edge of the contact.

Figure 2.3: Comparison of film thickness profiles for piezoviscous and isoviscous liquids. Due to the increase in viscosity, film thickness is greater for piezoviscous liquids [17].
Figure 2.4: Comparison pressure profiles for piezoviscous and isoviscous liquids. A pressure spike occurs for the piezoviscous while the isoviscous liquid behaves according to Hertz contact theory [17].

Figure 2.5: Mapper image of a lubricated contact.
This behavior can also be predicted by solving the Reynold’s equation for elastohydrodynamic lubrication [42]. Figure 2.6 shows the predicted film thickness obtained using the multilevel grid method presented by Venner and Lubrecht for these calculations [42].

![Figure 2.6: Inverse of film thickness profile as predicted using the code presented in Venner and Lubrecht, where film thickness is in nanometers.](image)

2.3 Hertz Contact Theory

Hertz contact theory involves the stresses in a contact between two nonconformal elastic solids, developed by Heinrich Hertz in 1888 while he was studying the contact of optical lenses and flats [21]. The assumptions necessary for Hertz contact analysis are [21]:

1. Contacting surfaces are continuous and non-conforming;
2. Strains are very small;
3. Contacting solids are considered as elastic half-spaces;
4. There is no friction between the surfaces.

In order for the assumption of elastic half spaces to be valid, the dimensions of the contact area must be small compared to both the dimensions of the bodies and the radii of curvature of the bodies. Hertz contact theory can be used to predict the pressure distribution in a contact, the deformation of the surfaces, and the size of the contact.

The pressure distribution predicted by Hertz contact is,

\[ p = p_0 \left[ 1 - \left( \frac{r}{a} \right)^2 \right]^{3/2} \]  \hspace{1cm} (2.3)

where \( p_0 \) is the maximum contact pressure, \( r \) is the distance from the center of the contact, and \( a \) is the radius of the contact area. The radius of the contact can be determined using the material properties and dimensions of the surfaces in contact. For the case of two contacting spheres, the contact radius is calculated using the equation,

\[ a = \left( \frac{3PR}{4E'} \right) \]  \hspace{1cm} (2.4)

where \( P \) is the applied load, \( R \) is the effective radius, and \( E' \) accounts for the material properties of the materials in contact [21]. The value of \( E' \) is calculated as

\[ \frac{1}{E'} = \frac{1-v_1^2}{E_1} + \frac{1-v_2^2}{E_2} \]  \hspace{1cm} (2.5)

where \( E_1 \) and \( E_2 \) are the elastic moduli and \( v_1 \) and \( v_2 \) are the Poisson’s ratios of the materials in the contact.

The pressure in a contact in EHL matches Hertz theory in general, but also includes a pressure spike. For a lubricant that is piezoviscous, pressure develops in the entry of the contact because of hydrodynamic effects. This leads to a significant increase in viscosity. At the end of the parallel zone, there is a decrease in viscosity in order to
maintain a finite pressure [12]. The behavior at the inlet and exit of the contact are joined with a discontinuity in the slope of the surface, causing the pressure spike that indicates EHL. This pressure spike is required to maintain flow throughout the contact because of the constriction. The reason for this constriction is that Grubin’s parallel zone approximation does not apply at the exit. Greenwood realized the pressure gradient is negative in this region, so the film thickness must be smaller than the film thickness in the parallel zone [12]. The minimum film thickness in the contact occurs at the constriction and is often 75-80% of the film thickness in the parallel zone [21].

Figures 2.3 and 2.4 show the difference in behavior between piezoviscous and isoviscous liquids. The piezoviscous liquid experiences a pressure spike at the trailing edge of the contact while the isoviscous liquid behaves according to Hertz contact theory, as shown in Figure 2.4. Figure 2.3 shows greater film thickness with the piezoviscous liquid due to the increase in viscosity. As the viscosity increases under pressure, the deformation of the contacting surfaces supports the load and the film thickness increases.

2.4 Hamrock Dowson Theory

Hamrock and Dowson created non-dimensional parameters to describe the speed, load, and material parameters of contacting surfaces, to determine how each of the parameters affected the minimum film thickness for a fully flooded EHL contact [17]. They developed equations to predict the central film thickness and the minimum film thickness for both hard and soft EHL, which exhibit different behavior based on the contacting materials. Soft EHL occurs for isoviscous liquids and in materials with a low elastic modulus, such as rubber, and hard EHL occurs for piezoviscous liquids and materials with properties similar to metals.
There are separate Hamrock Dowson equations for both soft and hard EHL. The Hamrock Dowson equation relates film thickness to dimensionless parameters associated with the system. The dimensionless parameters used are the speed parameter,

\[ U = \frac{u \eta_0}{E' R_x} \]  

(2.6)

where \( u \) is the rolling speed, \( R_x \) is the effective radius in the \( x \) direction, and \( \eta_0 \) is the viscosity of the lubricant. The load parameter is

\[ W = \frac{w}{E' R_x^2} \]  

(2.7)

where \( w \) is the applied load, \( E' \) is the effective modulus of elasticity, and \( R_x \) is the effective radius in the \( x \) direction. The material parameter is

\[ G = \alpha E' \]  

(2.8)

where \( \alpha \) is the pressure-viscosity coefficient and \( E' \) is the effective modulus of elasticity.

2.4.1 Hamrock Dowson for Hard EHL

In hard EHL, pressures reach 1 to 3 GPa with a film thickness generally greater than 0.1 \( \mu m \) [17]. The Hamrock Dowson equation for hard EHL is

\[ h_{\text{min}} = R_x 3.63 U^{0.68} G^{0.49} W^{0.073} (1 - e^{-0.68k}) \]  

(2.9)

In order to develop this equation, Hamrock and Dowson varied the dimensionless parameters for 34 cases based on geometries ranging from a ball on a plane to a rectangular contact for hard EHL [17]. The speed parameter varied over two orders of magnitude and the load parameter was varied over one full order of magnitude. This procedure incorporated simultaneous solutions of the Reynolds, rheology, and elasticity equations to calculate the minimum film thickness in a contact. Using this same method,
a Hamrock Dowson equation for central film thickness was also developed where the central film thickness could be predicted as

\[ h_c = R_x 2.69 U^{0.67} G^{-0.53} W^{-0.067} \left(1 - 0.61 e^{-0.73k}\right), \]  

using the same dimensionless parameters as before [17].

2.4.2 Hamrock Dowson for Soft EHL

In soft EHL involving soft polymers or rubbers, deformations are very large and pressures only reach around 1 MPa with film thicknesses less than 1 \( \mu \text{m} \) [17]. The viscosity in the contact is not significantly affected. The film thickness in soft EHL is dependent on the same speed and load parameters as hard EHL, but is not dependent on the material parameter, because there is no pressure-viscosity coefficient for isoviscous liquids. The Hamrock Dowson equation for minimum film thickness for soft EHL is,

\[ h_{\text{min}} = 7.43 U^{0.65} W^{-0.21} (1 - 0.85 e^{-0.31k}). \]  

and the center film thickness prediction for soft EHL is

\[ h_c = 7.32 \left(1 - 0.72 e^{-0.28k}\right) U^{0.64} W^{-0.22}. \]

2.5 Lubricating Properties of Ionic Fluids

Ionic liquids were first considered as lubricants in 2001 because of their nonvolatility, thermal stability, nonflammability, and low melting point [27, 33]. They have viscosities similar to oil and densities between 1 and 1.6 g/cm\(^3\) [26]. Studies have been conducted measuring film thickness of ionic liquids as lubricants. However, most studies conducted are difficult to compare because researchers use their own nonstandard methods, so there is a need for more standardized testing of ionic liquids as lubricants.
Additionally, the focus in many studies involving ionic liquids has been on chemistry and how to select the best anion to achieve certain characteristics [27]. The focus has also been on what will result in the best protective film on the surfaces in contact since the success of an ionic liquid as a lubricant often depends on this layer. Because ionic liquids have only recently been investigated as lubricants, researchers have focused on developing stable ionic liquids, considering chemical properties and whether hydrophobic or hydrophilic anions should be used. These are valid concerns for boundary lubrication, and important for machine startup. However, for typical operating conditions where EHL is important, pressure-viscosity coefficient will need to be considered in chemical synthesis.

More theoretical than experimental work has been done to determine pressure-viscosity coefficients for ionic liquids, but these theoretical values are typically 2.9 to 4 times higher than the few published experimental values [31]. In general there is little experimental data regarding ionic liquids as lubricants under high pressure.

Due to the variation in ionic liquids and the ability to control their properties, application-specific ionic liquids can be developed. Ionic liquids can be designed to have certain properties under different conditions, including high temperatures and pressures [1]. Based on the wide range of modifiable properties, developing an ionic liquid with high CO\textsubscript{2} solubility, desirable lubricating characteristics, and thermal properties comparable to existing refrigerants is a possibility.

Ionic liquids successfully form films between contacting surfaces, making them viable lubricants. In the contact area, ionic liquids can form cationic and anionic supramolecular aggregates [44]. These supramolecular aggregates form when the packing
density becomes high, resulting in an increase in viscosity because a larger force is required to move the liquid [44]. In a study by Qu et. al, in a ball-on-flat sliding test, it was determined that boundary film formation is dependent on mechanical stresses and thermal effects of the testing [33]. The mean film thicknesses measured were 60 nm, 200 nm, and 300 nm for steel, aluminum, and cast iron, respectively, where film thickness was measured with an SEM [33].

Xiao performed experiments measuring film thickness using optical interference intensity. They reported a nearly linear relationship between the log of film thickness and log of rolling speed. Additionally, the studies determined that film thickness decreases with pressure [44]. Film thickness measurements match linear curve fitting of log film thickness plotted against log speed above a critical speed, referred to as the critical film thickness. Experiments also showed that film thickness in elastohydrodynamic lubrication is related to viscosity. The study determined that film thickness increases with speed and decreases with applied pressure. The key result was that the ionic liquids studied had greater film thicknesses than silicone oils with similar viscosities [44].

Film thickness tests performed on an elastohydrodynamic lubrication (EHL) rig showed that ionic liquids have pressure-viscosity coefficients similar to hydrocarbons, with measured film thicknesses on the order of 100 nm. An elastohydrodynamic rig measures the film thickness between a steel ball and glass disc using optical interferometry. Pressure-viscosity coefficients were calculated by measuring the film thickness, then comparing that to the pressure-viscosity coefficient of a known liquid. The following equation was used to compare the two liquids to determine the pressure-viscosity coefficient,
\[
\frac{h}{h_{\text{ref}}} = \frac{(u\eta)\alpha^{0.53}}{(u\eta_{0.67}^0.53)_{\text{ref}}},
\]

(2.13)

where \( h \) is the film thickness, \( \alpha \) is the pressure-viscosity coefficient, \( u \) is the entrainment velocity, and \( \eta_0 \) is the viscosity [34].

In the same study, traction curves were created by measuring the friction coefficient using a similar set up on an EHL rig, in which the glass disc was replaced with a hardened steel disc and the slide-to-roll ratio between the ball and disc was varied. The ball and disc were driven independently to create the desired slide to roll ratio that increased from 0 to 0.5 during the test. Traction and Strubeck tests determined that ionic liquids are similar to polyalphaolefins [34]. The difference between the Strubeck test and the traction test was that in the Strubeck test, the slide to roll ratio remained constant at 0.5 while the speed increased slowly throughout the test. Like in Figure 2.1, the system transitioned from boundary lubrication, to mixed, and finally to hydrodynamic lubrication. Results from these tests are shown in Table 2.1.

Results from one study testing ionic liquids using an EHL rig demonstrated that the pressure-viscosity coefficients of BMI PF\(_6\) and EMI Im, two ionic liquids, are within the range of values for hydrocarbon base oils [34]. These ionic liquids exhibited lubricating properties similar to hydrocarbon base oils. Unlike other studies considering ionic liquids as lubricants, no preferential boundary layer was formed on either of the surfaces in contact. This study determined that ionic liquids could be suitable for use as lubricants because of their similarities to polyalphaolefins.
TABLE 2.1

LUBRICATING PROPERTIES OF TWO POLYALPHAOLEFINS AS CONTROLS COMPARED WITH TWO IONIC LIQUIDS, 1-ETHYL-3-METHYLLIMIDAZOLIUM BIS(TRIFLUOROMETHYLSULFONYL)IMIDE (EMI IM) AND 1-BUTYL-3-METHYLLIMIDAZOLIUM HEXAFLUOROPHOSPHATE (BMI PF₆) [34]

<table>
<thead>
<tr>
<th></th>
<th>Density [g/cm³]</th>
<th>Viscosity [mm²/s]</th>
<th>Pressure-Viscosity Coefficient [Pa⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAO A</td>
<td>0.80</td>
<td>15.2</td>
<td>1.2e-08</td>
</tr>
<tr>
<td>PAO B</td>
<td>0.83</td>
<td>68.5</td>
<td>1.7e-08</td>
</tr>
<tr>
<td>EMI Im</td>
<td>1.5</td>
<td>12.3</td>
<td>7.0e-09</td>
</tr>
<tr>
<td>BMI PF₆</td>
<td>1.3</td>
<td>78.7</td>
<td>1.1e-08</td>
</tr>
</tbody>
</table>

The two most important fluid parameters in characterizing the extent of lubrication are pressure-viscosity coefficient and viscosity at atmospheric pressure based on the Hamrock Dowson equation. While the viscosity at atmospheric pressure can be easily measured using a viscometer, the pressure-viscosity coefficient is more complicated to quantify, but can be determined using an EHL rig. Many studies have calculated this value theoretically, but an EHL rig gives a much more accurate value. Using optical interferometry, Gunsel measured film thickness. With these results, the pressure-viscosity coefficient was then determined from the equation

\[
h \propto \left( \frac{u_0 \eta_0}{w^{0.1}} \right)^{0.7} \alpha^{0.5}, \tag{2.14}\]

where \( h \) is the film thickness, \( U \) is the entrainment speed, \( \alpha \), the only unknown is the pressure-viscosity coefficient, and \( w \) is the applied load [13]. The results of these tests show a linear increase of log of film thickness with log of speed for several base oils.
Further tests need to be completed measuring film thickness and characterizing ionic liquids as lubricants. While the pressure-viscosity can be calculated using one of several different equations once the film thickness has been measured on an EHL rig, in all cases it is dependent on load, viscosity, entrainment speed, and film thickness.

To date, few studies measuring film thickness of ionic liquids have been conducted, as the focus has been predominately on chemical properties. Several studies have calculated pressure-viscosity coefficients based on density and viscosity measurements, but due to cost and equipment complexity, experimental values of pressure-viscosity coefficient are limited. The results of such studies are that thicker film thicknesses correspond to higher pressure-viscosity coefficients. However, higher viscosity results in an increase in friction [34]. Low pressure-viscosity coefficients decrease friction and stresses below the surfaces in contact. The two properties that best quantify film-generating capability are pressure-viscosity coefficient and viscosity. Because an increase in pressure-viscosity coefficient also corresponds to an increase in viscosity and an eventual increase in friction, the ideal properties are not straightforward.

2.6 Friction and Wear Performance of Ionic Fluids

Wear tests have been much more common than film thickness measurements to evaluate lubricating properties of ionic liquids. Four-ball tests and oscillating friction tests have been performed. One study comparing two ionic liquids with engine oil reported that friction coefficient was lower with the ionic liquids than with engine oil [32]. Like the results of many ionic liquid studies, these results were attributed to the boundary formed by the ionic liquid interacting with the surfaces in contact. This boundary layer was also reported in a four-ball wear test comparing three ionic liquids to
traditional lubricants. The ionic liquids exhibited higher load carrying potential, as shown in Table 2.2, and were adsorbed on the surfaces creating a lubricating boundary layer [24].

**TABLE 2.2**

RESULTS OF FOUR-BALL TESTS COMPARING THE IONIC LIQUIDS 1-ETHYL-3-HEXYLIMIDIAZOLIUM TETRAFLUOROBORATE (L206) AND 1-ETHYL-3-OCTYLIMIDIAZOLIUM TETRAFLUOROBORATE (L208) TO LIQUID PARAFFIN CONTAINING 1% ZINC DIALKYL DITHIOPHOSPHATE (LP+1%ZDDP) [24]

<table>
<thead>
<tr>
<th>Load [N]</th>
<th>Friction Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L206</td>
</tr>
<tr>
<td>196</td>
<td>0.039</td>
</tr>
<tr>
<td>294</td>
<td>0.058</td>
</tr>
<tr>
<td>392</td>
<td>0.054</td>
</tr>
<tr>
<td>490</td>
<td>0.045</td>
</tr>
<tr>
<td>588</td>
<td>0.039</td>
</tr>
<tr>
<td>686</td>
<td>0.037</td>
</tr>
<tr>
<td>784</td>
<td>0.037</td>
</tr>
</tbody>
</table>

Another study reported this boundary film on the surfaces of several metals in wear tests with ionic liquids and suggested that ionic liquids should be used as lubricant additives [25]. Tests compared the ionic liquid 1-ethyl-3-hexylimidiazolium hexafluorophosphate with varying amounts of the additive benzotriazole with dibasic acid esters with benzotriazole as a control. Wear tests were performed on an SRV oscillating friction and wear tester and showed that the wear volume for ionic liquids is much lower than wear volume for traditional lubricants [25]. The coefficient of friction
was also substantially lower for the 1-ethyl-3-hexylimidazolium hexafluorophosphate than for the dibasic acid esters.

Experiments have shown that ionic liquids can be used as base oils, additives, and lubricants. They can be used to lubricate a variety of pairs of engineering materials, including steel/steel, ceramic/ceramic, and steel/aluminum contacts [25]. For these surfaces, the coefficient of friction is lower with ionic liquids compared with synthetic lubricants, as shown in Table 2.3. The friction coefficient for the ionic liquid is consistently the lowest [47]. Additionally, the load carrying capacity of the ionic liquid, [C$_2$C$_6$im]BF$_4$, was much higher than that of the synthetic lubricants, PFPE and X-1P. While the synthetic oils could only carry 300 and 400 N before failing, the ionic liquid was able to support 600 N with a very low coefficient of friction [25].

**TABLE 2.3**

**COEFFICIENT OF FRICTION FOR SLIDING PAIRS COMPARING AN IONIC LIQUID TO 2 SYNTHETIC LUBRICANTS [47]**

<table>
<thead>
<tr>
<th>Load [N]</th>
<th>Friction Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[C$_2$C$_6$im]BF$_4$</td>
</tr>
<tr>
<td>200</td>
<td>0.060</td>
</tr>
<tr>
<td>300</td>
<td>0.055</td>
</tr>
<tr>
<td>400</td>
<td>0.050</td>
</tr>
<tr>
<td>500</td>
<td>0.045</td>
</tr>
<tr>
<td>600</td>
<td>0.045</td>
</tr>
</tbody>
</table>

Wear tests of ionic liquids in titanium/steel contacts also show a reduction in friction coefficient as compared to mineral oils. In a test comparing 6 ionic liquids to mineral oil as a lubricant between AISI 52100 steel and grade 3 titanium at room
temperature, all but one ionic liquid resulted in a 60% decrease in friction compared to the mineral oil [20]. In oscillating friction tests and ball on disc tests, synthetic ionic liquids reduce friction more effectively at high temperatures than at room temperature [48]. There are many studies comparing ionic liquids to standard lubricants in friction tests and ionic liquids designed to be lubricants typically perform better.

2.7 Ionic Liquids as Co-fluids

Ionic liquids can be used as the refrigerant in a refrigeration cycle in an effort to eliminate the harmful environmental effects of current refrigerants. In order to prevent ozone layer depletion, there was initially a shift from using R12 to R134a as a refrigerant. However, R134a will likely be phased out as well due to its high global warming potential [15, 46]. An ideal refrigerant would be CO$_2$, a natural refrigerant that is nontoxic, nonflammable, and inexpensive, with thermal conductivity data shown in Figure 2.7 [30, 43]. The refrigerating capacity per unit volume of CO$_2$ is close to 8 times higher than that of R134a, with a global warming potential that is 3100 times less than that of R134a [15]. For these reasons, CO$_2$ is being explored as a possible replacement for R134a to decrease environmental impact and increase the efficiency of existing refrigeration systems. Natural refrigerants were not considered before the environmental impact of chlorofluorocarbons and hydrochlorofluorocarbons were known because of the lower efficiency associated with them.
The challenge that arises when CO\textsubscript{2} is used as a refrigerant is that it requires extremely high operating pressures. In order to benefit from the refrigeration capabilities, using a co-fluid with CO\textsubscript{2} was considered to avoid high operating pressures. This co-fluid would have to reversibly absorb CO\textsubscript{2} in addition to having good lubricating properties. In a proof of concept study, Yongming et al. tested a co-fluid of CO\textsubscript{2} and C\textsubscript{5}H\textsubscript{9}NO in a current R134a vapor compression system [46]. While the coefficient of performance, which is the ratio of the cooling output to the energy input into the cycle, was lower than what is possible with R134a, this study determined that it is possible to use CO\textsubscript{2} as a refrigerant in a co-fluid.

2.7.1 Ionic Liquid Design and Modification

Ionic liquids are desirable as co-fluids because they can be designed to have specific characteristics based on the application. In a study by Oh et al. CO\textsubscript{2} was combined with polyol ester oils and polyalkylene glycol oil to reduce the operating
pressure requirements in a scroll compressor [30]. These liquids were selected for their lubricating properties, as the wear in a scroll compressor is very high. However, by increasing pressure, more CO$_2$ was dissolved in the polyol ester oil, which decreased the viscosity [30]. This was not an issue for the polyalkylene glycol oil, as the amount of dissolved CO$_2$ was constant for all pressures. This study showed that using a co-fluid with CO$_2$ has potential, but the liquids tested did not have the necessary properties. Because ionic liquids can be synthesized with very specific characteristics, they are considered here for use with CO$_2$ as co-fluids. Ionic liquids can be designed to have good lubricating properties. Wear reductions up to 99.5% compared to mineral oil have been measured with chloride imidazolium ionic liquids [20].

Ionic liquids can be modified to improve both their CO$_2$ solubility and lubricating properties. The anion in an ionic liquid has the greatest effect on CO$_2$ solubility, but there are many modifications that can be made to improve the CO$_2$ solubility of a given ionic liquid [28]. Anions containing fluoroalkyl groups have the highest CO$_2$ solubility, so increasing the number of fluoroalkyl groups increases CO$_2$ solubility [28]. Increasing the alkyl chain length on the cation also increases the CO$_2$ solubility. Adding ether groups in the alkyl chain increases the flexibility of the alkyl chain, which increases the free volume, leading to higher CO$_2$ solubility. While ionic liquids with a high level of fluorination also have improved CO$_2$ solubility, they may have more negative environmental effects [28].

2.7.2 CO$_2$ as a an Alternative to Current Refrigerants

CO$_2$ is a desirable alternative to current refrigerants because it is inorganic, non-toxic, and non-flammable [3]. It also exhibits an improved ODP, as shown in Table 2.4.
Even though the GWP is comparable, the recycled CO₂ can be used as refrigerants, and very little would be released into the air. The low specific volume of CO₂ means that a smaller volume would be required compared to current refrigerants [3]. Additionally, CO₂ has better thermo-physical properties at low temperatures compared to traditional refrigerants. At a given saturation temperature, the liquid viscosity, surface tension, and ratio of liquid to vapor density are all smaller than current refrigerants [2].

<table>
<thead>
<tr>
<th>Refrigerant</th>
<th>GWP</th>
<th>ODP</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCFC</td>
<td>0.05</td>
<td>3800</td>
</tr>
<tr>
<td>CFC-11</td>
<td>1</td>
<td>8100</td>
</tr>
<tr>
<td>CFC-12</td>
<td>1</td>
<td>9300</td>
</tr>
<tr>
<td>CFC-115</td>
<td>0.6</td>
<td>400-1800</td>
</tr>
<tr>
<td>CO₂</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

2.7.3 Viscosity of Ionic Liquid Mixtures

To date, ionic liquids developed to have ideal CO₂ carrying properties have been found to be quite viscous, with viscosities of up to 1000 mPa·s. It is important that the ionic liquid co-fluid selected has a sufficiently low viscosity so that it can be pumped through the compressor of an existing refrigeration system. In order to decrease the viscosity of an ionic liquid, it can be mixed with a less viscous ionic liquid or tetra glyme, an ethylene oxide based solvent [39]. Tetraglyme has good thermal and chemical stability so it can be used as a lubricant for refrigeration cycles. Mixing tetraglyme with ionic liquids could decrease the viscosity without diminishing the lubricating capabilities.
Viscosity predictions based on published data and equations that predict viscosity indicate that there is potential for drastically reduced viscosity when a small mole fraction of tetraglyme is added to an ionic liquid that has been designed to carry CO₂.

The Grunberg-Nissan equation has been determined to be the best equation for predicting viscosity of a mixture based on a comparison of 25 different equations completed by Irving in 1977 [38]. The equation determines the viscosity based on mole fraction and viscosities of the liquids in the mixture and can be written as

\[ \ln \eta_m = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G, \]  \hspace{1cm} (2.15)

where \( \eta_m \) is the viscosity of the mixture, \( \eta_1 \) and \( \eta_2 \) are the viscosities of the liquids in the mixture, and \( x_1 \) and \( x_2 \) are the mole fractions of the liquids. The value of \( G \) is an approximate measure of interaction strength between the two liquids.

Using the data in Table 2.5 reported by Sun, the Grunberg-Nissan equation can predict the viscosity of the mixture for any mole fraction of tetraglyme added to the ionic liquid \((n-\text{C}_7\text{H}_{15})(\text{C}_2\text{H}_5)(\text{i-}\text{C}_3\text{H}_7)_2\text{N}^+\text{N}^-\text{(SO}_2\text{CF}_3)_2\) [37]. The value of \( G \) was calculated to be 1.523 based on this data and was used to generate the plot in Figure 2.8. Reported values of \( G \) for binary mixtures, not including ionic liquids, range from about -1 to 7, so the value of 1.523 is reasonable [11].

In order to determine the effect of \( G \) and estimate the viscosity of mixing P66614 and tetraglyme, viscosity predictions with \( G \) values ranging from -1 to 5 were plotted in Figure 2.9. Viscosities of P66614 and the much less viscous tetraglyme are given in Table 2.6. Figure 2.9 shows that there is potential to significantly decrease the viscosity of P66614 if the actual value of \( G \) is sufficiently low. Because the value of \( G \) for the ionic liquid \((n-\text{C}_7\text{H}_{15})(\text{C}_2\text{H}_5)(\text{i-}\text{C}_3\text{H}_7)_2\text{N}^+\text{N}^-\text{(SO}_2\text{CF}_3)_2\) is 1.523, it is likely that the value of \( G \)
for P66614 could be low enough. This would result in a substantial decrease in viscosity as predicted by the Grunberg-Nissan equation.

TABLE 2.5

VISCOSITY DATA FOR TETRAGLYME AND THE IONIC LIQUID (N-
C7H15)(C2H5)(i-C3H7)2N+:+N- (SO2CF3)2 [37]

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Viscosity [mPa•s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetraglyme</td>
<td>3.5</td>
</tr>
<tr>
<td>(n-C7H15)(C2H5)(i-C3H7)2N+:+N- (SO2CF3)2</td>
<td>75.5</td>
</tr>
<tr>
<td>(n-C7H15)(C2H5)(i-C3H7)2N+:+N- (SO2CF3)2 with 40 wt% tetraglyme</td>
<td>17</td>
</tr>
</tbody>
</table>

While the Grunberg-Nissan equation is considered the best, other relationships have successfully predicted the behavior of mixtures with ionic liquids. The Bingham equation,

\[ \frac{1}{\eta} = \sum_{i=1}^{2} \frac{x_i}{\eta_i}, \]

(2.16)

where \( \eta_i \) and \( x_i \) are the viscosity and mole fraction of each liquid in the mixture, also fits published data for ionic liquids [23]. The Bingham equation predicts a rapid initial decrease in viscosity when tetraglyme is added, as shown in Figure 2.10. This suggests that adding small amounts of tetraglyme could significantly decrease the viscosity of P66614.
Figure 2.8: Predicted viscosity of a mixture of the ionic liquid \((\text{n-C}_7\text{H}_{15})\)(\text{C}_2\text{H}_5)(\text{i-C}_3\text{H}_7)_2\text{N}^+\text{N}^-\text{(SO}_2\text{CF}_3)_2\) and tetraglyme, which decreases as the mole fraction of tetraglyme increases based on the Grunberg-Nissan equation using data from Sun [37].

Figure 2.9: Viscosity predicted using the Grunberg-Nissan equation for a mixture of P66614 and tetraglyme with increasing mole fraction of tetraglyme for a range of \(G\) values, since the actual \(G\) value is unknown.
TABLE 2.6
VISCOSITY VALUES FOR P66614 AND TETRAGLYME USED TO GENERATE FIGURE 2.8 USING THE GRUNBERG-NISSAN EQUATION

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Viscosity [mPa•s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P66614</td>
<td>494.9</td>
</tr>
<tr>
<td>Tetraglyme</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Figures 2.10-2.13 show theoretical predictions in change in viscosity for mixtures. Experimental data of mixtures does not show such a significant initial decrease in viscosity, but the difference in the viscosities of the compared liquids was much smaller. Because P66614 has a viscosity two orders of magnitude higher than tetraglyme, the Bingham equation predicts a sudden decrease in viscosity for this mixture.
Figure 2.11: Change in viscosity based on mole fraction for mixtures of ionic liquids mixed with water [35].

Figure 2.12: Comparison of change in viscosity for an ionic liquid mixed with ethanol and water [45].
Figure 2.13: Change in viscosity of an ionic liquid mixed with several other liquids [6].

Figure 2.14 is a plot of viscosity data for a mixture of two ionic liquids reported by Larriba et. al. This data fits the Bingham equation and indicates that the Bingham equation could be used to predict the viscosity of ionic liquids [23]. Figure 2.12 shows that adding either ethanol or water can also lower the viscosity of an ionic liquid [45]. Further evidence that creating a mixture with an ionic liquid can decrease the viscosity of is shown in Figure 2.13, where ionic liquids are mixed with less viscous liquids [6].

Based on published results and predicted viscosity-mole fraction relationships, it is possible that adding a small amount of tetraglyme could sufficiently decrease the viscosity of the ionic liquid. The experiments in the literature were performed using liquids with viscosities that were within one order of magnitude of each other, while the
viscosities of tetraglyme and P66614 are three orders of magnitude apart. This could lead to different results that may not fit the Bingham or Grunberg-Nissan equation.

![Figure 2.14: Change in viscosity with mole fraction compared with the Bingham equation for a mixture of 2 ionic liquids [23].](image)

Using experimental viscosity data for a mixture of P66614 and tetraglyme at 25°C, the $G$ value was calculated for the Grunberg-Nissan equation for each data point and plotted in Figure 2.15. While more data is needed for small mole fractions of tetraglyme, this data suggests that adding small amounts of tetraglyme could significantly decrease the viscosity of an ionic liquid such as P66614.
Figure 2.15: Grunberg-Nissan equation plotted with experimental data for a mixture of P66614 and tetraglyme. Source: Data courtesy of Joseph Fillion, Chemical Engineering Department.
CHAPTER 3:
FUNDAMENTAL LIQUID PROPERTIES

3.1 Viscosity

In order to characterize the ionic liquids as a lubricant, the absolute viscosity must be determined. Newton’s postulate defines viscosity as

\[ \eta = \frac{\tau}{s}, \] (3.1)

where \( \tau \) is the shear stress and \( s \) is the shear strain rate. Viscosity is a measure of a liquid’s resistance to flow, with low viscosities associated with liquids that flow easily. Viscosity is important in lubrication, as an increase in viscosity results in an increase in friction \([17]\). However, if a lubricant is too inviscid, the film will not be thick enough to help support the load.

3.1.1 Viscometer

Using an Ubbelohde viscometer as shown in Figure 3.1, the kinematic viscosity was measured and converted to absolute viscosity. Lubricant was poured into tube A until the reservoir was filled between lines F and G. With tube B sealed, suction was applied to tube C until the bulb was filled and the lubricant was above line D. After removing the seal on tube B and the suction on tube C, the lubricant flowed back down tube C. The efflux time for the meniscus of the liquid to flow freely from line D to line E was then used to calculate the kinematic viscosity by multiplying the efflux time by the viscometer constant \([19]\).
The absolute viscosity desired has units of shear stress divided by shear rate \([17]\). This was achieved by multiplying the kinematic viscosity, measured with the viscometer, by the density of the lubricant.

### 3.1.2 Results

The results of the viscosity measurements are shown in Table 3.1. The ionic liquids P66614 and P44412 had viscosities that were orders of magnitude higher than desirable, so diluting with tetraglyme was considered. Future ionic liquids will be developed with an increased focus on a decreased viscosity.
### TABLE 3.1
EXPERIMENTAL VISCOSITY DATA

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Viscosity [mPa*s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffin</td>
<td>158</td>
</tr>
<tr>
<td>Bmim</td>
<td>81.7</td>
</tr>
<tr>
<td>P66614</td>
<td>494.9</td>
</tr>
<tr>
<td>P44412</td>
<td>1225</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>3</td>
</tr>
<tr>
<td>Dodecane</td>
<td>1.2</td>
</tr>
</tbody>
</table>

3.2 Thermal Conductivity

Because the ionic liquid selected will be used as the working fluid in a refrigeration system, the thermal conductivity must also be considered. Thermal conductivity measures the ability of a material to conduct heat. In operating conditions, the liquid would have CO$_2$ dissolved in it. Thermal conductivity tests were performed on the liquids without CO$_2$, as the thermal conductivity of the liquid will dominate.

3.2.1 Unitherm Thermal Conductivity Measurement System

Thermal conductivity measurements were conducted using a guarded heat flow thermal conductivity measuring system, the Unitherm Model 2022 shown in Figure 3.2 with a schematic in Figure 3.3. The guarded heat flow meter test method can measure the thermal conductivity of a small volume of liquid over a range of temperatures. The liquid sample is held in a container between two smooth surfaces. The thermal conductivity is measured across the depth of the liquid, 1.321 mm.
Figure 3.2: Unitherm Thermal Conductivity Measurement System used for thermal conductivity measurements.

Figure 3.3: Schematic of Model 2022 Unitherm Thermal Conductivity System used to measure thermal conductivity of ionic liquids [41].
Heat flows from the top surface through the sample to the bottom surface, which is part of a calibrated heat flow transducer, shown in Figure 3.4 [40]. Once the system reaches thermal equilibrium, the temperature difference across the sample is measured using temperature sensors on each side of the sample. The thermal conductivity is determined using this data, the output from the heat flow transducer, and the sample thickness.

Figure 3.4: Schematic of the test section of the Model 2022 Unitherm Thermal Conductivity System [40].

3.2.2 Results

The Unitherm was used to measure thermal conductivity over a range of temperatures for the ionic liquids Bmim, P66614, and P44412, with results shown in Figure 3.5. Ionic liquids tested have higher thermal conductivities than R134a, indicating
that they have the potential for use as the operating fluid in a refrigeration cycle [22]. Additionally, they have much higher thermal conductivity values than those reported for CO₂ [43]. In operating conditions, CO₂ would be dissolved in the ionic liquids, but the significantly higher thermal conductivity of the liquids will dominate.

Figure 3.5: Experimental thermal conductivity data for the ionic liquids Bmim, P66614, and P44412.
4.1 EHL Ultra Thin Film Measurement System

In order to make use of the Hamrock Dowson equation, the values for the dimensionless parameters are determined based on an experimental setup, with the pressure-viscosity coefficient as the only unknown. The EHL Ultra Thin Film Measurement System, shown in Figure 4.1, can be used to measure film thickness between a steel ball and a glass disk through optical interferometry. Based on the geometry of the system and the viscosity of the lubricant, the pressure-viscosity coefficient can be determined by fitting the Hamrock Dowson equation to film thickness vs. speed data, characterizing the liquid’s ability to form a thick film.

Pressure-viscosity and viscosity are the two parameters that characterize a liquid as a lubricant. A high pressure-viscosity coefficient corresponds to a thick film and a lubricant’s ability to carry part of the load [17]. However, viscous liquids that create thick films result in higher friction, so a balance between pressure-viscosity coefficient and viscosity is ideal for a lubricant.
4.2 Pressure-Viscosity Coefficient

The pressure-viscosity represents the piezoviscous behavior of a liquid, as described by the Barus Law,

\[ \eta = \eta_0 e^{\alpha p}, \]

where \( \eta \) is the absolute viscosity at a given pressure, \( p \), \( \eta_0 \) is the initial viscosity, and \( \alpha \) is the pressure-viscosity coefficient \([17]\). The pressure-viscosity coefficient cannot be measured directly, but by measuring the film thickness in a contact over a range of speeds and fitting the Hamrock Dowson equation, a value can be calculated.
4.3 Center Film Thickness Test

The center film thickness test measures the film thickness in the center of the contact over a range of speeds. A glass disc rests on a steel ball, loaded from below. For the center film thickness test, the disc is driven causing the ball to rotate with it, shown in Figure 4.2. The ball can spin freely with the disc as it rests on the ball carriage assembly, shown in Figure 4.3.

![Figure 4.2: Schematic of EHL rig test area during a center film thickness test [13].](image)

![Figure 4.3: Ball carriage assembly used for all tests on the EHL rig. The ball rests on this assembly and rotates with the disc in the Center Film Thickness and Mapper tests and is driven independently for the Traction and Stribeck tests.](image)
To determine the film thickness, a white light through a microscope is directed at the contact, through the glass disk, as shown in Figure 4.4. Figure 4.5 shows the output of the spectrometer in addition to the test set up. Part of the light is reflected by the chromium coating on the disk while part goes through the silica layer and lubricant film before being reflected back by the steel ball. The chromium layer on the glass disk is overlaid by a silica layer to optimize sensitivity for thin films [9]. The reflected light is recombined and passes through a spectrometer before going to a high resolution camera. The images are analyzed by software that determines the film thickness in the contact by analyzing the intensity vs. wavelength distribution to determine the wavelength of the maximum constructive interference [5]. The film thickness can then be measured over a range of speeds. The thickness of the spacer layer on the disc measured while the ball is stationary is subtracted from subsequent measurements, resulting in the film thickness profile.

Figure 4.4: EHL rig set up for a film thickness measurement with the green spacer layer disc.
Figure 4.5: Schematic of optical interference technique used on the EHL rig. White light shines through a glass disk so part of the of the light is reflected back from the chromium layer on the disk while the rest goes through the layer and lubricant to be reflected off the steel ball. The light paths are recombined to form an interference image that passes through a spectrometer and high resolution CCD black and white camera. The image goes through a spectrometer and central film thickness is measured using software [10].

The accompanying PCS Instruments software generates data for film thickness vs. speed. Fitting the Hamrock Dowson equation for hard EHL, shown in Equation 2.9, to this data can then determine the pressure-viscosity coefficient, which is the only unknown in the equation. Viscosity and pressure-viscosity coefficient data is used to characterize the lubricating properties of a liquid.

The addition of the spacer layer and improved analysis of the images have removed the previous limitations associated with optical interferometry. This improved disc, shown in the center film thickness test set up in Figure 4.5, uses a green spacer layer disc that results in a third order interference [9]. Film thicknesses as low as 10 nm have
been measured using this device and it can be used for low viscosity fluids, two-phase lubricants, and in tests with very thin films due to high pressure or starved contacts.

4.4 Center Film Thickness Test Results

The center film thickness test was performed for paraffin, hexadecane, dodecane, Bmim, P66614 and P44412. The viscosity, measured before each test, and the pressure-viscosity coefficient, determined by fitting the Hamrock Dowson equation, are presented in Table 4.1. No pressure-viscosity coefficient is reported for P44412, as this liquid does not exhibit piezovisco behavior consistent with Barus Law predictions so the film thickness does not increase with speed according to the Hamrock Dowson equation. This can be accounted for based on the chemical structure of P44412, which has short alkyl chains resulting in tighter ion pairs. The other liquids all behaved as expected, with linear log film thickness vs. log speed. Based on the results presented in Table 4.1, all liquids tested would be a suitable lubricant. However, they have viscosities that would result in too much power loss when pumped through the heat exchanger. The chemistry of the ionic liquids developed so far is sufficient for use as a CO2 carrier, but the viscosities are too high.
### TABLE 4.1

LUBRICATING CHARACTERISTICS OF THE LIQUIDS TESTED

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Center Film Thickness [nm]</th>
<th>Viscosity [mPa*s]</th>
<th>Pressure-Viscosity Coefficient [Pa^{-1}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffin</td>
<td>757</td>
<td>158</td>
<td>6.919e-8</td>
</tr>
<tr>
<td>Bnim</td>
<td>257</td>
<td>81.7</td>
<td>1.806e-8</td>
</tr>
<tr>
<td>P66614</td>
<td>705</td>
<td>494.9</td>
<td>1.587e-8</td>
</tr>
<tr>
<td>P44412</td>
<td>692</td>
<td>1225</td>
<td>--</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>37</td>
<td>3</td>
<td>3.7e-8</td>
</tr>
<tr>
<td>Dodecane</td>
<td>24</td>
<td>1.2</td>
<td>1.3e-8</td>
</tr>
</tbody>
</table>

4.5 Mapper Test

Optical interferometry has also been used to measure the film thickness throughout the entire contact area for a ball on disc geometry. This procedure was developed after the center film thickness measurement, and is based on the same concept. The range and resolution of detectable film thicknesses vary based on the type of light used and the coating on the glass disc [14, 18]. Using a glass disc with a chromium coating, white light measures film thickness between 0.1 µm and 1 µm with a resolution of close to 3 nm [18]. Using monochromatic light, the range is much larger, measuring values from 0.1 µm to several µm, but sacrificing resolution.

In order to visualize the entire contact, an image of the contact can be captured and analyzed because the film thicknesses are visible as third order interference colors as a result of the silica layer. The images can then be converted to film thickness measurements using a calibration that correlates film thickness and color. Subtracting the thickness of the glass disc results in the film thickness [5]. The calibration is based on results from the center film thickness test that relates wavelength and intensity. Using
constructive interference, the film thickness can be determined. Once a given film thickness is determined, the thin film optics can be replaced by a color camera. The hue values were matched to the film thicknesses measured using the thin film method [5]. To analyze the images and convert them to film thickness, red, green, and blue signals are stored and converted to a hue value between 0 and 255. A value of 0 indicates pure red, 240 indicates pure blue, and 120 indicates pure green [5]. Using a hue/film thickness look up table, a film thickness is assigned based on the red, green, and blue values.

While the film thickness test measures the film thickness and generates data to determine the pressure-viscosity coefficient, the mapper test can be used to measure film thickness values for the entire contact area. The glass disc used in the mapper test only has a blue silica spacer layer. This layer is roughly 130 nm thick, resulting in a first order interference as compared to the third order interference in the center film thickness measurements [9]. As for the center film thickness test, the thickness of the spacer layer is measured at the beginning of each test and subtracted from the measurement to determine the actual film thickness.

The mapper test shines a white LED through the disc from above, illuminating the Hertz contact area. Some of this light is reflected back from the spacer layer while some shines through the layer and lubricant before being reflected off the steel ball. An interference image is formed from the recombined light paths and is captured using a high-resolution full color camera [9]. The images of the contact area are captured over a range of speeds for each test.
4.6 Mapper Test Results

As speed increases, the constriction becomes more visible as lubricant gathers in the center of the contact indicating that the system is in the EHL regime and that a pressure spike is present. This can be seen in Figure 4.6 for BMIM.

![Mapper Test Results](image)

Figure 4.6: Images of the mapper test as rolling speed is increased from 0 mm/s to 1000.2 mm/s. As the speed increases, the constriction that develops at the trailing edge demonstrates the piezoviscous behavior of the liquid.

4.7 Traction and Strubeck Tests

Traction and Strubeck tests are both run for contacts between a highly polished steel disc and a steel ball. In film thickness tests using the glass discs, the disc is driven by a motor while the ball rolls due to its contact with the disc. In the traction and Strubeck
tests, a separate motor drives the ball. The disc and driven ball used for both of these tests are shown in Figure 4.7. In the traction test, the rolling speed of the disc is constant and the test is conducted for a range of slide-to-roll ratios. The Stribeck test uses a constant slide-to-roll ratio and the speed is varied. Both tests measure the friction coefficient between the ball and disc.

![Figure 4.7: Traction and Stribeck tests use a ball driven by a motor and a highly polished steel disc.](image)

4.8 Traction and Stribeck Test Results

As shown in Figures 4.8 and 4.9, the friction coefficients are sufficiently low, indicating that all ionic liquids considered would be viable lubricants. Figure 4.8 shows the results of the Stribeck test that indicates that the friction coefficients for all tested liquids are very low. Higher coefficients of friction would have indicated that the liquids are traction liquids and therefore not suitable as lubricants.

The traction test shows that an increase in sliding would increase the friction coefficient. The increase in sliding also results in an increase in shear strain. This behavior is expected, as the friction coefficient should initially increase before remaining
constant. Figure 4.9 shows the range of slide-to-roll ratios over which the coefficient of friction is increasing.

Figure 4.8: Coefficient of friction measured by a Strubeck test, demonstrating that the coefficient of friction remains sufficiently low as the rolling speed is increased for a constant slide-to-roll ratio of 0.5.
Figure 4.9: Traction test demonstrating the initial increase in friction coefficient as the slide to roll ratio is increased.
CHAPTER 5:
CONCLUSIONS

5.1 Results and Future Work

Experiments have determined that the ionic liquids developed as CO₂ co-fluids so far are effective lubricants. While the mechanical properties of the considered ionic liquids make them effective lubricants, their viscosities are too high for them to be efficiently pumped through the existing heat exchanger. However, dissolving CO₂ in the ionic liquids should lower the viscosity significantly. This was not possible for the initial testing conditions, but will be considered in the future.

As future ionic liquids are developed, the goal is that their characteristics will be modified so that in addition to being viable lubricants and CO₂ carriers, they will also have sufficiently low viscosities to be pumped through the heat exchanger in a refrigeration system. An ideal ionic liquid would significantly increase the efficiency of the refrigeration system and decrease the harmful environmental effects.
REFERENCES


