IONIC LIQUID / CO₂ CO-FLUID REFRIGERATION:
CO₂ SOLUBILITY MODELING AND LIFE CYCLE ANALYSIS

A Dissertation

Submitted to the Graduate School
of the University of Notre Dame
in Partial Fulfillment of the Requirements
for the Degree of

Doctor of Philosophy

by
Jared E. Peterson

____________________________________
Mark A. Stadtherr, Co-Director

____________________________________
Joan F. Brennecke, Co-Director

Graduate Program in Chemical and Biomolecular Engineering
Notre Dame, Indiana
September 2013
Ionic Liquid / CO₂ CO-Fluid Refrigeration: CO₂ Solubility Modeling and Life Cycle Analysis

Abstract

by

Jared E. Peterson

Improving our current refrigeration systems is important from an energy standpoint as well as from an environmental standpoint. One method of improving our refrigeration systems is developing new working fluids that reduce the energy required for operation, and have less of an environmental impact. One of the possible types of working fluids that displays a great deal of potential is a mixture involving CO₂ (the refrigerant) and an ionic liquid (the co-fluid). The ionic liquid co-fluid greatly reduces the pressure that would be required if CO₂ alone was used. To identify appropriate ionic liquids, two important aspects are the properties of ionic liquid / CO₂ mixtures and the potential environmental impact of the ionic liquid / CO₂ co-fluid refrigeration system over its entire life cycle. In this work properties of various ionic liquids are modeled using the SAFT equation of state. This modeling has been done for both pure component and CO₂ solubility and it shows the effects of impact of the association term for these
compounds in regards to the goodness of fit. Furthermore properties of untested ionic liquids are predicted using the same model. Synthesis routes are also predicted for the synthesis of both 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and trihexyl(tetradecyl)phosphonium 1,2,3-triazolide. From these synthesis routes, and from an estimation of the refrigeration systems theoretical efficiencies, environmental impacts can be determined and analyzed.
This dissertation is dedicated to my children, Landon, Torilynn, Ellalyn, and Levi whom I love very much

but, especially to my wife Kerstin,

who has had the love to not realize that she is way out of my league

or at least the decency to not point it out.
# TABLE OF CONTENTS

**FIGURES.** .......................................................... v  
**TABLES.** .......................................................... viii  
**ACKNOWLEDGMENTS.** ............................................. x  
**CHAPTER 1: INTRODUCTION.** ..................................... 1  
  1.1 Motivation. .................................................... 1  
  1.2 Introduction to Ionic Liquids. .............................. 2  
  1.3 Reasons for Modeling. ......................................... 3  
  1.4 Reasons for Life Cycle Analysis Modeling. ................. 5  
  1.5 Outline. ....................................................... 7  
  1.6 Works Cited. .................................................. 8  
**CHAPTER 2: MODELING BACKGROUND.** ......................... 10  
  2.1 Model Types. ................................................ 10  
  2.2 Models that have been used for Ionic Liquids. ............. 11  
    2.2.1 Cubic Equations of State. ............................. 11  
    2.2.2 Group Contribution Models. ............................ 20  
    2.2.3 Other Models. .......................................... 28  
  2.3 How the SAFT Model Works. .................................. 28  
  2.4 Variations in the SAFT Model. .............................. 30  
  2.5 Previous Ionic Liquid work with the SAFT Model. ........ 57  
  2.6 Works Cited. ................................................ 65  
**CHAPTER 3: SAFT MODELING.** ................................... 71  
  3.1 Project Scope. ............................................... 71  
  3.2 Procedure. .................................................. 72  
  3.3 Results and Discussion. .................................... 74  
  3.4 Concluding Remarks. ........................................ 105  
  3.5 Works Cited. ................................................ 106  
**CHAPTER 4: LIFE CYCLE ANALYSIS BACKGROUND.** ............. 108  
  4.1 Reasons for doing a Life Cycle Analysis. ................ 108  
  4.2 Types of Life Cycle Analysis. ............................. 109  
  4.3 Refrigeration Process. ..................................... 114  
  4.4 ISO 14000. ................................................... 116  
  4.5 Works Cited. ................................................ 118
FIGURES

1.1 Some ionic liquid cations and anions. ............................... 2

2.1 Lee et al. group contribution ionic liquid divisions. .... 25

2.2 Peters et al. group contribution ionic liquid divisions. .... 27

2.3 SAFT self-association example. ................................. 34

3.1 Total volume as a function of molecular weight for the SSAFT model. . 76

3.2 BF$_4$ series density fits. ........................................ 79

3.3 PF$_6$ series density fits. ........................................ 79

3.4 TF$_2$N series density fits. ....................................... 80

3.5 PC-SAFT parameters; number of segments vs. molecular weight. .... 81

3.6 PC-SAFT parameters; total volume vs. molecular weight. ........... 81

3.7 PC-SAFT parameters; total energy vs. molecular weight. ........... 82

3.8 CO$_2$ solubility comparison with Karakatsani et al. ................. 93

3.9 CO$_2$ solubility comparison with Andreu and Vega. ............... 94

3.10 [emim][TF$_2$N] solubility plots. ............................... 95
3.11 [bmim][Tf$_2$N] solubility plots. ........................................... 96
3.12 [hmim][Tf$_2$N] solubility plots. ........................................... 96
3.13 [bmim][PF$_6$] solubility plots. ........................................... 97
3.14 [hmim][PF$_6$] solubility plots. ........................................... 97
3.15 [omim][PF$_6$] solubility plots. ........................................... 98
3.16 [emim][BF$_4$] solubility plots. ........................................... 98
3.17 [bmim][BF$_4$] solubility plots. ........................................... 99
3.18 [hmim][BF$_4$] solubility plots. ........................................... 99
3.19 [omim][BF$_4$] solubility plots. ........................................... 100
3.20 [P$_{2444}$][DEP] solubility plots. ........................................... 100
3.21 [emim][DEP] solubility plots. ........................................... 101
3.22 [emim][MeSO$_3$] solubility plots. ........................................... 101
3.23 [emim][MeSO$_4$] solubility plots. ........................................... 102
3.24 [hmim][OTf] solubility plots. ........................................... 102
3.25 [emim][HSO$_4$] solubility plots. ........................................... 103
3.26 [OHemim][TFA] solubility plots. ........................................... 103
3.27 [emim][SCN] solubility plots. ........................................... 104
TABLES

2.1 Critical Value Predictions for Ionic Liquids. ......................... 14

3.1 Simplified SAFT Parameters and Ratios. ............................ 75

3.2 PC-SAFT Parameters and Fits. ......................................... 78

3.3 Constants for [Tf$_2$N] anion. ....................................... 83

3.4 [Tf$_2$N] Predicted Values. ........................................... 83

3.5 CO$_2$ PC-SAFT Parameters. ........................................... 84

3.6 Binary Interaction Parameter Temperature Dependence. ............ 86

3.7 New Ionic Liquid PC-SAFT Parameters. ............................... 88

3.8 [P$_{66614}$][Tf$_2$N] PC-SAFT Parameters. ............................ 90

3.9 New Ionic Liquid Binary Interaction Parameters. ................. 91

5.1 Grams of CO$_2$ Equivalent for Eastern U.S. Blend. ............... 128

5.2 Grams of CO$_2$ Equivalent for Western U.S. Blend. .............. 129

5.3 Grams of CO$_2$ Equivalent from Nuclear Power. .................. 130

5.4 Energy Required for Heating. ......................................... 132
5.5 Cubic Meters of Water Required for Cooling. .............................. 133
5.6 Environmental Impacts of [hmim][Tf$_2$N] Synthesis. ..................... 138
5.7 Environmental Impacts of Running an [hmim][Tf$_2$N] Air Conditioner. 139
5.8 Environmental Impacts of Synthesizing an Air Conditioner. .............. 140
5.9 Overall Impacts for [hmim][Tf$_2$N] / CO$_2$ System. ...................... 141
5.10 Heating Required for [P$_{66614}$][3 triazolide] Synthesis. .................... 144
5.11 Cooling Required for [P$_{66614}$][3 triazolide] Synthesis. ................. 145
5.12 Environmental Impacts of [P$_{66614}$][3 triazolide] Synthesis. ............ 146
A.1 Simplified SAFT Parameters and Ratios. .................................... 156
B.1 PC-SAFT Initial Ionic Liquids; Initial Estimates, Parameters, and Fits. ... 157
C.1 Initial Ionic Liquids; Binary Interaction Parameter ($k_{ij}$) Tables. ......... 159
D.1 Newer Ionic Liquids; Initial Estimates, Parameters, and Fits. .............. 161
ACKNOWLEDGMENTS

I would like to sincerely thank all of the following for their assistance and support and all of their contributions to my studies and research at Notre Dame:

Dr. Mark Stadtherr, for his patience, guidance and direction. For his time, effort and help in all of this and more. His professional knowledge and desire for perfection has made me learn so much in my research, studies, and life.

Dr. Joan Brenencke for her assistance and guidance. For her willingness to put up with my confusion.

The Faculty at Notre Dame for their assistance in my graduate educational development.

The Department Secretaries, both current and former, who were always willing to help out, regardless of how busy they were.
CHAPTER 1

INTRODUCTION

1.1 Motivation

In the United States alone approximately $2.4 \times 10^{15}$ BTUs are used on cooling. A further complication that can arise from this is the fact that the majority of the energy provided for cooling comes from the burning of fossil fuels, which releases a great deal of CO$_2$ into the atmosphere. In fact, an additional 420 million metric tons of CO$_2$ are evolved in this way [1-2]. Furthermore, many of the cooling systems that are used are vapor compression air conditioners which use refrigerants that are high in global warming potential, much higher than CO$_2$, and that can potentially leak or be otherwise released into the atmosphere. Combining these factors yields the fact that our current air conditioners generate a great deal of emissions, which results in a large amount of global warming potential.

While there are many factors involved in the global warming potential thus generated, not all of them are easily solved. For example, while changing the type of power stations that are used in the United States from fossil fuels to a more environmentally friendly type would result in lower emissions; such a change would require many decades. In order to change the amount of cooling used it would require a
great many people to give up certain conveniences for long term gains. One thing that can be done, however, is to change the air conditioner itself. In designing a better air conditioner finding a good suitable working fluid is critical. One of the possible types of working fluids that displays a great deal of potential is a mixture involving CO$_2$ (the refrigerant) and an ionic liquid (the co-fluid) [3-4]. The ionic liquid co-fluid greatly reduces the pressure that would be required if CO$_2$ alone was used.

1.2 Introduction to Ionic Liquids

Ionic liquids (ILs) are salts that are liquid at room temperature. They are composed of a cation and an anion and tend to have a bulky cation group. They have

![Figure: 1.1](image_url)
been shown experimentally to have very low vapor pressures and tend to have relatively large liquid ranges [5-8]. Some of the more commonly encountered cations and anions are shown in Figure 1.1.

Ionic liquids, in addition to their other attractive properties, are also very appealing due to their flexibility; meaning their ability to be changed in order to meet certain design specifications. In general the properties of ionic liquids could be changed by changing out the anion or the cation, or by simply changing the length of alkyl group attached to the ionic liquid, if there is an alkyl group in the liquid. For example, the density of [hmim][PF₆] at atmospheric pressure and 15 Celsius is approximately 1.30 g/cm³, [10] whereas the density of [bmim][PF₆] is approximately 1.37 g/cm³ [11]. So with the simple change of removing 2 carbons, the density increased by about 5%, and it is not only the density that can be changed in this way, but practically any property can be changed by modifying the various parts of the compound. Another example of a minor change causing a reasonably large difference is in CO₂ solubility. One way to examine this is to compare the solubilities of these same compounds at the same pressure and temperature. At 333.15K and 10MPa the solubilities are approximately 67 mole percent for [bmim][PF₆] and approximately 55 mole percent for [hmim][PF₆] (once again with the only change being the addition of two carbons and some hydrogens). For this flexibility ionic liquids have been referred to as designer solvents [12].

1.3 Reasons for Modeling
The extreme flexibility of ionic liquids, however, does create a problem, namely the time required to make and test each of these individual ionic liquids. This problem can lead to a severely limited selection of compounds which can, and would, be tested. As an example of this point, imagine that there are only one hundred different ionic liquids which can be formed. If synthesizing and testing each one took three months, within the span of a year only four would be made, which would require approximately 25 years to test them all. Considering that the cost of a project is related to the time required to do the project, this sort of project would be very expensive. Furthermore, if you were looking for a particular compound to perform a specific job, it would probably be easier to work around that function rather than make and test each compound for use in that situation. In reality there are a number of complications to the simple situation described above, and of course multiple compounds can be tested at once, but the basic premise stands and in reality there are orders of magnitude more combinations of ionic liquids than simply the one hundred previously mentioned.

The solution to this problem of time and money is to use molecular modeling to speed up the process and predict the compounds that would be most useful to actually create and test. This would, of course, vastly speed up the time required to find an ionic liquid that would work well in a given situation. Furthermore, molecular modeling would require little more than a computer, which could potentially save on a great number of compounds and expensive equipment. While the molecular model wouldn’t be as accurate as making each compound, it could give a good starting location to begin testing. Obviously some work would have to be done in order to test various models for accuracy, and some compounds would have to be done before, but the time and money
saved would be quite evident. In my work, as reported in Chapters 2 and 3, I have studied the use of a molecularly-based equation-of-state model based on statistical associating fluid theory (SAFT) for predicting CO₂ solubility in ionic liquid co-fluids. This approach offers the potential to predict the properties of new and untested ionic liquids with no additional fitting involved. This model has shown itself to be good at fitting both pure component and multicomponent systems[13-15].

1.4 Reasons for Life Cycle Analysis Modeling

As stated before, one of the attractive features of ionic liquids is their low vapor pressures [5-8]. This is attractive for a number of reasons, one of the foremost being their potential for use as green solvents. They emit no appreciable vapors into the atmosphere and are, therefore, considered less environmentally damaging than similar more volatile solvents. However, it is worth asking the question; Are they, in actuality, less damaging when all aspects of their manufacture and use are considered?

A clearer example of this is seen in the common question of paper or plastic. In many locations this is mostly an irrelevant issue today, but it was once common in grocery stores to be asked whether you wanted a paper bag or a plastic bag. Some thought that it was obvious that paper was the clear choice in this circumstance. It was biodegradable, and came from trees which are renewable. Plastic, on the other hand, was non-biodegradable and came from a non-renewable resource. So is paper the better choice? When we apply a life cycle analysis to the entire system we come up with a somewhat different picture. While paper is, in reality, biodegradable and does come from
a renewable resource, paper bags also require approximately twenty six times more water to make than plastic bags and require about three times the energy to manufacture [16-18]. Also, since plastic compresses better than paper, it would require approximately seven times more trucks to transport a similar quantity of paper bags as plastic bags. Even in the landfill, where biodegradable paper ought to have the edge, it turns out that plastic may be the better choice, since modern landfill construction limits the amount of biodegrading that actually occurs, plastics lower volume again becomes an advantage. Additionally, even if you choose to recycle your waste it turns out that recycling plastic bags requires only a small fraction of the energy that recycling paper bags takes. It remains true that paper does come from trees whereas plastic comes from oil, and if you accidentally lose a bag in the wind, the paper bag will eventually biodegrade, whereas the plastic one will still be blowing around (which may be considered aesthetically offensive in many locales). As we can see from this discussion, once a larger picture is looked at and examined it may be that plastic bags, despite some issues, are actually more environmentally friendly than paper bags.

A similar question can then be asked for an ionic liquid as a solvent rather than a conventional solvent. Even though it may appear that the ionic liquid is more attractive, is this actually true once everything is taken into account? Even though their air emissions are less than with conventional solvents, perhaps their ground waste is more hazardous? Or perhaps the energy required to synthesize them is extremely high and would produce more pollution than the ionic liquid would save? For these reasons it is important that a clear and precise life cycle analysis is completed for the proposed ionic liquids. In my work, as reported in Chapter 5, I have performed a life cycle analysis for
two ionic liquids, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf₂N]) and trihexyl(tetradecyl)phosphonium 1,2,3-triazolide ([P₆₆₆₁₄][3 triazolide]), that have been proposed as co-fluids for refrigeration.

1.5 Outline

The work that has been accomplished has been broken up into the five following chapters. In Chapter 2 a modeling background will be given. Various models that have been used to model ionic liquids will be discussed, with a focus on modeling ionic liquid solubilities, as well as a history of the SAFT model and some of its uses. Finally the various SAFT models that have been used to model ionic liquids will be examined. In Chapter 3 the modeling work I have done will be presented beginning with work on pure components followed by work on multicomponent systems. Chapter 4 will give an account of the reasons for performing a life cycle analysis as well as some of the various types of life cycle analysis that can be performed. Furthermore various metrics for evaluating environmental impact will be discussed as well as the actual ionic liquid / CO₂ cofluid refrigeration process that will be analyzed. In Chapter 5 the actual process of synthesizing the ionic liquids and performing a life cycle analysis on the ionic liquids will be examined. Furthermore, the overall life cycle analysis of the refrigeration system will be examined and conclusions will be drawn from these analyses. In Chapter 6 conclusions will be drawn from both the SAFT modeling and the life cycle analyses, and recommendations will be made for future work.
1.6 Works Cited


CHAPTER 2

MODELING BACKGROUND

2.1 Model Types

With all of the potential that ionic liquids present it is only natural that there is a lot of interest in the behavior of ionic liquids at various temperatures and pressures as well as how they react to other molecules. This has led to a much experimental work being done to determine these properties. However, there is much more to do. While experiments are accurate and, currently, the only way to know for sure how a compound will behave, discovering all of the properties solely through experimentation would be extremely time consuming. Modeling has the answer to this, because it is able to estimate the properties of the ionic liquids in a variety of conditions with significantly less time in the lab.

The increased interest in ionic liquids has led to an increasing interest in the desire to model them. Several different methods have been employed, including activity coefficient models, equations of state, and molecular models. Each of these different methods has its own strengths and weaknesses, but in the interest of brevity only equations of state are examined in depth. Equations of state are equations that provide a mathematical relationship between two or more state functions, such as temperature, pressure, volume, or internal energy. These are of interest because, in order to examine
the solubility of CO₂ within the ionic liquid as a function of temperature, the equation
must at least explicitly account for each of these two things. While other types of models
might account for these terms, equations of state were chosen because the calculations are
relatively quick.

2.2 Models that have been used for ILs

Due to this interest in ionic liquids various methods have been used to model them. Some of the methods that have been tried are Cubic Equations of state[1-21], Group Contribution models [22-31], and various others[32-36]. An alternative model to those mentioned above is the SAFT model, which was the model chosen for this paper and will be described in greater detail in some of the following sections.

2.2.1 – Cubic Equations of State

One of the cubic equations of state that has been used to model ionic liquids is the Peng-Robinson equation of state with the Wong-Sandler mixing rule. This model has been used extensively by Dr. Carvalho of the University of Aveiro, in Portugal, with good results. The Peng-Robinson equation of state is an equation of state that attempts to predict the properties of a compound through the use of its critical properties and its accentric factor. For most compounds these properties are well known. However, in the case of ionic liquids it is difficult, if not nearly impossible, to find these values experimentally due to the extremely low vapor pressure of these types of liquids. This
problem is compounded by the fact that ionic liquids begin to decompose as the temperature approaches what would be assumed to be their normal boiling point. If a particular compound doesn’t have a real vapor phase, finding the point at which the liquid and the vapor phase are the same is a difficult proposition at the very least. This problem was solved through the use of a group contribution model designed to predict critical properties and tailored specifically for ionic liquids proposed by Valderrama and Robles [37].

Additionally this paper modifies the equation somewhat more through the use of the Wong-Sandler mixing rule [38]. The use of the Wong-Sandler mixing rule allows them to use this equation even if you have, “incomplete PTxy data” [3]. The final models that were used, after some simplifications were made, were of the following form:

\[ P = \frac{RT}{V-b_m} + \frac{a_m}{V(V+b_m)+b_m(V-b_m)} \]  \hfill (2.1)

\[ b_m = \frac{\sum \sum x_i x_j (b - \frac{a}{RT})_{ij}}{1 - \sum x_i a_i \frac{A_{so}^E(x)}{\Omega RT}} \]  

\[ = \frac{1}{2} [b_i + b_j] - \sqrt{\frac{a_i a_j}{RT}} (1 - k_{ij}) \]  \hfill (2.2)

\[ a_m = b_m (\sum x_i \left[ \frac{a_i}{a_j} \right] + \frac{A_{so}^E(x)}{\Omega}) \]  \hfill (2.3)

And these models, while somewhat complicated, are reasonable to do with the assistance of UNIQUAC. With these models complete, and a method of using them ascertained, data was measured and results obtained various compounds, with good
results. After measuring and fitting the data for CO₂ solubility for various
[Cₙmim][Tf₂N]s, [bmim][dicyanamide(DCA)], [triethyltetradecylphosphonium
(THTDP)][Tf₂N] and [Cl], and a few others, the results showed that their model was
able to predict the solubilities with errors of generally, but not always, lower than 20%. For all of its strengths, however, this model is somewhat impractical from a sheer predictive standpoint because in order to fit the model well it requires a reasonable amount of solubility data before any predictive work can be done.

Using the work of Valderrama and Robles isn’t the only method of using the Peng-Robinson in order to do predictive work with ionic liquids though. Another method that was applied by Hwayong Kim et al., and again in separate papers by Byung-Chul Lee et al., and J.S. Lim et al., is a method that has been termed the Joback method [39] to predict the critical temperature and pressure, and the Ambrose-Walton method [40] to find the acentric factor. Unfortunately the Joback method requires a boiling point in order to predict the critical values. Fortunately, within the Joback method there is a means of predicting the boiling point of a compound. Unfortunately, it is mentioned that it is often an inaccurate estimation of the boiling point, but that it was used anyway. Once these values are determined a standard Peng-Robinson approach can be taken. Regardless of the somewhat suspicious values, this method, applied by Kim, also had reasonable results with the error being less than 7% for the compound that was tested. Unfortunately no method of prediction was attempted by these authors and this method was used strictly to fit the data.

Since both of these methods, the pure Peng-Robinson with critical value prediction through the Joback method and the Peng-Robinson with the Wong-Sandler
mixing rule and critical value prediction through Valderrama and Robles method, require critical values, it is interesting to compare the two values. The values chosen for comparison are various bis(trifluoromethylsulfonyl)imides taken from Lee’s and Valderrama’s papers.

Table 2.1:

CRITICAL VALUE PREDICTIONS FOR IONIC LIQUIDS

<table>
<thead>
<tr>
<th>Author</th>
<th>Compound</th>
<th>Tc (K)</th>
<th>Pc (MPa)</th>
<th>ω</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valderrama</td>
<td>[emim][Tf2N]</td>
<td>1244.9</td>
<td>3.26</td>
<td>.1818</td>
</tr>
<tr>
<td>Lee</td>
<td>[emim][Tf2N]</td>
<td>788.05</td>
<td>3.31</td>
<td>1.225</td>
</tr>
<tr>
<td>Valderrama</td>
<td>[bmim][Tf2N]</td>
<td>1265.0</td>
<td>2.76</td>
<td>.2656</td>
</tr>
<tr>
<td>Lee</td>
<td>[bmim][Tf2N]</td>
<td>831.39</td>
<td>2.69</td>
<td>1.289</td>
</tr>
<tr>
<td>Valderrama</td>
<td>[hmim][Tf2N]</td>
<td>1287.3</td>
<td>2.39</td>
<td>.3539</td>
</tr>
<tr>
<td>Lee</td>
<td>[hmim][Tf2N]</td>
<td>876.24</td>
<td>2.22</td>
<td>1.327</td>
</tr>
</tbody>
</table>

Upon even a brief inspection of these two values it is clear that there is a fair amount of discrepancy between the values predicted through the Joback method and Valderrama’s. The trends are somewhat similar, but the temperature values that Valderrama predicts are more than 30% greater than the values predicted by the Joback method, and the acentric factors differ by almost an order of magnitude, although the
critical pressures are similar. One method is probably more accurate than the other, and since Valderrama specifically designed his method to predict the values of ionic liquids for equation of state models, that is probably the better choice to use. However, the Joback method has been around for a longer time and is, consequently more common, there are certain merits for that method as well. As far as that goes, however, the critical values to choose for ionic liquids depend greatly on the tastes of the researcher.

The Peng-Robinson has also been used with alternate mixing rules. In a paper by Yoonkook Park et al. [11] the Peng-Robinson equation of state was used, but rather than using either no special mixing rule or the Wong-Sandler rule, the choice was made to use the two parameter mixing rule. The critical values for the ionic liquids were taken from the work of Valderrama. The two parameter mixing rule is the basic mixing rule that has been used in some of the previously mentioned papers and the governing equations are as follows:

\[
P = \frac{RT}{V-b_m} + \frac{a_m}{V(V+b_m)+b_m(V-b_m)}
\]

(2.4)

\[
a_i = \frac{0.45724 R^2 T_e^2}{p_c} \left[ 1 + \beta \left( 1 - \left( \frac{T_r}{T_e} \right)^{\frac{1}{2}} \right) \right]^2
\]

(2.5)

\[
\beta = 0.37464 + 1.54226 \omega - 0.26992 \omega^2
\]

(2.6)

\[
b_i = \frac{0.0778 RT_e}{p_c}
\]

(2.7)

With the basic mixing rule being given as:

\[
a_m = \sum_{i=1} \sum_{j=1} x_i x_j a_{ij}
\]

(2.8)
\[ b_m = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j b_{ij} \]  
(2.9)

\[ a_{ij} = (a_i a_j)^{1/2} (1 - k_{ij}) \]  
(2.10)

\[ b_{ij} = \frac{b_i + b_j}{2} (1 - l_{ij}) \]  
(2.11)

The major difference between the approach taken by Park vs. Kim and Lee is that the previous authors that had used it had chosen to use the Joback method to determine the critical, whereas Park has chosen to use the values given by Valderrama. Ideally the minor difference between using Valderrama’s critical values and the values found from the Joback method would be an ideal means of testing the difference between the two methods, however as in the previous cases, there was no attempt at prediction and, as an added complication, Park used this method for a system of an alkyl-imidazole tetrafluoroborate mixed with CO\(_2\), which is a system untested by the previous authors. Much like the previous authors, the fit was reasonable, but lacking any sort of prediction makes it unclear as to whether this would be a good model for predictive work.

Fortunately this question is somewhat resolved in the work of Aaron Scurto [12-13]. In his work he uses the same model as used by Park et al. to predict the solubilities of CO\(_2\) within various imidazolium based ionic liquids. His predictions involve the fitting the model to the experimental data and testing to see whether the model under these circumstances predicted the point at which the compounds go from being a VLE system to a VLLE system. In other words, to see if the model was able to predict, after fitting the model, the point at which the ionic liquid + CO\(_2\) liquid mixture became an ionic liquid rich liquid phase and a CO\(_2\) rich liquid phase. This phase is noticeable by a
distinct increase in the slope of the Px diagram. It is worth reiterating, however, that the model had already been previously fit with fairly good results, even at high pressures, and thus it should come as no particular surprise that it was fairly good at predicting the point at which the liquid system undergoes a split.

Despite the many previous mentions of the Peng-Robinson equation, and several more that haven’t been mentioned in detail, other cubic equations of state have been used. One of the equations of state that have been used fairly heavily is the Redlich-Kwong equation of state. This equation has been used fairly heavily by Shiflett and Yokozeki [14-18]. This is a fairly basic equation of state that, much like the Peng-Robinson equation, has a fairly large degree of mobility in terms of potential modifications. The equation used by Shiflett and Yokozeki is as follows for the single component case:

\[
P = \frac{RT}{V-b} \left( \frac{\alpha(T)}{V(V+b)} \right)
\]

(2.12)

\[
\alpha(T) = 0.427480 \frac{R^2T_c^2}{P_c} \alpha(T)
\]

(2.13)

\[
b = 0.08664 \frac{RT_c}{P_c}
\]

(2.14)

\[
\alpha(T) = \sum_{k=0}^{\infty} \beta_k \left( \frac{1}{T_r} - T_r \right)^k
\]

(2.15)

Once again as the model is examined it is apparent that once again there are critical values that are required. Despite the other common methods that other authors have used and created, Shiflett and Yokozeki use the method proposed by Alessandro Vetere [41]. This method is a modification of the Rackett equation which allows
prediction of the critical values through changes in density as the temperature changes. This has the advantage over the Joback method in that the Joback method requires a boiling point, which is quite difficult to determine experimentally for ionic liquids, but density changes are simple to measure and calculate. However, the method proposed by Vetere was designed around, and tested for, organic compounds. So, while the predictive power of this method is quite good for these organics, with the vast majority of the errors less than 5%, there is no real way of telling whether this particular method is equally as accurate with ionic liquids. Comparing these values to the previous values of [hmim][Tf2N] yields us a critical temperature that is somewhat lower than the Joback method at 815K, and a critical pressure that is quite a bit lower than the other two methods at 1.611MPa. There was no attempt to predict the acentric factor, as their primary equations had no need of them.

For the multi component case the equations are somewhat similar with generally standard style mixing rules and mixing constants. Upon examination of the equations as they stand it is apparent that they share certain similarities to the Peng-Robinson equation of state but is clearly a unique equation. With these equations Shiflett and Yokozeki have modeled a fair number of different things including the solubility of CO2 in [hmim][Tf2N], the use of [bmim][BF4] to separate N2O and CO2, the separation of H2S and CO2 through the use of [bmim][PF6] and [bmim][MeSO4], and the separation of CO2 and SO2 with [hmim][Tf2N].

For these different compounds the fits were quite good, which is what one would expect considering that there are 4 binary interaction parameters for each set of 2 compounds. However, what makes this model useful is that it has been used for
predictive work in addition to its fitting. For the [hmim][CO$_2$] system there was a wide array of data fit to the system and then the fit was analyzed in alternate scenarios and the predictive capabilities were fairly good. The prediction at temperature in between the fit temperatures was fairly good, and the model was able to accurately predict a point at which the VLLE system became immiscible. For the ternary systems little predictive work was done, but the model was able to accurately fit the data, including the VLLE case for H$_2$S/[bmim][MeSO$_4$], which has a very narrow LLE window (between .97 and .99). So for this case, as in the previous works, the fits using these cubic equations of state are fairly good, in general, but the ability to predict a previously untested compound, or a compound with only minimal work done, remains somewhat lacking.

There are other works that have been used to model ionic liquids, either singly or with additional compounds, but they tend to follow the trends previously established. Indeed, there is an additional work done by Yokozeki and Shiflett [19] where they test the generic Van Der Waals equation with similar results. The generic Van Der Waals equation is similar to the previously mentioned equations but somewhat simpler and is given as follows:

$$ P = \frac{RT}{V-b} - \frac{a(T)}{V^2} $$

(2.16)

Where the values of a and b are determined the same as in equations (2.13) and (2.14) with the only difference being that the constant on b is 0.125 rather than 0.08664. From this we can see that this equation is practically identical to equations (2.1) and (2.12), with the difference being the way the second exponent is handled in the latter half of the equation and some differences in the method of calculating the values of a and b.
From the similarities in these equations it would be unsurprising should it be found that these equations all have similar results, and this observation was in fact made in the same paper. In fact Shiflett and Yokozeki come to the conclusion that, regardless of modifications and/or base equation, all cubic equations of state work equally well for modeling PTx phase behavior. While that may not necessarily be true across all cubic equations of state it certainly seems to hold true for the Peng-Robinson, Modified Peng-Robinson, Redlich-Kwong, and Van Der Waals, and all of these appear to work equally well, or equally poorly depending on the desired results, regardless of which mixing rule is chosen or the method chosen to determine the critical values used within the equation. The implication of this appears to be that, when using cubic equations of state, the simpler of an equation one chooses to use the better since the results will be practically identical.

2.2.2 – Group Contribution Models

Despite the amount of work that has been done modeling ionic liquids with cubic equations of state, they are hardly the only means of modeling them and other means have been employed. One method that has been employed reasonably often and with a fairly good degree of success has been various group contribution models.

One model that was used was proposed by Ye and Shreeve [22]. The approach that they attempted was a fairly logical and straightforward approach. They initially analyzed the Cambridge Structure database, in particular the objects that either looked like or could be used in the formation of ionic liquids. From these values the volume of
the anion and the cation could be calculated, and the volume of the structure as a whole could be calculated by summing the volume of each of the different parts, often referred to as the $V_+$ and $V_-$. The density of the system was then calculated from the rather simple, and logical, equation of:

$$ \rho = \frac{W}{NV} $$

(2.17)

Where $W$ is the molecular mass in kg/mol, $N$ is Avogadro’s number, and $V$ is the molecular volume of the salt in m$^3$/molecule, which leaves the density in kg/m$^3$. As previously mentioned this is a very logical and simple approach, and yet it is able to achieve effective results. Across a wide variety of different ionic liquids this method was able to predict the densities with a fairly small margin of error. Specifically, across the ninety four different ionic liquids tested the average deviation was under 4%, and oftentimes much lower than that, which is close enough for most uses. The major issue that this method has is the inability to check for density changes due to temperature and/or pressure variations. The modeled is predicated on the use of room temperature initial volume measurements, and if such measurements are lacking or the density is desired at a different temperature, either a new system must be determined, or new measurements need to be taken.

The room temperature and atmospheric pressure limitation on the model proposed by Ye and Shreeve need not be final however. In a paper by Gardas and Coutinho [24] they took the model of Ye and Shreeve and modified it to allow for the density to be a function of temperature and pressure. This, somewhat obviously, adds to the complexity of the model while allowing for a greater degree of prediction than was previously
allowable allowing for temperatures of between 273.15 and 393.15K and pressures of between 0.10 and 100 MPa. This spectrum is basically the entire practical range of ionic liquids as well because as the temperature of the ionic liquid rises the rate of decomposition increases making it impractical to use the ionic liquid at high temperatures, and 100MPa is beyond the scope of most industrial processes. This was done by including the isothermal compressibility and isobaric expansivity within the volume term as follows:

\[
\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T
\]  

(2.18)

\[
\alpha_P = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P
\]  

(2.19)

Where \( \kappa_T \) is the isothermal compressibility and \( \alpha_P \) is the isobaric expansivity. These equations can then be combined and solved set equal to the volume which yields:

\[
V = V_0 e^{(x + \alpha_P T + \kappa_T P)}
\]  

(2.20)

With \( V_0 \) being the molecular volume at the reference temperature, and \( x \) being equal to initial conditions given as:

\[
x = -(\alpha_P T_0 + \kappa_T P_0)
\]  

(2.21)

Equation (2.20) can then be expanded as a Taylor series for simplicity and with only the first members of the series surviving gives us the simpler equation of:

\[
V = V_0 (a + bT + cP)
\]  

(2.22)
With $a$ being $(1+x)$, $b$ being equal to $\alpha P$, and $c$ being equal to $\kappa T$. This can be combined with the original equation to give the temperature and pressure dependent equation which is:

$$\rho = \frac{W}{NV_0(a+bT+cP)}$$

(2.23)

In order for this equation to be more accurate for each different ionic liquid, each of these parameters would be different and have to be determined experimentally. However, a simpler method, which was the method chosen by Gardas and Coutinho, involved fitting each of these three parameters as fit constants rather than experimentally determined values. This allows for a simpler equation to use, as well as allowing for the prediction of unmade compounds. The values of $a$, $b$, and $c$ were determined by fitting equation (2.23) across a variety of different temperatures and pressures for nine different ionic liquids.

Once all of the equations had been determined and the required parameters found the process of testing the model was done, with good results. The model was tested across a wide variety of ionic liquids including a variety of imidazoles with various anions attached, various phosphonium, pyridinium and pyrrolidinium-based ionic liquids. The results were quite good with the mean percent deviation across a variety of temperatures and pressures lower than 4% in all cases, and usually lower than 1%. The model was then attempted for a small sampling of binary mixtures of ionic liquids that had either a common anion or a common cation, with similarly good results. This is good because, as mentioned previously, there is a method, the Vetere method that can be used to predict critical values based on density changes which could be combined with this...
model to allow the prediction of critical values for compounds that had been only looked at. These critical values could then be used to run a cubic equation of state, such as the ones previously used to allow for prediction on these completely new and untested compounds.

The last couple of group contribution models focused solely on the prediction of the density of untested compounds, but this isn’t the only thing that group contribution models have been used for. In a paper by Lee et al. [25] a group contribution, lattice fluid equation of state was applied to the prediction of the solubility of gasses within ionic liquids. In this model the ionic liquids were broken up into segments, and each segment was assigned three different group segment numbers, a bulkiness parameter, and three different group interaction energy parameters. Then, when these compounds were combined through a number of equations mentioned within their paper, final values can be obtained which give an overall segment number and segment interaction energy, from which solubility data can be produced.

In theory this is a somewhat ideal model, allowing for the prediction of untested compounds from little more than knowledge of its basic formula. In practice though this model leaves somewhat to be desired. For one thing the authors chose somewhat odd segments to use, having each alkyl chain being one segment, and then the bulky cation plus the anion be another as shown in the following Figure:
The implications of this are that this model as presented are that, while yes it can be used for predictive work, it can only predict new solubilities due to a change in alkyl chain length. As soon as the major cation or anion are changed new parameters need to be determined. Further complicating this issue is the fact that each segment has seven fit parameters, meaning that in order to fit the bulky group initially a reasonably large amount of data needs to be known.

Once these values had been determined though, Lee et al. were able to predict the solubilities of a small smattering of ionic liquids with various gasses within them. The results, unfortunately, were decidedly average. The fits for the binary systems (gas + ionic liquid) were good, but not necessarily better than one might find for the cubic equations of state while the fits for the ternary systems (two gasses plus ionic liquid) were decidedly sub-par with predicted values that could have errors of higher than 25%, which is worse than some of the previously suggested models. In regards to this model I wouldn’t recommend using it as is, but it has been included due to its attempt at
predicting solubilities in the ionic liquids from a pure predictive standpoint, and not due to its effectiveness.

As mentioned previously combing a group contribution model with an equation of state could prove fruitful, and this approach has been tried. In a series of papers that has Cor J. Peters as a common author [27-29] an interesting group contribution-equation of state model is used in order to predict both binary and ternary parameters. The model is expressed in terms of the residual Helmholtz energy as a sum of an attractive term and a free volume term with the attractive term defined in an NRTL type equation and the free volume term described as follows:

\[
\left( \frac{\alpha^R}{RT} \right)_{T,V,n} = \left( \frac{\alpha^R}{RT} \right)_{att} + \left( \frac{\alpha^R}{RT} \right)_{fv}
\]

\[
\left( \frac{\alpha^R}{RT} \right)_{T,V,n} = 3 \left( \frac{\lambda_1 \lambda_2}{\lambda_3} \right) (Y - 1) + \left( \frac{\lambda_3^2}{\lambda_3^3} \right) (Y^2 - Y - \ln Y) + n \ln Y
\]

Where

\[
\lambda_k = \sum_{j}^{NC} n_j d_j^k
\]

\[
Y = \left( \frac{1 - \pi \lambda_3}{6V} \right)^{-1}
\]

Where \( n \) is the total number of moles, \( NC \) is the number of components, \( V \) is the total volume, and \( d \) is the hard sphere diameter per mole. It is worth noting that many of these equations bear certain resemblances to the SAFT equation of state that will be mentioned further in, namely that it is expressed in terms of the residual Helmholtz energy, and that the overall equation is broken up into component pieces, one of which is
an attractive energy term. It would be interesting to attempt to reconcile this equation even more closely with the SAFT model, but doing so is beyond this work, but perhaps an attempt could be made by another.

As it might be, correctly assumed a model of this type with multiple groups would have a multiplicity of interaction parameters, and this model fits that assumption. These papers break each ionic liquid into a variety of parts that is best represented in the following Figure:

![Figure 2.2: Peters et al. group contribution ionic liquid divisions](image)

With the anion being a group unto itself. It is interesting to note that the bulky cation wasn’t assumed to be a group in and of itself, but was instead assumed to be a set of smaller groups from which a larger group could be calculated. Additionally however, for certain of the calculations used within the model the larger group of the bulky cation plus the anion was used. This large number of groups led to an even larger number of parameters, but these parameters could then be used, if they and the model were
sufficiently accurate, to calculate new compounds without much necessary in the way of experimental work. As it so happens, this model was indeed sufficiently accurate as well. For the binary solubility tests of [bmim][emim] and [hmim][PF$_6$] the model proved its ability to both fit and predict with an error of less than 4% and pressures ranging higher than 70MPa for temperatures of over 350K. For ternary systems the model proved a good fit as well, with errors that were higher than with the binary systems, but still generally below 10%.

2.2.3 – Other Models

In addition to cubic equation of states and group contribution methods, other methods have been used to evaluate ionic liquids including, but not limited to the COSMO method, COSMO-RS, and a neural network approach. These methods had varying degrees of success but will not be mentioned in great detail here due to their larger deviation from the primary model to be focused on, the SAFT model.

2.3 How the SAFT Model Works

One of the models that appear to show a great deal of promise for modeling ionic liquids is the SAFT model [42]. The SAFT model is, in essence, the idea that an excess thermodynamic property can be broken up into various parts and, when all the parts are summed together, yield a correct total excess property.
There are, for a basic SAFT model, three basic parts. Initially the modeled is examined and general expectations are set. The compound is then modeled as a hard sphere fluid. Then dispersion forces are added which cause the spheres to have a preference for each other. Then a chain term is added which causes the spheres to link together into molecules. Finally for many models association sites are added to the molecules which cause the molecules to link together. Now, it is important to note that these steps aren’t set in stone and the method of calculating the various parts are subject to change, in fact many different SAFT models either add new parts to the model, or do away with parts altogether. An example of the former case would be polar SAFT, wherein a Polar term is added to the mix to explicitly account for dipole-dipole attraction. An example of the latter is when the SAFT model is applied to compounds that are generally considered non-self-associating, such as alkanes. In this case the association term is left off.

The SAFT equation of state is generally represented in terms of the residual Helmholtz energy per unit mole of mixture. For most SAFT models there are four terms that make up the total residual energy and so the overall energy is calculated as:

\[
\mathcal{a}^{res} = \mathcal{a}^{hs} + \mathcal{a}^{chain} + \mathcal{a}^{disp} + \mathcal{a}^{assoc}
\] (2.28)

With the terms representing the hard-sphere energy, the chain energy, the dispersion energy, and the association energy respectively. As mentioned previously, all of these terms need not be included, and additional terms can be added. The following section will describe some of the deviations that might be seen across the model.
2.4 Variations in the SAFT Model

As mentioned previously, there are many variations on the SAFT model depending on how each of these expressions are represented and while a comprehensive list of all of the various SAFT models and changes wrought to it throughout its life is beyond this work, some of the more prominent models and types will be mentioned and discussed. The initial model was initially presented by Chapman et al. [43] in 1990 and consisted of these four terms, although in this paper the hard sphere and the dispersion terms were combined into a single term called the segment energy. The basic expression as given in (2.28) was then applied in the following format.

\[
\frac{a_0^{hs}}{RT} = \frac{4\eta-3\eta^2}{(1-\eta)^2}
\]  

(2.29)

Which equation came from the hard sphere model presented by Carnahan and Starling [44] and which had \( \eta \), the segment packing fraction or the reduced density, being represented by the following expression:

\[
\eta = \frac{\pi N_{AV}}{6} \rho d^3 \sum_i X_i m_i
\]

(2.30)

Where \( X_i \) is the mole fraction of the species, \( m_i \) is the number of that particular segment type, and \( d \) is the hard sphere diameter of the segment. The dispersion term can be determined as for any Lennard-Jones type fluid, but was initially determined from a correlation initially determined by Cotterman et al. [45] and is as follows:

\[
\alpha_0^{disp} = \frac{er}{k} \left( \alpha_{01}^{disp} + \frac{\alpha_{02}^{disp}}{T_R} \right)
\]

(2.31)
Where

\[
a_{01}^{\text{disp}} = \rho_R \left[ -8.5959 - 4.5424 \rho_R - 2.1268 \rho_R^2 + 10.285 \rho_R^3 \right] \quad (2.32)
\]

\[
a_{02}^{\text{disp}} = \rho_R \left[ -1.9075 + 9.9724 \rho_R - 22.216 \rho_R^2 + 15.904 \rho_R^3 \right] \quad (2.33)
\]

Where \( \varepsilon \) is a Lennard-Jones intermolecular force (a fit parameter), \( k \) is the boltzmann constant \( T_r \) is a reduced temperature, and \( \rho_r \) is a reduced density defined as:

\[
\rho_R = \left[ \frac{6}{\sqrt{\pi}} \right] \eta \quad (2.34)
\]

It is interesting to note that the dispersion term and the hard sphere can be combined to form a Lennard-Jones segment, but for the SAFT model it is often more advantageous to leave them as separate terms, even though many times they are written as a single term. The chain term was applied in the following manner:

\[
\frac{a_{\text{chain}}^{\text{chain}}}{RT} = \sum_i X_i \left( 1 - m_i \right) \ln(g_{ii}(d_{ii})^{hs}) \quad (2.35)
\]

Where \( g_{ii} \) is the hard sphere distribution function and is given in the following equation as derived by Reed and Gubbins [46]:

\[
g_{ii}(d_{ii})^{hs} = \frac{1}{1-\xi_3} + \frac{3d_{ii}}{2} \frac{\xi_2}{(1-\xi_3)^2} + 2 \left[ \frac{d_{ii}}{2} \right]^2 \frac{\xi_2^2}{(1-\xi_3)^3} \quad (2.36)
\]

With the hard sphere distribution function dependent on the effective hard sphere diameter and on the density as follows:

\[
\xi_k = \frac{\pi N_A}{6} \rho \sum_i X_i m_i a_{ii}^k \quad (2.37)
\]
The association term for mixtures is given as follows:

\[
\frac{a_{\text{assoc}}}{RT} = \sum_i X_i \left[ \sum_A \left[ \ln X^A_i - \frac{X^A_i}{2} \right] + \frac{1}{2} M_i \right]
\] (2.38)

Where \( X^A_i \) is the mole fraction of molecules \( i \) that are not bonded at site \( A \) in a mixture and is given by:

\[
X^A_i = \left[ 1 + N_{AV} \sum_j \sum_B \rho_j X^B_j \Delta^{A_i B_j} \right]^{-1}
\] (2.39)

Which is summed over all of the sites and where \( \rho_j \) is the component density defined as:

\[
\rho_j = X_j \rho_{\text{mixture}}
\] (2.40)

and \( \Delta^{A_i B_j} \) is the association strength and given by:

\[
\Delta^{A_i B_j} = d_{ij}^3 g_{ij}(d_{ij})^3 \kappa^{A_i B_j} \left[ \exp \left( \frac{\xi_{ij}^{A_i B_j}}{kT} \right) - 1 \right]
\] (2.41)

With \( d_{ij} \) equal to the arithmetic mean of the pure components \( d_{ii} \) and \( d_{jj} \), and \( g_{ij} \) being the radial distribution function, and set as approximately equal to the hard sphere distribution function, given by:

\[
g_{ij}(d_{ij})^{\text{seg}} \approx g_{ij}(d_{ij})^{\text{hs}} = \frac{1}{1-\xi_3} + \frac{3d_{ii}d_{jj}}{d_{ii}+d_{jj} (1-\xi_3)^2} + 2 \left[ \frac{d_{ii}d_{jj}}{d_{ii}+d_{jj}} \right]^2 \frac{\xi_2}{(1-\xi_3)^3}
\] (2.42)

Which equation simplifies to equation (2.36) for the single component case.

It is important to note that even with this being the basic equation, terms can be left out depending on the compounds modeled. The associating term, for example, is
often left out when the compounds are non-associating, such as in the case of methane or propane.

Throughout this model there are three parameters that need to be fit for each compound, if the compounds is non-associating, $\sigma$, the temperature independent diameter, which is used to determine the temperature dependent value, $\varepsilon/k$, which is the Lennard-Jones intermolecular force over boltzmann’s constant, and $m$, which is the number of segments within that particular compound and, in the initial uses of this model, was often forced to be an integer or a logical fraction. If the compound is associating two additional terms are added, namely $\kappa_{AB}$, which is the bonding volume from sites A and B, and $\varepsilon_{AB}/k$, which is the bonding energy from sites A and B. Note that this equation would allow both self-associating, as in the case of pure water or the basic alcohols, and cross association, as one would expect from two compounds with a strong interaction such as water and methanol.

Several compounds were attempted with this model, and it did a reasonable job for its complexity and newness, but ultimately there were several flaws that were apparent in it. For example, the authors modeled methane, ethane, and propane with it and were able to predict both density and vapor pressure with a reasonable degree of accuracy, however this model was designed to be theoretically correct equation of state and so the parameters should fit a logical order and be predictable. However, this wasn’t necessarily the case. One would expect that for these three compounds the segment diameter to remain the same, or very similar, as well Lennard-Jones intermolecular force, and only the number of segments really changing over the course of the compound, however, this wasn’t the case. While the force was relatively constant over the three
compounds, the temperature independent segment diameter changed by almost 20%. This may, in part, be due to the fact that number of segments was forced to increase linearly, 1, 2, 3, but nevertheless this showed that there was yet some room for improvement in the model.

One of the difficulties that exists within this model is, in particular, the association term. In order to use the association term one must find the $X^{Ai}$, or the fraction of molecules, $i$, that are not bonded to site $A$. This calculation can, however, be simplified when one examines particular cases as demonstrated within a paper by Huang and Radosz [47]. For example in the case of a self-associating acid, such as acetic acid, where the molecules and sites appears as follows:

![Figure 2.3: SAFT self-association example](image)

The equation for $X^A$ can be simplified as the following:

$$X^A = \frac{-1 + \sqrt{1 + 4 \rho A}}{2 \rho A}$$

(2.43)

Which is simply a rearrangement of the equation given in (2.39). Since the derivation isn’t necessarily intuitive, nor is the equation necessarily explanatory the following is a
derivation for this case and the other equations given will be given without explanation should they be needed.

Initially equation [2.39] must be written for the case of only a single association site for a single component which is written as follows:

$$ X^A = (1 + X^A \rho \Delta )^{-1} \tag{2.44} $$

Which can be rewritten and solved according to the following steps:

$$ X^A + X^A^2 \rho \Delta = 1 \tag{2.45} $$

$$ X^A \rho \Delta + (X^A \rho \Delta)^2 = \rho \Delta \tag{2.46} $$

$$ 4X^A \rho \Delta + 4(X^A \rho \Delta)^2 = 4\rho \Delta \tag{2.47} $$

$$ 1 + 4X^A \rho \Delta + 4(X^A \rho \Delta)^2 = 4\rho \Delta + 1 \tag{2.48} $$

$$ 1 + 2X^A \rho \Delta = \sqrt{4\rho \Delta + 1} \tag{2.49} $$

Which becomes our initial expression given in (2.43). This will be our most important derivation as far as self-association is concerned as ionic liquids tend to follow this particular pattern of self-associating, but other derivations exist and, should a particular problem prove itself to be difficult beyond its worth to obtain a closed form solution, equation (2.39) can be solved directly through an iterative approach.

Should one desire an even simpler model there are alternate methods as well. In 1995 a modification to the SAFT model was proposed by Fu and Sandler [48]. In their
paper it was determined that a simplification could be made to the dispersion term by changing it to a model based on the work of Lee et al. [49]. The dispersion term was modified thusly:

\[
\frac{a^{\text{disp}}}{RT} = mZ_m \ln\left(\frac{\nu_s}{\nu_s + (\nu^*Y)}\right)
\] (2.50)

Where \(\nu_s\) is the segment molar volume calculated by \(\nu_s = 1/\rho_m\) and \(Z_m\) is the maximum coordination number and, in the original paper by Lee was treated as an adjustable parameter. Fu and Sandler used something of this approach and, rather than attempting to find the theoretical coordination number simply set it to 36 which is the maximum value in simplified perturbed hard chain theory as defined by Kim et al. [50]. For pure components \(Y\) is defined as:

\[
Y = \exp\left(\frac{u}{2kT}\right) - 1
\] (2.51)

With \(u\) calculated from the fit parameter \(u^0\) from the equation:

\[
u = u^0 \left[ 1 + \left(\frac{e}{kT}\right) \right]
\] (2.52)

With \(e/k\) set to -10K based on the fitting of the vapor pressure and liquid density of ethane. For mixtures \(Y\) is defined in conjunction with \(\nu\) as follows:

\[
\langle \nu \ast Y \rangle = \frac{N_{AV} \sum_i \sum_j x_i x_j m_i m_j (d_{ij}^3/\sqrt{2}) [\exp(u_{ij}/kT) - 1]}{\sum_i \sum_j x_i x_j m_i m_j}
\] (2.53)

With \(u_{ij}\) and \(d_{ij}\) being calculated as follows:

\[
u_{ij} = \left(1 - k_{ij}\right) \sqrt{u_i u_j}
\] (2.54)
With the other terms, namely the hard sphere, chain, and association terms, as described in the beginning of the section.

After this model was set forth it was tested for a variety of both associating and non-associating fluids, as well as for a small smattering of binary systems. The results for this model were quite good fitting the compounds used, and compared to the original SAFT model fit the compounds with approximately 25% less error in general. Furthermore, for binary mixtures it proved robust and capable of accurately predicting the azeotropes of the compounds tested. Unfortunately this model hasn’t been used by other authors for purposes of testing ionic liquid solubility, the model proved sufficiently intriguing that it was tested for ionic liquids later in this paper.

Another modification that has been made to the SAFT model, in particular the dispersion term, is allowing the hard-core segments of chain molecules to have attractive potentials of variable range. This model is often called SAFT-VR [51]. In this model the hard sphere and dispersion terms are written as a single term, called the monomer term as follows:

$$A_{mono}^{m} = m \frac{A_{m}^{m}}{N_{s}kT} = m \alpha_{m}^{m} \quad (2.56)$$

Where $N_s$ is the total number of spherical monomers and $\alpha_{m}^{m}$ is the excess free energy per monomer and can be written in the following expansion:

$$\alpha_{m}^{m} = \alpha_{HS}^{m} - \frac{\alpha_{VDW}^{m}\rho_{s}}{kT} \quad (2.57)$$
Where $a^{HS}$ is the standard Carnahan-Starling equation and $\alpha^{VDW}$ is the Van Der Waals attractive constant and can be obtained from the monomer-monomer interactions and is often calculated using the Barker and Henderson perturbation expansion as explained previously when the SAFT model was set forth in this paper. However, for in the original SAFT model, this dispersion term was done for the case of a Lennard-Jones type potential well, but the authors of the original paper solved this equation for alternate cases, such as case of a square-well, the Sutherland fluid case, the Yukawa case, and the Soft Repulsive fluid case. While going into each of these cases is generally unnecessary unless one has a specific case of interest, it may be beneficial to the reader to examine a particular case more in depth to understand in general how the other systems would change.

For the case of a square-well potential we begin with the generic expansion as mentioned previously, namely with monomer set as:

$$a^M = a^{HS} + \beta a_1 + \beta^2 a_2 + \cdots,$$  \hspace{1cm} (2.58)

With $\beta = 1/kT$. In the original SAFT model this back part of $a_1$ and $a_2$ was calculated for Lennard-Jones type potentials, but this can be modified. For the square well case, however, a number of changes result namely that $a_1$ and $a_2$ are changed to:

$$a_1^{SW} = a_1^{VDW} g^{HS}(1; \eta_{eff})$$  \hspace{1cm} (2.59)

$$a_1^{VDW} = -4 \eta \epsilon (\lambda^2 - 1)$$  \hspace{1cm} (2.60)

With $\eta_{eff}$ parameterized for energy between within $1.1 \leq \lambda \leq 1.8$, $\lambda$ being range and set as a fit parameter and $a_2$ given as the first density derivative of $a_1^{SW}$. As mentioned, the full
derivation of this model is unnecessary, as it adds little value for the effort, it is worth looking at these final results and comparing them to the original model. Note that they are both expansions of the same function and only the square well attractive potential function changed. This means that, even if one should have a model that behaves in some unusual fashion the SAFT model would be capable of dealing with it, with only minor shifts in the dispersion term.

This model, speaking of the SAFT-VR model specifically, is unusual in the fact that it is not a single equation, but instead a series of models that can be substituted into a particular facet of an overarching model. There are several ramifications of this, but from the accuracy standpoint it means that each of the different model types could potentially have a different accuracy for the types of compounds they were designed to model, which makes generic statements about the quality of the model difficult to make, and so specific SAFT-VR types need to be examined separately. Within the original paper n-alkanes and n-perfluoroalkanes were evaluated using the square well depth approach and compared to a basic SAFT-HS (Hard sphere only, meaning that the dispersion term was left off it) model. The results showed that the addition of the variable range attractive forces, the VR term in this model, improved the quality of the model in its ability to model and predict vapor-liquid coexistence curves and vapor pressures. However, while the fits are good it doesn’t appear to add a great deal of additional accuracy above what a simpler SAFT model might be able to do. However, in the years since the models inception it has proven itself capable of performing a number of powerful things, such as modeling a number of binary systems without the need for a binary interaction parameter [52], the ability to accurately measure and predict binary systems accurately with
pentafluorochemicals using only a single binary interaction parameter [53], and modeling
the adsorption properties of various gasses [54]. Furthermore, since the SAFT-VR model
only impacts the dispersion term, or the second part of the monomer term as used within
the original VR model, additional terms can be added onto the model, or other terms can
be changed, allowing for many other SAFT variations to change from a Lennard-Jones
type potential to another type.

Another form of SAFT that has been created is the soft SAFT equation [55] which
was created by Andreu and Vega. In this form of the model the chain term is set up to be
able to handle heteronuclear Lennard-Jones chains, in other words rather than using a
hard sphere model (Square well potential model), the model was based on a soft sphere
(Lennard-Jones model), which modified the chain term as follows:

$$\frac{A_{chain}}{N m k_B T} = \sum_{i=1}^{n} x_i (1 - m_i) \ln y_{ii}^R(\sigma_{ii})$$  (2.61)

where $y_{ii}^R(\sigma_{ii})$ is related to the pair radial distribution function for a Lennard-Jones fluid
by the equation:

$$y_{ii}^R(\sigma_{ii}) = g_{ij}^LJ(\sigma_{ii}) \exp(\varphi_{LJ}(\sigma_{ii})/k_B T)$$  (2.62)

with $\varphi_{LJ}$ being the potential energy between the various Lennard-Jones chain molecules
as follows:

$$\varphi_{LJ} = 4 \sum_i \sum_j \varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right]$$  (2.63)
and $g_R$ being the pair distribution function. In order to obtain a closed form solution, results were obtained from Johnson and Gubbins [56] which gives the results of:

$$ g_R^{LJ} = 1 + \sum_{i=1}^{5} \sum_{j=1}^{5} a_{ij} \rho^* i T^* j $$

(2.64)

With $T^*$ being a reduced temperature given by $T^* = k_B T / \epsilon$ and $\rho^*$ being a reduced density given by $\rho^* = \rho \sigma^3$. The values $a_{ij}$ are constants given by Johnson et al. [57].

This model did reasonably well during testing for the prediction of phase diagrams, but was generally less accurate than other SAFT models. That being said, the model used in the initial paper had only used the first-order perturbation expansion for the Lennard-Jones term (often done as the hard sphere - dispersion expansion) and that could easily be correct for should one have an interest in further exploring this model. Additional work has been done with this model as well, including the use of this model to predict the properties of ionic liquids, and an examination of that is including in the following section.

Another model that was developed for the SAFT model is the PC-SAFT model. This model, like some of the previous ones, proposes and modification to the dispersion term. This model, however, has shown itself to be somewhat more accurate than the previous models and so it has been used more than the other models. Furthermore, this model is the one that has had the most work done to it by this author and, thus, it behooves us to go into somewhat more depth and greater detail in this explanation than has been done with many of the previous examples. The model used here is the basic model as proposed by Gross and Sadawski [58]. The hard sphere contribution is based on the hard sphere model as presented by Carnahan and Starling [44].
where \( \eta \) is the close packing fraction, \( \rho_s \) is the molar density of the hard spheres, and \( d \) is the temperature dependent hard sphere diameter of a segment. The diameter of the segment is derived from the square well depth of the hard sphere, \( u_0 \), the radius of the temperature independent diameter, \( k \) is Boltzmann’s constant, \( \tau = \pi \sqrt{2} \), or the packing fraction for close packed spheres, and \( c \) is a constant of 0.12 based on the work of Chen and Kreglewski [59].

The chain term, as derived by Chapman et al. [43], is given by

\[
a_{\text{chain}}^{\text{hs}} = \frac{4\eta - 3\eta^2}{(1-\eta)^3}
\] (2.65)

with

\[
\eta = \frac{\pi N_{AV}}{6} \rho_s d^3
\] (2.66)

\[
d = \sigma (1 - c \ast e^{-\frac{3u_0}{k T}})
\] (2.67)

\[
\sigma = (\nu_0^0 \frac{6\tau}{\pi N_{AV}})
\] (2.68)

where \( \eta \) is the close packing fraction, \( \rho_s \) is the molar density of the hard spheres, and \( d \) is the temperature dependent hard sphere diameter of a segment. The diameter of the segment is derived from the square well depth of the hard sphere, \( u_0 \), the radius of the temperature independent diameter, \( k \) is Boltzmann’s constant, \( \tau = \pi \sqrt{2} \), or the packing fraction for close packed spheres, and \( c \) is a constant of 0.12 based on the work of Chen and Kreglewski [59].

The chain term, as derived by Chapman et al. [43], is given by

\[
a_{\text{chain}}^{\text{chain}} = (1-m) \ln\left(\frac{1-\frac{1}{2} \eta}{(1-\eta)^3}\right)
\] (2.69)

with all of the variables as defined previously.
The dispersion term for PC-SAFT is based off of the perturbation theory of Barker and Henderson [60] and expressed in terms of the SAFT parameters by Gross and Sadowski.

\[ \frac{a_{\text{disp}}}{RT} = \frac{A_1}{RT} * \frac{A_2}{RT} \]  

(2.70)

with

\[ \frac{A_1}{RT} = -2\pi \rho * I_1(\eta, m) \sum_i \sum_j x_i x_j m_i m_j \left( \frac{u_{ij}}{kT} \right) \sigma_{ij}^3 \]  

(2.71)

\[ \frac{A_2}{RT} = -2\rho \bar{m} * \left( 1 + Z^{hc} + \rho \frac{\partial Z^{hc}}{\partial \rho} \right)^{-1} * I_2(\eta, \bar{m}) \sum_i \sum_j x_i x_j m_i m_j \left( \frac{e_{ij}}{kT} \right) \sigma_{ij}^3 \]  

(2.72)

where \( Z^{hc} \) is the sum of the hard sphere and the chain term expressed as compressibility factors and \( I_i \) is the radial distribution function expressed as a power series.

\[ \left( 1 + Z^{hc} + \rho \frac{\partial Z^{hc}}{\partial \rho} \right)^{-1} = 1 + \bar{m}^{8\eta - 2\eta^2} \frac{(1-\eta)^4}{(1-\eta)(2-\eta)^2} + (1 - \bar{m})^{\frac{20\eta - 27\eta^2 + 12\eta^3 - 2\eta^4}{(1-\eta)(2-\eta)^2}} \]  

(2.73)

\[ I_2(\eta, \bar{m}) = \sum_{j=0}^{6} b_j(m) \eta^j \]  

(2.74)

\[ I_1(\eta, \bar{m}) = \sum_{j=0}^{6} a_j(m) \eta^j \]  

(2.75)

These equations show the final forms of the previously mentioned expressions where \( a_i \) and \( b_i \) are given by.
\[
\begin{align*}
  a_i(m) &= a_{0i} + \frac{m-1}{m} a_{1i} + \frac{m-1}{m} \frac{m-2}{m} a_{2i} \\
  b_i(m) &= b_{0i} + \frac{m-1}{m} b_{1i} + \frac{m-1}{m} \frac{m-2}{m} b_{2i}
\end{align*}
\]

(2.76)

(2.77)

where \(a_{ij}\) and \(b_{ij}\) are constants Gross and Sadowski obtained by fitting a variety of pure component density data.

Finally the association term is written as

\[
a_{\text{assoc}}^{RT} = \sum_{A} \left( \frac{\ln(X_A)}{2} - X_A \right) + \frac{1}{2} M
\]

(2.78)

with

\[
X_A = (1 + N_{AV} \sum_B \rho B X_B \Delta^{AB})^{-1}
\]

(2.80)

\[
\Delta^{AB} = g^{hs} \left( e^{\frac{\varepsilon_{AB}}{kT}} - 1 \right) d^3 \kappa^{AB}
\]

(2.81)

\[
g^{hs} = \frac{1 - \frac{1}{2} \eta}{(1 - \eta)^i}
\]

(2.82)

where \(g^{hs}\) is the pair correlation function as given by boublik [61], \(X_A\) is the fraction of association sites that are not bonded, \(\Delta^{AB}\) is the association strength, \(\varepsilon_{AB}\) is the association energy and \(\kappa_{AB}\) is the association volume.

These equations for PC-SAFT were initially presented by Gross and Sadowski and the equations used in this model have been unchanged since its inception. In these equations, although there is much that could be discussed about them, there are several
more important things to note from them. Amid these variables there are only five fit parameters $m$, which is the total number of segments per molecule, $v_{oo}$, the temperature independent segment molar volume in a close packed arrangement, $u_o/k$, the square well depth of each segment, $\varepsilon_{ij}/k$, the energy of association between two self-associating molecules, and $\kappa^{AB}$, which is the volume of association. In order to further minimize the number of parameters used the association term was removed leaving a total of 3 fit parameters for a single pure component and a single binary interaction parameter.

As mentioned previously, this model has shown itself to be somewhat more accurate than many of the previous dispersion modifications and since its inception it has been applied to many different types of systems from polar compounds, to organic compounds, to somewhat more esoteric compounds and it has shown itself to be able to predict and fit these compounds with reasonable accuracy. However, simply because this model has shown itself to be a robust model, does not mean that other modifications haven’t been made in an attempt to improve it even further, or apply additional modifications in order to allow it to more accurately model a particular type of party. Additionally this model has been used to model ionic liquids previously, and a more in depth look at the results of that is done in the following section.

Another model that hinges heavily on the PC-SAFT model is the ePC-SAFT model, or electrolyte PC-SAFT model [62] developed by Held et al. This model was designed, as one might infer from the name, for the use in modeling and predicting the properties of electrolytes. In this model, rather forcing the system make hard chains, the system allows the ions exist separately as well as allowing molecules to exist within chains should that be more appropriate as shown in the following equation:
\[ \frac{A^{res}}{N} = a^{res} = a^{hc} + a^{disp} + a^{assoc} + a^{ion} \]  

(2.83)

where the hard chain term (\(a^{hc}\) in the above expression) is simply the sum of the hard sphere and chain term and \(N\) is the total number of molecules. The addition of the ion term allows for the inclusion of coulombic interactions, in addition to the dispersive and associative already included. The ion term can be calculated using a Debye-Hukel term as defined by Held et al. [62] and can be included by charging species \(j\) as follows:

\[ \frac{a^{ion}}{k_B T} = -\frac{\kappa}{12\pi k_B T \varepsilon} \sum_j x_j q_j^2 \chi_j \]  

(2.84)

where \(q_j\) represents the charge of ion \(j\) and \(\varepsilon\) represents the dielectric constant. The ions within this model are modeled as if they were spherical species in a uniform dielectric continuum. The molecules can approach each other up to the diameter of the ion as given by \(\sigma_j\) or \(a_j\) as used within the ion term. Within that framework \(\chi_j\) is given by:

\[ \chi_j = \frac{3}{(\kappa a_j)^3} \left[ \frac{3}{2} + \ln(1 + \kappa a_j) - 2 \left( 1 + \kappa a_j \right) + \frac{1}{2} \left( 1 + \kappa a_j \right)^2 \right] \]  

(2.85)

where \(\kappa\) is the inverse Debye screening length given by:

\[ \kappa = \sqrt{\frac{N_A}{k_B T \varepsilon} \sum_j q_j^2 c_j} = \sqrt{\frac{\rho_N e^2}{k_B T \varepsilon} \sum_j z_j^2 \chi_j} \]  

(2.86)

with \(c_j\) being the molar concentration and \(\rho_N\) being the number density of the system. The effects of the ion with water are assumed to be completely accounted for within the hard chain and dispersion terms and therefore unnecessary.
This model once fully developed and established, was tested for its ability to predict ion behavior within water. Initially parameters were found for water, and then for various ions that one might encounter within a system. Then, once individual ion values were determined, the model was tested against various salts dissolved within water such as various fluorides, chlorides, and bromides among others. Once these values were obtained they were compared to experimental results, in the categories of density, vapor pressure, and activity coefficients. The results were shown to be quite good as well, with average relative deviations in density of less than 1%, less than 3.5% for vapor pressures, and less than 10% for activity coefficients. Furthermore, these values showed to be reasonable at a variety of temperatures showing its predictive power. Unfortunately, this model was only tested for relatively simple ions and no attempt has been made to model ionic liquids with them.

Another modification that has been made to the PC-SAFT model is the inclusion of a polar term [42]. While the attraction between particles has been modeled within other parts of the model, or at least accounted for within the fitted parameters, it has heretofore been an implicit fit within the models. Recognizing this weakness Karakatsani and Economou added a term that could handle this using a model pioneered by Larsen et al. [64] With the inclusion of this polar term, the model can explicitly model dipole-dipole, quadrupole-quadrupole, and dipole-quadrupole interactions through the use of the pade approximation as follows:

\[
\frac{a_{\text{polar}}}{RT} = m \frac{a_2^{\text{polar}}}{1 - a_3^{\text{polar}} / a_2^{\text{polar}}}
\] (2.87)
where \(a_2^{\text{polar}}\) and \(a_3^{\text{polar}}\) are the second and third order perturbation terms respectively and can be found using the following equations:

\[
\frac{a_3^{\text{polar}}}{RT} = \frac{a_2^{\text{polar}}}{RT} + \frac{a_3^{\text{polar}}}{RT} \tag{2.88}
\]

which, for spherical fluids Larsen et al. proposed the following solutions:

\[
\frac{a_2^{\text{polar}}}{RT} = -\left(\frac{1}{T_{\text{tilde}}}\right)^2 \frac{\eta}{K^3} \left[\frac{4}{3} \mu^4 + \frac{12 \mu^2 Q^2}{5 K^2} + \frac{12 Q^4}{5 K^4}\right] \tag{2.89}
\]

\[
\frac{a_{3.2}^{\text{polar}}}{RT} = \left(\frac{1}{T_{\text{tilde}}}\right)^3 \frac{\eta}{K^6} \left[\frac{6}{5} \mu^4 Q^2 + \frac{144 \mu^2 Q^4}{175 K^2} + \frac{72 Q^6}{245 K^4}\right] \tag{2.90}
\]

\[
\frac{a_{3.3}^{\text{polar}}}{RT} = \left(\frac{1}{T_{\text{tilde}}}\right)^3 \frac{\eta^2}{K^6} \left[\frac{10}{9} \mu^6 + \frac{159 \mu^4 Q^2}{125 K^2} + \frac{689 \mu^2 Q^4}{1000 K^4} + \frac{243 Q^6}{800 K^6}\right] \tag{2.91}
\]

where ref stands for the reference fluid, or the hard sphere fluid for Larsen et al. and the SAFT model and the other terms are defined as shown below:

\[
\mu = 85.12 \frac{\mu/m}{\sqrt{(u/k)\sigma^3}} \tag{2.92}
\]

\[
Q = 85.12 \frac{Q_{\text{basic}}/m}{\sqrt{(u/k)\sigma^3}} \tag{2.93}
\]

\[
\rho^* = \rho \sigma^3 \tag{2.94}
\]
where $\mu$ is the dipole moment, $Q$ is the quadrupole moment, and $K$ is a dimensionless quantity that accounts for the range of polar interactions as compared to hard-sphere interactions, meaning that $K = \sigma_p / \sigma$.

Additionally, it is known that within a charged system it is possible to induce dipoles and Karakatsani and Economou address this as well within the same paper by adding yet another term, an induced dipole term giving an overall expression that appears as:

$$
\frac{a^{res}(T, \rho)}{RT} = \frac{a^{hs}(T, \rho)}{RT} + \frac{a^{chain}(T, \rho)}{RT} + \frac{a^{assoc}(T, \rho)}{RT} + \frac{a^{disp}(T, \rho)}{RT} + \frac{a^{polar}(T, \rho)}{RT} + \frac{a^{ind}(T, \rho)}{RT}
$$

(2.95)

where, once again, these terms can be defined separately from each other yielding a veritable grab bag of equations that can be chosen to fit a particular compound or set of compounds. The induced dipole term here is the term as defined, again, by Larsen et al. as follows:

$$
a^{ind} = m \frac{a_2^{ind}}{1-a_3^{ind}/a_2^{ind}}
$$

(2.96)

Where $a_2^{ind}$ and $a_3^{ind}$ are also found through the use of the pade approximation and are defined as follows:

$$
\frac{a_2^{ind}}{RT} = -\frac{8}{T_{tilde}} \frac{\eta}{K^3} \mu^2 a
$$

(2.97)

$$
\frac{a_3^{ind}}{RT} = 10 \left( \frac{1}{T_{tilde}} \right)^2 \frac{\eta^2}{K^3} \mu^4 a
$$

(2.98)
with the other terms as defined previously.

Throughout all of these additional equations it is worth mentioning though that only one additional fitted parameter is added, namely the $Q_{\text{basic}}$, or the quadrupole moment. From a practical standpoint, this means that should a particular system have no quadrupole moment, or only the dipole moment is relevant, this system of equations simplifies dramatically and loses all need for additional fitted parameters. However, this is predicated on knowing the dipole moment of the system before modeling, but should that not be known the dipole moment, $\mu$, could be used as a fitted parameter, albeit with a minor loss to the integrity of the system. Furthermore, it is worth mentioning that, even though this model is displayed in the form previously shown, all of those terms need not be included. Should it be decided or determined that the induced dipole moment is small or irrelevant that term can be excluded with no loss to the overall integrity of the system.

At the inception of this model it was tested against a variety of different pure compounds. The values tested for all compounds were saturated pressure and density at a variety of different temperature ranges, as well as against a smattering of somewhat more unusual values, such as the second virial coefficient, $B$, the Joule-Thompson coefficient, and isochoric specific heat for a small sampling of these compounds. As it turns out, this model was quite good at predicting these values with only small (<2.5% AAD) deviations from the experimental values.

Another model that has been created and used is a model that is called SAFT1 by its creators Adidharma and Radosz [65]. The model created here is what can be termed a hetero-model, as opposed to the previous models, which were homo-models. What this
means from a practical standpoint is that in the previous models given, all of the spheres within a compound have the same size and energy terms or, in other words, all of the spheres within the compound are homogenous. Recognizing the limitations inherent in this sort of model, SAFT1 was created to allow the spheres within a particular compound to be different and distinct from the other if necessary creating a heterogeneous mixture of spheres. That is not to say that they need to be different, but for a particular compound they can be allowed to differ.

This model, at its heart, looks much like some of the other models, with the main equation being represented as the Helmholtz energy and being a sum of the pieces and terms that we have already seen in the previous models, namely the hard-sphere term, the dispersion term, and the chain term. The dispersion term is then simplified by assuming that the potential is a square well. However, at this point though the model begins to look, while somewhat similar, noticeably different from the previous versions seen to allow for a hetero distribution of spheres. The basic equations appear as follows with the “a” here being the dimensionless Helmholtz energy:

\[ a_{res} = \frac{\bar{a}_{res}}{RT} = a_{seg} + a_{chain} \]  
\[ (2.99) \]

\[ a_{seg} = (\sum_i X_i m_i) a_{0}^{seg} \]  
\[ (2.100) \]

\[ a_{0}^{seg} = a_{0}^{sw} = a_{0}^{hs} + \sum_{n=1}^{\infty} \frac{a_n}{(T^*)^n} \]  
\[ (2.101) \]

where \( a_n \) is the \( n \)th order perturbation term and \( T^* \) is the dimensionless temperature of \( kT/u \) where \( k \) is the Boltzmann constant. The hard sphere term is then defined as:
It is worth mentioning that, so far, this is the exact same equation that the previous SAFT models have used for mixtures. The difference between this equation and the ones used heretofore is in the way that the variables within the equation are defined. In particular the $\xi_k$ is defined as:

$$
\xi_k = \pi N_A \rho \frac{\sum_i X_i m_i \sum_\alpha x_\alpha (\sigma_\alpha)^k}{6} 
$$

where the symbol $\alpha$ denotes different segments, $\sigma_\alpha$ is the segment diameter, and $x_\alpha$ is the segment fraction defined as the number of moles of segment $\alpha$ divided by the total number of moles of all segments. In essence what was done here by Adidharma and Radosz is they took the same base equation but added an additional “mixing rule” to account for the mixing the different segments within the variables that make up the main equation. In theory such an approach could be taken for the other terms as well, allowing for, for example, the use of the PC-SAFT dispersion equation, or any of the various Soft SAFT dispersive terms if one could but find a theoretically reasonable mixing rule.

For the first perturbation term, or the first dispersive element, the energies need to be summed over all the segment pair interactions as shown.

$$
a_1 = \sum_\alpha \sum_\beta x_\alpha x_\beta a_{1,\alpha \beta} 
$$

Where we have $\alpha$ and $\beta$ as notations representing the different segment types and $a_{1,\alpha \beta}$ is the first order binary term for $\alpha$-$\beta$ segment interactions and is given by:
\[ a_{1,\alpha \beta} = -4 \left( \frac{\pi}{6} \sigma^{3} N_{AV} \rho \sum_{i} X_{i} m_{i} \right) u_{\alpha \beta} \left( \lambda^{3}_{\alpha \beta} - 1 \right) g_{\alpha \beta}^{hs} \left( \sigma_{\alpha \beta}, \xi_{3,\text{eff}} \right) \] (2.105)

Where the various terms designated as \((-\))_{\alpha \beta} represent the interactions between the various segments. For the most part all of these terms have been seen, and used, before, albeit possibly with some different mixing rules. The exception to this is the term \(\lambda_{\alpha \beta}\), which is the reduced range of the potential well for the segment interactions and is found by simply taking the arithmetic mean of the individual segments potential wells.

The hard-sphere radial distribution function, \(g_{\alpha \beta}^{hs}\) is determined in a process similar, but not identical, to what is done in other SAFT models as follows:

\[
g_{\alpha \beta}^{hs} \left( \sigma_{\alpha \beta}, \xi_{3,\text{eff}} \right) = \frac{1}{1-\xi_{3,\text{eff}}} + \frac{3\sigma_{\alpha} \sigma_{\beta}}{\sigma_{\alpha} + \sigma_{\beta}} \frac{\xi_{2,\text{eff}}}{(1-\xi_{3,\text{eff}})^{2}} + 2 \left[ \frac{\sigma_{\alpha} \sigma_{\beta}}{\sigma_{\alpha} + \sigma_{\beta}} \right]^{2} \frac{(\xi_{2,\text{eff}})^{2}}{(1-\xi_{3,\text{eff}})^{3}} \] (2.106)

where the values of \(\xi_{3,\text{eff}}\) and \(\xi_{2,\text{eff}}\) are found through the use of the reduced range of the potential well of the segment-segment interactions.

Should one desire there are further perturbation expansions that can be done for the dispersion term, and indeed within their paper Adidharma and Radosz go on to do the second perturbation expansion, but perhaps it might be more beneficial to note that such expansions can be made and, and indeed have even more terms than what is done in that work, should one desire it. The chain term, however, will be mentioned and its first order expansion looked at.

\[
a_{\text{chain}} = - \sum_{i} X_{i} (m_{i} + 1) \left[ \ln \left( g_{i}^{sw} (\sigma_{\alpha \beta}) \right) - \ln \left( g_{0,i}^{sw} (\sigma_{\alpha \beta}) \right) \right] \] (2.107)

\[
\ln \left( g_{i}^{sw} (\sigma_{\alpha \beta}) \right) = \sum_{\beta \geq \alpha} B_{\alpha \beta,i} \ln \left( g_{\alpha \beta}^{sw} (\sigma_{\alpha \beta}) \right) \] (2.108)
With \( g_{a\beta}^{sw} = g_{a\beta}^{hs}(\sigma_{a\beta}) + \beta u_{a\beta}g_{1a\beta}(\sigma_{a\beta}) \) where the second part of that equation is the perturbation from the Barker-Henderson perturbation theory as mentioned earlier and the hard-sphere radial distribution function given previously.

From these equations one can then begin to test the model on non-associating fluids for accuracy and predictive power. The model itself, while appearing a good deal more complex than some of the previous models, includes only one additional fitted parameter per segment, and that is the reduced potential range, \( \lambda \). In the initial paper the only compounds that were tested were alkanes, admittedly a reasonably large amount of them, but nevertheless no additional compounds were tested in its initial phase. Interestingly enough, due to the simple nature of alkanes, only one type of segment was needed per alkane as well, so while the model was developed to allow different segments within the compound it was initially only tested for homo species.

The hetero-SAFT model while accurate, was further improved upon, and made more useful for the modeling of ionic liquids, through the works of Tan et al. [66-67]. In this model this basic framework of SAFT1 was used, meaning the hard-sphere, dispersion, association, and chain terms, but additionally an ion term was added. The ion term was added specifically to account for free ions within a solution and, compared to the other four terms, is a long range interaction. The ion term is derived from what is called a Restricted Primitive Model [68], which leads to the name of this SAFT model, SAFT-RPM, or SAFT-Restricted Primitive Model. Within this model the long range coulombic interactions are given by:

\[
a_{ion} = -\frac{3x^2 + 6x + 2 - 2(1+2x)^{3/2}}{12\pi \rho N_A d^3}
\]  

(2.109)
with \( x \) being the dimensionless quantity defined as \( x = \kappa d \), where \( d \) is the hydrated diameter and \( \kappa \) is the Debye inverse screening length which is found from:

\[
\kappa^2 = \frac{4\pi}{\epsilon_w kT} \sum_j \rho_n q_j^2 = \alpha_0^2 \sum_j \rho_n z_j^2
\]  

(2.110)

\[
\alpha_0^2 = \frac{4\pi e^2}{\epsilon_w kT}
\]  

(2.111)

With \( \epsilon_w \) being the permittivity of water, \( \rho_{n,j} \) being the number density of ion \( j \), \( q_j \) being the valence of the charged ion, and \( e \) being the charge of an electron in esu. Furthermore, within the model the various fitted parameters are allowed to vary with temperature according to fixed equations with the initial fittings being done at 25°C.

This model was initially tested for five different ions in a variety of combinations, with anions and 2 cations. The fittings were tested against things such as density, osmotic coefficient, mean ionic activity coefficient, and vapor pressure. The final results were then compared to two other models and the results were generally significantly worse (At times >5x the error) even though it admittedly had more parameters having one salt parameter and 3 ion parameters. However, since the majority of the parameters were ion parameters this implies that the model would be ideal for property prediction of new compounds, having only one joint parameter that would need to be fit. Furthermore, while the comparison values were somewhat bad, the absolute percent errors were fairly small, being generally less than 1% error.

From SAFT-RPM sprang another model from Tan et al. called SAFT2 [69]. One of the major weaknesses of the SAFT-RPM model is the fact that the model is only valid when the reduced potential range is between 1.1 and 1.8, which simply is not a large
enough range for many ions. For example, during the fitting of the lithium ion the reduced potential range came out to two, which was a minor problem. Fortunately the average range of the lithium when paired with water was within the range of the possible, but there are other segments that have larger values that aren’t so easy to solve, such as Mg$^{2+}$ ($\lambda = 2.3$) or Ca$^{2+}$ ($\lambda = 2.2$). This problem is solved through modifying the hard-sphere radial distribution function or, more accurately, taking a step backwards to the more basic integral and solving that with different boundary conditions. Furthermore, while the authors were improving the model they also chose to improve the truncation term on their dispersion expansion. While the original and modified values look the same at first glance, namely:

\[
\alpha_t = \sum_{m=2}^{5} \sum_{n=1}^{2} D_{mn} \left( \frac{u}{kT} \right)^m \left( \frac{\eta}{\tau} \right)^n
\]

the difference lies in the fitted coefficients $D_{mn}$. In the original version by Chen and Kreglewski [59] the coefficients were fit to pure argon data, which makes less sense for the SAFT model as it is generally used for organic chains. So, in order to better reflect this, the new parameters were refit to the liquid saturation curve of n-alkanes.

These changes, while seeming fairly minor, resulted in impressive improvements in accuracy to this model over the SAFT1 model and the SAFT-RPM model. The model was able to, with good accuracy, predict osmotic coefficients, densities, and activity coefficients of a variety of different ions and alkanes. These changes also paved the way for the modeling of ionic liquids with this model as all the parts of an ionic liquid that might be desired to model are already set up.
While there are other SAFT modifications that can be, and have been made, the ones mentioned here are some of the most prevalent or seem like that would be well suited towards the modeling of ionic liquids or have been used to model ionic liquids.

2.5 Previous IL Work with the SAFT Model

As mentioned earlier in the previous section the SAFT model has been used to model ionic liquids. Previously several authors have used various models in order to simulate ionic liquid data. These works will be mentioned here as well as several potential issues that can be seen within the various author’s models.

In Andreu’s work she used a soft SAFT model [55] to attempt to predict CO$_2$ solubility [70-71] in ionic liquids and to show that the ionic liquid parameters could, in theory, be predicted. The soft SAFT model that Andreu used involved the three standard parameters used in this paper m, or the number of segments per chain, $\sigma$, the segment size, and $u^o/k$, the energy parameter. It is worth mentioning that $u^o$ is referred to as $\epsilon$ in Andreu’s works. Additionally Andreu uses the association term which adds two more parameters, the association energy, $\epsilon_{AB}$, and the association volume, $\kappa_{AB}$. In addition to these five parameters two additional were included for the inclusion of a polar term. However, this polar term was only used for the CO$_2$, which didn’t use the association term, and wasn’t part of the pure ionic liquid fitting. In the interest of completeness the two parameters used were the value for the quadrupole Q, and the molecular parameter $\chi_p$. Not all of these parameters were fit, however. For both the ionic liquid three main parameters were fit to temperature density data, but the association parameters were
derived from the parameters that had previously been used for alkanols [72] in order to avoid further fitting. No assessment is made as to whether this approach was acceptable or not, but the second paper used the same association parameters for the ionic liquid, implying that this approach was sufficiently reasonable so as to bear repeating. The fitting of the CO$_2$ parameters involved the fitting of the basic three parameters as the polar term parameters were either fixed, as in the case of $x_p$, or derived from literature [73-74], as with Q.

These papers show that this model does a good job in both of the primary purposes of its work, namely both modeling the solubility of the CO$_2$ well and having the parameters be ordered in such a fashion that different alkyl chains could be easily predicted. What this means in other words is that the parameters of untested ionic liquids with the same cations and anions could be predicted from earlier (or later) compounds of differing alkyl chain lengths. So, for example, the properties of [hmim][Tf$_2$N] could be predicted from the values of [emim][Tf$_2$N] or [omim][Tf$_2$N]. This prediction was set up so it could be done easily from knowledge of only the molecular weight of the compound according to the follows equations:

$$m = 0.0188M_w - 0.7590$$  \hfill (2.113)

$$m\sigma^3 = 1.926M_w - 221.350$$  \hfill (2.114)

$$\frac{m\epsilon}{k_B} = 8.540M_w - 514.820$$  \hfill (2.115)

However, despite these impressive accomplishments there are a few more desirable qualities that this work is lacking. Chief among these is the fact that, while
these parameters can predict different alkyl chain lengths easily, prediction becomes impossible if either the cation or the anion changes. Furthermore, even though it is mentioned that the parameters are easy to make predictions with, no predictions are actually with it leaving the results of any such prediction in doubt. As an added issue the model does not account for the exceedingly low vapor pressures of ionic liquids when the parameter fitting is done, this results in the ionic liquids having vapor pressures, which are simply ignored in the fitting.

Another group that used the SAFT model to model ionic liquids was Economou et al., in their work with tPC-PSAFT [75-77], where they attempt to fit parameters and solubility data without any real attempt at prediction, to see if their models could predict the correct shapes and flows of the real fluids. The major difference between the model I used and the one used in this paper is the inclusion of an association term and a polar term, whereas this paper attempts a similar model without these terms, resulting in a simpler, more succinct, model. In his work there are four parameters, the number of segments, $m$, a segment energy parameter, $u^0/k$, the segment volume, $v_{oo}$, and the segment polar diameter. These parameters were fit using density data over a wide temperature range. Furthermore, the segment energy that was used was the same across all ionic liquids of the same family, resulting in a slightly simpler fit. It is important to note that in addition to fitting the pure ionic liquid parameters to density data an additional term was added in order to cause the ionic liquid to exhibit a low vapor pressure. Since the exact vapor pressures of the ionic liquids aren’t known the fit that was attempted was order of magnitude only. In addition to these parameters three additional derived parameters were used, those being the association terms, energy and volume, and the dipole moment of the
polar term. The association terms that were used were estimated from literature data [78] using the dissolution enthalpy and entropy of CO$_2$ in the ionic liquid in accordance with the following equations:

$$\frac{\varepsilon^{AB}}{k} \approx -\Delta H^{\text{dissol}}$$

$$\kappa^{AB} \approx \exp\left(\frac{\Delta S^{\text{dissol}}}{R}\right)$$

The polar terms were decided to be the same as the dipole moment and effective polar interaction diameter as methanol. [79]

Within Economou’s work with ionic liquids it is interesting to note that his earliest paper is fit without regards for the low vapor pressure that ionic liquids exhibit and, instead, simply ignore the resulting ionic liquid vapor phase, much like Andreu’s previous work. However, in his later works his parameters were changed in order to better show this property. In these papers Economou modeled the solubility of ionic liquids with various solutes including, among others, water, CO$_2$, benzene, O$_2$, and CHF$_3$. The results obtained were generally good with $k_{ij}$s, or the binary interaction parameters, for ionic liquids in the range of ~.01 - .075 and had a slight upward trend with temperature. While the exact numerical fits weren’t given the values appeared to follow similar curvatures to experimental data, according to the plots given, at pressures of as high as 90MPa.

Another approached that has been done is the modeling of ionic liquids using a hetero-SAFT model, called SAFT2 [65,69,80]. Within the hetero-SAFT model the segments need not have similar sizes or properties, which seem to be the ideal for ionic
liquids as they are composed of several parts, namely the cation, the alkyl chain, and the anion, with each part having significantly different properties from the parts. The advantage to this approach is that once the properties of each part is determined, it is a simple matter of combining the various parts into new and untested ionic liquids, and thus easily estimate their properties. The hetero-SAFT model used, SAFT2, is somewhat unique and so a slightly more detailed discussion of the parameters will be mentioned as well as the method used for fitting these parameters. The parameters for the alkyl chain are \( v^0 \) (The segment volume), \( u/k \) (Energy of a segment), and \( \lambda \) (the reduced range of the square well potential). These parameters were fit by fitting, first, the values for ethane. Then, dividing that into two pieces, where logical, yielded the values for 2 methyl groups. Then, the values for other alkanes were calculated and the parameters for a methyl group were removed, leaving only the parameters for the alkyl group. This approach is known as the backbone-branch group approximation [81]. This yields a nice linear fit for these parameters that is easily derived. For the cation and the anion the fitting process became more difficult. The ionic liquids tested were fit to a large range of temperature and pressure density data and from this the myriad of parameters for each of these parts were determined. For the cation the parameters fit were \( v^0 \) (Segment volume), \( \lambda \) (the reduced range of the square well potential), \( n_B \) (group bond number), \( \epsilon^{AB}/k \) (association energy), \( \kappa^{AB} \) (association volume), and \( c_1, c_2, c_3 \). These last three parameters are unique as they are used to calculate a more commonly seen parameter, \( u/k \), according to the following equation.

\[
\frac{u}{k} = c_1 + c_2 T + c_3 T^2
\]  

(2.118)
where T is the temperature in Kelvin. For each anion the parameters are similar except that to determine \( u/k \) only \( c_1 \) and \( c_2 \) are used and the \( n_B \) for each anion is simply set to 0.

In short, fitting each ionic liquid involves a great deal of testing and available data because, unfortunately, the approach used by Ji resulted in an exceptionally large number of parameters, 17 per pure ionic liquid, with three for the alkyl chain, eight for the imidazolium, and six for the anion. However, once all of the properties for each of the pieces were determined the model showed an ability to predict the densities of the tested ionic liquids at higher pressures, and even predict the densities of new ionic liquids with the same cation and anion, but differing alkyl chain lengths with ARDs of less that .2%. In theory this method could even be used to predict entirely new ionic liquids using the pieces that had been constructed, but such work wasn’t done.

The fitting of the ionic liquid to \( \text{CO}_2 \) solubility was a similarly complicated affair [63]. \( \text{CO}_2 \) had its parameters fit to a combination of vapor pressure and density data. There were then 6 parameters fit to the \( \text{CO}_2 \) molecule, namely \( m \) (number of segments), \( \nu^\infty \) (segment volume), \( u^0/k \) (segment energy), \( \lambda \) (reduced range of the square well), \( \epsilon^{AB}/k \) (association energy), and \( \kappa^{AB} \) (association volume). Then, for the solubility modeling the assumption was made that all of the vapor phase was \( \text{CO}_2 \). Whether the model would naturally show no volatility in the vapor phase, or whether this artificial constraint was necessary to eliminate traces of ionic liquid from the vapor is unclear, but for the calculations the vapor was purely \( \text{CO}_2 \). Then additional parameters were added for the solubility prediction, namely additional association parameters \( \epsilon_L \) and \( \kappa_L \) for the cross association between \( \text{CO}_2 \) and the anion, and an additional three parameters for each of the
anion and the cation, $c_1$, $c_2$, and $c_3$ used to find the binary interaction parameters for the CO$_2$ and them according to the equation:

$$k_{\alpha\beta} = c_1 + c_2T + c_3T^2$$  \hspace{1cm} (2.119)

Finally one additional binary interaction parameter was included for the binary interaction between the CO$_2$ and the alkyl chain. This means that, not including the pure component CO$_2$ parameters an additional 7 parameters, (three for the anion, three for the cation, and one for the alkyl chain) were required to get the binary interaction parameters. However, despite this large number of fit parameters, or perhaps because of it, the model did what appears to be a reasonably good job of fitting the experimental data at pressures up to 20MPa. However, the large number of fit parameters as a whole makes this model extremely complicated causes it to require a very large amount of data in order to fit, but once obtained the model had heretofore unmatched versatility compared to the other SAFT models.

These SAFT models that have been used to model ionic liquids show a high degree of potential. In each of the cases presented here the model showed the ability to fit density data and CO$_2$ solubility data, as well as other data based on the paper in question. Furthermore, each of these models showed the ability to predict the properties of unmade or untested ionic liquids and hints at the ability to do so with a high degree of accuracy. Unfortunately, each of them has a number of issues that could be improved upon. In the case of Soft-SAFT some of the parameters were fit to somewhat random compounds, such as fitting the association parameters within the ionic liquid to alkanol data, even though such compounds associate differently than ionic liquids. Furthermore
the models and parameters that they used, while high ordered, showed that the ionic liquids would have a vapor pressure, which is clearly not accurate. In the case of tPC-SAFT while the model showed a great deal of promise and power, it was determined possible that a simpler model might well have a similar predicting power, allowing for a better fit with less fit parameters. The final model examined for ionic liquid / CO₂ solubility was the SAFT2 model. This model showed incredible predictive power, able to construct ionic liquids from simply basic parts. Unfortunately, using the model for new parts would require a great deal of new information and new fitting. Furthermore, each segment would have various interaction parameters with other segments requiring even greater number of fit parameters. The conclusion was that a new model could be developed that would allow similar predictive power and fitting ability without the requirement of so many parameters.
2.6 Works Cited


2 - P.J. Carvalho, V.H. Alvarez, I.M. Marrucho, M. Aznar, J.A.P. Coutinho, High pressure phase behavior of carbon dioxide in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and 1-butyl-3-methylimidazolium dicyanamide ionic liquids. Journal of Supercritical Fluids 50 (2009) 105-111


13 – S.O. Nwosu, J.C. Schleicher, A.M. Scurto, High-pressure phase equilibria for the synthesis of ionic liquids in compressed CO2 for 1-hexyl-3-methylimidazolium bromide with 1-bromohexane and 1-methylimidazole. J. of Supercritical Fluids 51 (2009) 1-9


20 – M. Yazdizadeh, F. Rahmani, A.A. Forghani, Thermodynamic modeling of CO2 solubility in ionic liquid ([Cn-mim] [Tf2N]; n=2, 4, 6, 8) with using Wong-Sandler mixing rule, Peng-Rabinson equation of state (EOS) and differential evolution (DE) method. Korean J. Chem. Eng. 28 (2011) 246-251


41 – A. Vetere, Again the Rackett equation. The Chemical Engineering Journal 49 (1992) 27-33


68 - Lee, L. L. Molecular Thermodynamics of Nonideal Fluids; Butterworth Publishers: Stoneham, MA, 1988


81 – S. Tan, Doctoral Dissertation, University of Wyoming, 2004
CHAPTER 3

SAFT MODELING

3.1 Project Scope

As mentioned in the previous chapter the SAFT model seems to offer greater predictive power than other equation of state models that have been used with no real loss in fitting ability or in the ability to model solubilities. However, the models that have been used to model gas solubilities in ionic liquids, though valid, could be improved upon. It was decided that one of the major improvements that could be made was a streamlining of the process, or a simplification of the process in such a way as to reduce the number of fit parameters required by the model.

Before accomplishing these objectives it was determined that a SAFT model would first need to be selected. This model would need to have a history of accuracy and good fitting as well as imply that it has the ability to model ionic liquids. Furthermore, the model would need to show that it could do so with a smaller number of fitted parameters than previously used. It was potential models that could be used were, first the Simplified SAFT model, and second the tPC-SAFT model without the association and polar terms.
The Simplified SAFT model was chosen because it was a simple model that appeared to have the pieces necessary to model ionic liquids with a minimum number of parameters. The simplified SAFT model also had a modification to the dispersion term that appeared to be an improvement over the basic dispersion term. The model had also shown itself to be an accurate model and was widely used for heavier organic chains which, while not identical to ionic liquids, bore enough similarities that there were expectations that the model would yield good results. However, for the simplified SAFT model no solubility fitting work was done and because of this, when the procedures are discussed later any mention of fitting or using CO$_2$ does not apply to the fitting of the Simplified SAFT model and only applies to the PC-SAFT model. The PC-SAFT model was chosen due to its frequent use in a wide variety of compounds. It had also been previously used to model ionic liquids and it was desirable to use an already proven model and attempt to improve it. In this case the improvement was made by limiting the number of required parameters, thereby simplifying the model.

3.2 Procedure

As a first step in developing a SAFT based model for CO$_2$/IL systems it was necessary to estimate values for these three pure component parameters. The parameters found needed to meet the following criteria: One, the model should fit the experimental pure IL density vs. temperature data well. This was accomplished by minimizing an AARD value. Two, the model should predict an appropriately low vapor pressure for the pure IL. This restriction was put into place because it quickly became apparent that were
the model fit to pure density data there would be a fair amount of vapor pressure associated with each of the ionic liquids. To assess this feature threshold value that the vapor was used which pressure was not allowed to exceed. If the model did predict a vapor pressure higher than the threshold, a large penalty to the optimization function was enacted. The vapor pressure cutoff that was used was selected based on the work of Earle et al. [1] showed that ionic liquid vapor could be obtained for extremely low pressures and that these pressures were less than .001 mbar. The third desired quality was that for a family of closely-related ILs, the SAFT parameters should also be closely related and correlated to molecular weight. To assess this criterion we consider how well \( \rho, m^*v_{oo} \) (total segment volume) and \( m^*u_o \) (total segment energy) correlate with molecular weight (each quantity should in principle increase monotonically with molecular weight for closely related ILs). Since there are multiple criteria for determining the parameter values, this is essentially a multi-objective optimization problem. I used a multi-level approach to address this multi-objective problem. In the innermost level the objective is to obtain the best fit in the density vs. temperature data; in the next level the parameters may be adjusted to meet the vapor pressure threshold; and in the outermost level adjustments were made to better match the molecular weight relationships. Once the values for the pure ILs have been obtained the next step was to attempt to obtain binary VLE data fit the data with binary interaction parameters (\( k_{ij} \)) as small as possible. Should the previously obtained values prove impractical or poorly indicative of the vapor pressure of the CO\(_2\) / IL mixture new IL parameter values were attempted.
The fitting of the pure ionic liquids was done to a wide variety of density data [2-15] while the fitting of the CO₂ solubility binary interaction parameters was fit to solubility data. In the case of fitting the CO₂, literature values were obtained from a work by Gross and Sadowski [16]. Gross and Sadowski report that these parameters describe, “the densities of the fluid region of carbon dioxide with good precision up to elevated pressures.” This statement has been confirmed through personal testing.

3.3 Results and Discussion:

The results for the simplified SAFT model were interesting and unlike anything that had been seen in the SAFT to date. Ultimately though it was decided that this Simplified SAFT model was the worse of the two models chosen and unfit for CO₂ solubility fitting and testing. As mentioned previously it was fit to density data for a variety of pure component ionic liquids, namely [hmim][eFAP], [hmim][Tf₂N], [hmpy][Tf₂N], [bmim][Tf₂N], [TMG][Tf₂N], and [TSILmpy][Tf₂N]. See table 3.1 for the fitted values.

The number of segments found, m, is quite low but the overall volume of the molecule, v₀₀, is fairly high. This means that the model is predicting that the ionic liquid is best composed of a small number of very large segments. Initially this was a cause for concern because all of the previous models had shown a larger number of segments than this, generally in the range of 10+, while this model showed the number of segments in the range of one to two. It was also concerning because there was no particularly discernible pattern that the segments followed, making prediction difficult. Fortunately,
after some data mining, it became apparent that there was a trend that could be seen, in that the number of segments correlated with a reasonable degree of accuracy to the ratio in sizes of the cation compared to the anion or visa-versa based on whichever one was larger. Results for this are reported in Table 3.1.

Table 3.1:

SIMPLIFIED SAFT PARAMETERS AND RATIOS

<table>
<thead>
<tr>
<th></th>
<th>[hmim]</th>
<th>[hmim]</th>
<th>[hmpy]</th>
<th>[bmim]</th>
<th>[Tf2N]</th>
<th>[Tf2N]</th>
<th>[Tf2N]</th>
</tr>
</thead>
<tbody>
<tr>
<td>m</td>
<td>1.36</td>
<td>1.46</td>
<td>1.49</td>
<td>1.34</td>
<td>1.62</td>
<td>1.51</td>
<td></td>
</tr>
<tr>
<td>v^oo</td>
<td>189.67</td>
<td>104</td>
<td>150.1</td>
<td>143.73</td>
<td>106.69</td>
<td>124.78</td>
<td></td>
</tr>
<tr>
<td>u^o</td>
<td>248.12</td>
<td>280.14</td>
<td>240.73</td>
<td>253.34</td>
<td>219.22</td>
<td>258.65</td>
<td></td>
</tr>
<tr>
<td>MW</td>
<td>612.28</td>
<td>241.33</td>
<td>460.46</td>
<td>421.38</td>
<td>398.28</td>
<td>433.39</td>
<td></td>
</tr>
<tr>
<td>m*v^oo</td>
<td>257.59</td>
<td>152.28</td>
<td>223.14</td>
<td>192.1</td>
<td>173.07</td>
<td>188.05</td>
<td></td>
</tr>
<tr>
<td>tot to cat ratio</td>
<td>3.66</td>
<td>1.44</td>
<td>2.58</td>
<td>3.03</td>
<td>3.43</td>
<td>2.87</td>
<td></td>
</tr>
<tr>
<td>tot to an ratio</td>
<td>1.38</td>
<td>3.26</td>
<td>1.63</td>
<td>1.49</td>
<td>1.41</td>
<td>1.54</td>
<td></td>
</tr>
<tr>
<td>dif ratio to m</td>
<td>1.30%</td>
<td>1.50%</td>
<td>9.80%</td>
<td>11.70%</td>
<td>13.00%</td>
<td>1.90%</td>
<td></td>
</tr>
<tr>
<td>dif from 0</td>
<td>0.01</td>
<td>-0.01</td>
<td>0.1</td>
<td>0.12</td>
<td>-0.13</td>
<td>0.02</td>
<td></td>
</tr>
</tbody>
</table>
The segment number, \( m \), corresponds with some precision to the number of ratio of the larger ion to the smaller. This implies that the Simplified SAFT model is, without any sort of prompting or training, “drawing” a segment around the larger ion and then discerning the mass fraction of the smaller ion. To a certain degree this could be viewed as a confirmation of the validity of the model, even with these difficult, fairly unrelated, components. As a further testament the total volume of the model was shown to increase with molecular weight with some accuracy as shown in Figure 3.1.

![Figure 3.1: Total volume as a function of Molecular Weight for the SSAFT model](image)

Unfortunately this model was eventually deemed unfit for use in ionic liquids. The main reason to choose a different model was that predicting the parameters of unmade compounds would be nearly impossible because, while there was a pattern to the
properties of the volume and the segment number, these associations were weak. For example, while the segment number did seem to follow the trend of ion size ratio, the model is highly sensitive to a change in the number of segments. Therefore if the prediction was off by 10%, the final result could be off significantly. Furthermore, in order to predict a new compound the segment number would be used to estimate the total volume of the segment. The final reason that this model was rejected is that with this model the total energy of the compound, or the number of segments multiplied by the segment energy $u^0$, behaved contrary to what was expected. Namely as the molecular weight increased, the total energy of the system trended downward or, at best remained relatively constant. For these reasons it was determined that a shift from this model to the aforementioned PC-SAFT model would be beneficial.

Initially some of the older ionic liquids were run in the PC-SAFT model to attempt to determine the strengths and weaknesses of this particular model type and to determine the overall validity of the model. The testing was done initially for a series of ILs that had been reasonably well tested so that comparisons could be drawn as to whether this model was within acceptable bounds for accuracy. The ILs chosen were various molecules across the $\text{Tf}_2\text{N}$ series, the $\text{BF}_4$ series, and the $\text{PF}_6$ series. The parameters determined for these ILs are shown in Table 3.2 below. The AARDs given are the values for the fit of the density compared to the experimental data.
Table 3.2:

PC-SAFT PARAMETERS AND FITS

<table>
<thead>
<tr>
<th></th>
<th>Ti2N</th>
<th>BF4</th>
<th>PF6</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>emim</td>
<td>bmim</td>
<td>hmim</td>
</tr>
<tr>
<td>Fit Values</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>uo/k</td>
<td>253.0111</td>
<td>250.5477</td>
<td>224.8754</td>
</tr>
<tr>
<td>AARD</td>
<td>4.50E-03</td>
<td>5.30E-03</td>
<td>3.00E-03</td>
</tr>
</tbody>
</table>

Notice that the most inaccurate fit that was obtained from this method was only about 1%, which can be seen in the following charts.
Figure 3.2: BF₄ series density fits

Figure 3.3: PF₆ series density fits
There would be little gained if the fitting of the pure density data was the only positive. Fortunately these results also show very linear and predictable fits, meaning that from these values new compounds and parameters should be able to be predicted according to the following expressions:

\[ m = C_1 M_w + C_2 \]  \hspace{2cm} (3.1)

\[ m v_{00} = C_3 M_w + C_4 \]  \hspace{2cm} (3.2)

\[ \frac{m u_0}{k_B} = C_5 M_w + C_6 \]  \hspace{2cm} (3.3)

Where \( C_n \) is found from fitting the known values in the series. Note that these are linear equations and thus should be easy to find and determine accuracy. A graphical example of the linearity of these expressions is given in Figures 3.5 - 3.7.
Figure 3.5: PC-SAFT parameters; number of segments vs. molecular weight

Figure 3.6: PC-SAFT parameters; total volume vs. molecular weight
Based on these results predicting the next point in the series would be simple. Once these trends were determined the next step was to test this seemingly obvious predictability. Since Tf₂N is generally the most studied ionic liquid it was chosen for use in testing the predictive power and the compounds tested were [C₃mim][Tf₂N] and [C₅mim][Tf₂N]. The fits for the previous equations used for Tf₂N left us with the values in Table 3.3:

Figure 3.7: PC-SAFT parameters; total energy vs. molecular weight
Table 3.3:

CONSTANTS FOR [Tf₂N] ANION

<table>
<thead>
<tr>
<th>C₁</th>
<th>C₂</th>
<th>C₃</th>
<th>C₄</th>
<th>C₅</th>
<th>C₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0193</td>
<td>5.8029</td>
<td>0.6297</td>
<td>-89.414</td>
<td>-3.1318</td>
<td>4718</td>
</tr>
</tbody>
</table>

These results allowed us to predict the parameters that would be used for [C₃mim][Tf₂N] and [C₅mim][Tf₂N]. These fitted parameters are found in Table 3.4. Then once the fitted parameters had been estimated the actual densities were used to predict to the same parameters as shown below:

Table 3.4:

[Tf₂N] PREDICTED VALUES

<table>
<thead>
<tr>
<th></th>
<th>m</th>
<th>v₀₀</th>
<th>u₀/k</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C₃mim][Tf₂N] (predicted)</td>
<td>13.63</td>
<td>12.17</td>
<td>253.02</td>
</tr>
<tr>
<td>[C₅mim][Tf₂N] (predicted)</td>
<td>14.17</td>
<td>12.95</td>
<td>237.17</td>
</tr>
<tr>
<td>[C₃mim][Tf₂N] (calculated)</td>
<td>13.86</td>
<td>12.06</td>
<td>259.80</td>
</tr>
<tr>
<td>[C₅mim][Tf₂N] (calculated)</td>
<td>14.32</td>
<td>12.82</td>
<td>237.53</td>
</tr>
</tbody>
</table>
Note how close the predicted values are to the calculated values. From this we can determine that estimation of new parameters is well within the reach of this model. Additionally, this model is simpler than many of the previous models and shows the extremely low vapor pressures expected of an ionic liquid.

Once these density-obtained parameters were determined the next step was attempting to fit the CO₂ solubility data to the model to verify that this model and these parameters could be used to fit this data using only a single binary interaction parameter, $k_{ij}$. It was also desirable to have this model be able to fit the solubility data at a variety of temperatures and it was decided to allow the binary interaction parameter to vary with temperature. Additionally it was determined that the density and saturation pressure values used for CO₂ were very important when determining the solubility of CO₂ within the ionic liquid, and the fitness parameters were adjusted accordingly. The values that were determined for CO₂ are given in Table 3.5.

Table 3.5:

CO₂ PC-SAFT PARAMETERS

<table>
<thead>
<tr>
<th></th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>m</td>
<td>3.9323</td>
</tr>
<tr>
<td>voo</td>
<td>1.689</td>
</tr>
<tr>
<td>uo/k</td>
<td>144.5643</td>
</tr>
</tbody>
</table>
It is worth mentioning that for these values, and for all of the values determined and mentioned so far, there is more than one value that can be found. The method that was used was used to determine local minimums and so the exact fit parameter values that can be determined depend somewhat on the initial conditions used. The values given and reported are the values that were determined to be the best fit among those local minimums obtained based on the previously mentioned criteria.

The values for the binary interaction parameter, $k_{ij}$, were initially fit at a variety of temperatures. The binary interaction parameters then obtained were allowed to vary linearly with temperature according to the equation (3.4).

$$k_{ij} = C_1 T + C_2$$  \hspace{1cm} (3.4)

The parameters were fit per compound as no discernible pattern was found across the “families” of ionic liquids and are given in Table 3.6.
Table 3.6:

BINARY INTERACTION PARAMETER TEMPERATURE DEPENDENCE

<table>
<thead>
<tr>
<th>IL</th>
<th>C1</th>
<th>C2</th>
</tr>
</thead>
<tbody>
<tr>
<td>[emim][BF₄]</td>
<td>0.0002</td>
<td>0.1271</td>
</tr>
<tr>
<td>[bmim][BF₄]</td>
<td>0.0004</td>
<td>0.0572</td>
</tr>
<tr>
<td>[hmim][BF₄]</td>
<td>0.0006</td>
<td>0.0095</td>
</tr>
<tr>
<td>[omim][BF₄]</td>
<td>-0.0006</td>
<td>0.4227</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[bmim][PF₆]</td>
<td>-0.0006</td>
<td>0.4118</td>
</tr>
<tr>
<td>[hmim][PF₆]</td>
<td>0.0002</td>
<td>0.1715</td>
</tr>
<tr>
<td>[omim][PF₆]</td>
<td>-0.0011</td>
<td>0.6088</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[emim][Tf₂N]</td>
<td>0.0002</td>
<td>0.1682</td>
</tr>
<tr>
<td>[bmim][Tf₂N]</td>
<td>0.0002</td>
<td>0.1563</td>
</tr>
<tr>
<td>[hmim][Tf₂N]</td>
<td>0.0005</td>
<td>0.0767</td>
</tr>
</tbody>
</table>

As mentioned there was no discernible mathematical pattern found across the families of ionic liquids. It did not seem to matter whether the compounds had similar anions or whether they had similar cations. However, in all of these cases the slopes, or the C₁ values, are a small number meaning that the temperature dependence, while important for accurate fitting, is not very strong. From a practical standpoint this means that once a single binary interaction parameter is determined one could use it for a variety
of different temperatures and expect that the value that would be found from fitting would be no more than a few percent different, assuming that the temperature variation was not too great (approximately <40K). For greater temperature variations it would be advisable to find an approximate slope in order to estimate a more accurate binary interaction parameter.

Once these well tested systems had been modeled using this simple version of SAFT they were compared to the results obtained by other SAFT researchers, where possible. The results were generally favorable and it was determined that this method was an acceptable method for modeling ILs. Once the accuracy had been verified this method was further used to model ionic liquids whose data had recently been determined in an attempt at modeling and doing predictive work with a different variety of ionic liquids. The first layer of the work, much as was done in the work described above, was fitting the parameters of these ionic liquids to the pure component density data of that liquid and verifying that the resulting pressures were suitably low. The parameters that were determined are shown below in Table 3.7.
Table 3.7:
NEW IONIC LIQUID PC-SAFT PARAMETERS

<table>
<thead>
<tr>
<th></th>
<th>[OHemim][TFA]</th>
<th>[emim][HSO4]</th>
<th>[emim][MeSO4]</th>
<th>[emim][MeSO3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(m)</td>
<td>13.7737</td>
<td>12.9439</td>
<td>13.6005</td>
<td>3.3602</td>
</tr>
<tr>
<td>(v_\infty (mL/mol))</td>
<td>8.1547</td>
<td>7.6153</td>
<td>8.2513</td>
<td>36.073</td>
</tr>
<tr>
<td>(u_0 (K))</td>
<td>315.2721</td>
<td>335.1047</td>
<td>312.3337</td>
<td>826.0939</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>[hmim][Otf]</th>
<th>[emim][DEP]</th>
<th>[emim][SCN]</th>
<th>[P2444][DEP]</th>
<th>[P66614][Tf2N]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(m)</td>
<td>3.081</td>
<td>2.725</td>
<td>12.9668</td>
<td>2.4381</td>
<td>74.8623</td>
</tr>
<tr>
<td>(v_\infty (mL/mol))</td>
<td>56.4108</td>
<td>57.0986</td>
<td>7.5755</td>
<td>101.3755</td>
<td>5.2252</td>
</tr>
<tr>
<td>(u_0 (K))</td>
<td>576.5044</td>
<td>591.7358</td>
<td>335.3713</td>
<td>502.5612</td>
<td>288.3967</td>
</tr>
</tbody>
</table>

Note that the results for these newer ionic liquids differ radically from the results determined for the older ionic liquids given previously. There are a variety of reasons why this might be, but the most compelling reason is most likely that there is less data available. When doing fitting for a single temperature density series, or even two temperatures, the results tend to be different than for larger temperature ranges. It is also worth mentioning that these compounds are so widely different that no particular attempt was made to fit these parameters into any sort of predictable pattern.

Among the newer ionic liquids for which modeling was attempted [P\textsubscript{66614}][Tf\textsubscript{2}N] bears a particular mention for its abnormal behavior as shown below in Table 3.8.
attempting to model $[\text{P}_{66614}][\text{TF}_2\text{N}]$ it, like all the other liquids modeled, was first fit to pure component density data. However, as the modeling was attempted, it was quickly found that the parameters that were converged to were highly unusual compared to the other ionic liquid parameters. The number of segments were approximately five times larger and had less segment volume than the others measured. While other parameters were discovered that could model the density of $[\text{P}_{66614}][\text{TF}_2\text{N}]$ reasonably well, all of the found parameters were just as unusual. While the reasons for this are currently unknown, as this is the only compound of this type that has been tested, it is hypothesized that the reason is that $\text{P}_{66614}$ is being broken up by the model into a series of $-\text{CH}_3$- and $-\text{CH}_4$ sized spheres. This theory is somewhat supported by the fact that this hypothesis would yield approximately thirty four spheres for the anion and the cation would yield close to fifteen or so. Admittedly this only accounts for about fifty spheres, but that is significantly closer than the average of ten to fifteen that is normally achieved for the ionic liquids. Additionally the average volume that is obtained for this compound is less than a standard ionic liquid.
Table 3.8:

\[[P_{6614}]\text{[Tf}_2\text{N]} \text{ PC-SAFT PARAMETERS}\]

<table>
<thead>
<tr>
<th>[P_{6614}\text{[Tf}_2\text{N]} ]</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>74.8623</td>
<td></td>
</tr>
<tr>
<td>5.2252</td>
<td></td>
</tr>
<tr>
<td>288.3967</td>
<td></td>
</tr>
<tr>
<td>0.0013</td>
<td></td>
</tr>
</tbody>
</table>

With these pure component IL parameters, as well as previously determined CO\(_2\) parameters, the modeling of the solubility, with attempts at prediction, were done using a single binary interaction parameter \(k_{ij}\). The results for the binary interaction parameters are shown in Table 3.9.
Table 3.9:

NEW IONIC LIQUID BINARY INTERACTION PARAMETERS

<table>
<thead>
<tr>
<th>[Ohemim][TFA]</th>
<th>[emim][HSO₄]</th>
<th>[emim][MeSO₄]</th>
<th>[emim][MeSO₃]</th>
</tr>
</thead>
<tbody>
<tr>
<td>k&lt;sub&gt;ij&lt;/sub&gt;</td>
<td>T</td>
<td>k&lt;sub&gt;ij&lt;/sub&gt;</td>
<td>T</td>
</tr>
<tr>
<td>0.148</td>
<td>299.3</td>
<td>0.1316</td>
<td>313.28</td>
</tr>
<tr>
<td>0.1678</td>
<td>313.75</td>
<td>0.1219</td>
<td>333.65</td>
</tr>
<tr>
<td>0.1544</td>
<td>333.5</td>
<td></td>
<td>1.0157</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>[hmim][OTf]</th>
<th>[emim][DEP]</th>
<th>[emim][SCN]</th>
<th>[P₂₄₄₄][DEP]</th>
</tr>
</thead>
<tbody>
<tr>
<td>k&lt;sub&gt;ij&lt;/sub&gt;</td>
<td>T</td>
<td>k&lt;sub&gt;ij&lt;/sub&gt;</td>
<td>T</td>
</tr>
<tr>
<td>0.1606</td>
<td>298.2</td>
<td>0.1331</td>
<td>298.5</td>
</tr>
<tr>
<td>0.1956</td>
<td>313.13</td>
<td>0.1343</td>
<td>313.73</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.0199</td>
</tr>
</tbody>
</table>

Note that this data was not fit to equation (3.4), given previously. This was done because in many cases there are only two data points and, while a line can be made with only two points, there would be serious concerns about the accuracy of any data extrapolated from such a line. In some of the cases where there are three points, which is still a small size for making a linear fit, the points often seem to follow no particular reasoning and therefore any line formed would be suspect as well.
As the simulations were run for these systems several interesting points were noticed. In particular one point that became markedly noticeable was the effect that the CO₂ parameters had on the system. Initially parameters were used that had been fit to the density and bubble point pressure data. However, it was soon found that these values were exceptionally poor at predicting higher pressure data and, in fact, it would not predict a significant increase in the slope of the pressure until concentrations were quite a bit higher than what has been observed experimentally. This was problematic and so different values for CO₂ were selected based on the work of Garcia, as mentioned previously.

The results seemed surprisingly good at lower pressures and, with the proper $k_{ij}$, could predict the point at which the pressure began to increase rapidly. It was found, however, that the curve was unable to match the pressures after the increase in slope, predicting pressures based on a less steep curve. Since changing the CO₂ parameters changes the curvature, as previously discussed, it may be that there is a set of CO₂ values that would match the ionic liquid data at higher pressures. Should such a value exist though, it is currently unknown. In addition to these observations it was noticed that the $k_{ij}$s found in the fitting generally were generally found to be a function of temperature and, in most cases, increased slightly as temperature rose. This was found to be the case for most of the systems run regardless of their anion or cation.

Once these older ionic liquids had been modeled it became apparent that perhaps it would be advantageous to do a more in depth comparison to some of the other SAFT models that had been run on the same systems. Therefore, systems were selected that had been modeled by other authors in order to better gain an idea of how similar the models
are. A randomly chosen system ([omim][BF₄]) from previously referenced author, Karakasani et al., was selected first. For this system, since the same experimental data was used in both cases, a careful attempt was made to imitate the data presented. While this attempt is as accurate as can be reasonably done, there are no guarantees as to the exactness of their data as shown in Figure 3.8. Comparing these plots it can be seen that, in particular for low pressures the values are nearly identical and it is only once the pressure begins to increase that the advantages to Karakasani’s method become evident. Greater accuracy can be expected from their model though because, as mentioned previously, this paper uses significantly less parameters, and yet the lower pressure fits are comparable.

![Figure 3.8: CO₂ solubility comparison with Karakatsani et al.](image-url)
The next comparison that was attempted was a comparison between the method presented here and the soft SAFT method employed by Andreu and Vega. The attempt at doing the comparison was similar to the previous comparison, except that different experimental data was used. The system was run again using the method previously described and the data that they reported [17]. For this system the accuracy of this model shines through somewhat more clearly than in the previous comparison because the experimental data used was strictly low pressure data and, therefore, well within the bounds of this models capabilities as seen in Figure 3.9. It is unknown why there are no data points from Andreu and Vega in the extreme low pressure range, it is apparent that this model is comparable, if not better, despite having less parameters.

![Andreu and Vega vs Peterson data](image)

Figure 3.9: CO$_2$ solubility comparison with Andreu and Vega

Once the solubility data was run and compared to other authors it became apparent that the model was, indeed, a good model, particularly in the lower pressure regions where most of the data was taken from, it was attempted on the newer ionic
liquids. The results for the newer ionic liquids were, unfortunately, subpar. Due to lower number of data points and the fact that many of the data points were taken on or near the point of rapidly increasing slope, it was difficult to model them as around that point is where the model begins to show itself to be weaker. Nevertheless, the fits are generally good and could probably be used to extrapolate the lower pressure data points with a fairly good accuracy. However, unlike the old ionic liquids previously discussed the AARD values tend to be significantly higher, with an average of about 13% error. This greater amount of error is assumed to be curvature of some of the plots and the difficulty in modeling the systems after the increase in slope.

In the interest of completeness all of the remaining solubility fits have been included below, without comparisons in order to showcase the strengths and weakness of this model with a graphical format.

Figure 3.10: [emim][Tf2N] solubility plots
Figure 3.11: [bmim][Tf2N] solubility plots

Figure 3.12: [hmim][Tf2N] solubility plots
Figure 3.13: [bmim][PF₆] solubility plots

Figure 3.14: [hmim][PF₆] solubility plots
Figure 3.15: [omim][PF$_6$] solubility plots

Figure 3.16: [emim][BF$_4$] solubility plots
Figure 3.17: [bmim][BF₄] solubility plots

Figure 3.18: [hmim][BF₄] solubility plots
Figure 3.19: [omim][BF4] solubility plots

Figure 3.20: [P2444][DEP] solubility plots
Figure 3.21: [emim][DEP] solubility plots

Figure 3.22: [emim][MeSO₃] solubility plots
Figure 3.23: [emim][MeSO₄] solubility plots

Figure 3.24: [hmim][OTf] solubility plots
Figure 3.25: [emim][HSO$_4$] solubility plots

Figure 3.26: [OHemim][TFA] solubility plots
3.4 Concluding Remarks

The results for this particular version of SAFT, simplified PC-SAFT, were determined to be satisfactory. This can be said for a variety of reasons. First, the fit
parameters are predictable and linear with molecular weight. This is important because new ionic liquids are synthesized with a fairly high rate. Unfortunately, it is difficult to determine in a laboratory setting the properties and solubilities of each of these new compounds. Second, if the properties of new ionic liquids can be easily and accurately predicted a great deal of work, time, and money can be saved. Furthermore, these results, both from prediction and fitting, result in good single component data yielding good results for density predictions with the additional benefit of predicting the extremely low vapor pressures that ionic liquids exhibit. Additionally these models do a relatively good job of modeling the solubility of CO$_2$ within the ionic liquid once a suitable binary interaction parameter has been determined. The only major problem that the model experienced was that at high pressures, generally pressures above 20 MPa, the model shows its weakness by failing to fully match the increased curvature of the solubility data. In summary this model, while simpler and with less parameters than the other SAFT models that have been used to model ionic liquid solubility, was able to model single component and multi-component data with accuracy that is comparable to other models.
3.5 Works Cited


12 – A. Shariati, C.J. Peters, High-Pressure Phase Behavior of Systems with Ionic Liquids: Part III. The Binary System Carbon Dioxide + 1-hexyl-3-methylimidazolium hexafluorophosphate. J. of Supercritical Fluids 30 (2004) 139-144


CHAPTER 4

LIFE CYCLE ANALYSIS BACKGROUND

4.1 Reasons for Doing a Life Cycle Analysis

Initially the only desire was to attempt to create a good working SAFT model and test it against various ionic liquids. After a model was found and tested it was determined that this was not enough. As mentioned previously one of the great hopes for ionic liquids is that they will prove themselves to be green chemicals, meaning that they would produce less waste and have less of an environmental impact than many currently used compounds. This information is included to specifically ask the question of whether using ionic liquids in a CO$_2$ \ ionic liquid co-fluid air conditioner could be used with less environmental impact. This is already partially accomplished and verified by realizing that ionic liquids have little to no vapor pressure. In other words, should a leak occur within the system and the working fluids escape, the ionic liquid would not get into the atmosphere in any appreciable amount. However, this is not enough information to determine whether ionic liquids are more environmentally friendly or not. Indeed, when determining the whether the ionic liquid \ CO$_2$ air conditioner was more environmentally conscious there are several concerns that are of greater import because the relative volatilities only matter when the air conditioner is allowed to leak out of the system, whether through a regular leak or because the device was improperly disposed of. The
First, and arguably the most important reason why volatility is a poor metric as to whether or not the ionic liquid is a green compound, is that in an air conditioning system the biggest source of waste is not from the leakage of the refrigerants, but from simple use of the system. Therefore, the big question is whether or not the new air conditioner is more efficient. Efficiency is so important because the vast majority of environmental waste is generated through the power plant as the system consumes power. The second reason, which is mainly important in a country that uses power sources with low environmental impact, is that the environmental impact of synthesizing and transporting the compound is greater than the impact the refrigerant would have on the environment if it were to escape and leak out into the atmosphere. For these reasons, it is important to complete a life cycle assessment of an ionic liquid / CO$_2$ co-fluid air conditioner.

4.2 Types of Life Cycle Analysis

There are several different types of Life Cycle Assessments. The most common types that one might see are the Cradle-to-Gate assessment, Open Loop Production, Gate-to-Gate, Well-to-Wheel, and Cradle-to-Grave. Cradle-to-Gate assessment is the analysis of a product from its inception, defined as the materials used to make the product existing in their raw states before they are harvested, to a stopping point. That stopping point, or gate, is determined by the one doing the assessment. For example, if a lumberjack were to perform a life cycle assessment, they would most likely evaluate the waste from the tree, until they have finished cutting and processing the wood, with no regard for what would occur after that point. A paper mill doing a Cradle-to-Gate life cycle assessment,
would be more likely to track their process from the tree to the moment that they had the paper ready to ship. So, what the gate is can vary widely from system to system. The Open Loop Production Assessment, also called the Cradle-to-Cradle Assessment, is designed in such a way that allows the disposal of the final product to be used in the creation of the new product. In essence, this type of life cycle analysis assumes a very particular type of recycling in which the recycled product is identical to the initial product. An example of this might be the recycling of glass bottles in which new glass bottles are formed. It may be argued that any sort of recycling constitutes an Open Loop Production, however this is technically incorrect unless each of the products that could be formed are analyzed in their entirety as well. Gate-to-Gate assessments consist of analyzing the environmental impact of a particular step within a process. For example, for the synthesis of [hmim][Tf$_2$N] there is a step in which hexanol is formed. If this step were to be analyzed as the entirety of the system it would be considered a Gate-to-Gate assessment. Well-to-Wheel assessments are designed specifically to analyze the transportation of either fuels or vehicles. This system can be used to evaluate the environmental impact of various modes of transportation and can be used to determine the environmental effects of differing fuels or vehicles. For the purposes of this paper the most important method is going to be the Cradle-to-Grave assessment. In this method the materials are analyzed from the raw materials to the moment in which the product reaches its end of life and is disposed. Whether this disposal is sending the material to be recycled or whether it is deposited in a landfill, when the initial product is complete and removed the life cycle assessment ends.
Each of these assessments are useful for analyzing either a particular type of process or a particular phase of a process. Completed, these assessments would analyze every possible environmental impact, whether it be land, air, water, radiation, or some more obscure type. However, often evaluating each of these types is difficult and so simplifications are made. Furthermore, within each of these methods there is some debate as to which materials might cause more impact than others. For example, if a product at its end of life has to leave behind either NO\textsubscript{x} or SO\textsubscript{x}, which of these would be the more environmentally friendly choice? One commonly used method is the CO\textsubscript{2} equivalent method, which will be used throughout the remainder of this paper. In this method any gasses that escape through the system have their global warming potential compared to the global warming potential of CO\textsubscript{2} and the units are the mass of CO\textsubscript{2} required for an equivalent amount of global warming potential. Global warming potential is calculated by finding the amount of energy that is absorbed by the greenhouse gas over an area for a fixed length of time that would otherwise escape into the vacuum of space. This value is then compared to the value that is obtained in a similar test for a reference material, in most cases CO\textsubscript{2}. For the sake of simplicity CO\textsubscript{2} has been determined to have a value of exactly one global warming potential unit. With this unit as a base the global warming potential, or GWP, of other compounds can be determined and in some cases is very high. For example, in the case of Sulphur hexa-fluoride, SF\textsubscript{6}, the global warming potential is approximately 23,000 times greater than carbon dioxide \cite{1} over a 100 year time span. However, this isn’t the only value that matters when analyzing the overall impact of a particular compound. Another important factor to determine is the length of time that a particular compound will exist in the atmosphere.
For example, carbon tetrachloride, $\text{CCl}_4$, it has an average expected life time in the atmosphere of 47 years. This means that if one were to analyze the same sample of air for a long period of time the effect of carbon tetrachloride would become less and less and the study went on longer and longer. So, if one were to analyze the effects of carbon tetrachloride in the environment as a function of time they would notice that the effects would begin to dissipate as time went on.

As a life cycle analysis is examined it becomes apparent that global warming potential isn’t the only method of evaluating environmental impact. Another method of evaluating impact is examining the acidification of a process. Acidification, in this work, will be measured in grams of H\(^+\) equivalent. What this means is that, during a process, a certain amount of waste is generated and this waste can be analyzed to determine the amount of either direct hydrogen ions, or show the potential to react with electrons. In essence, Lewis acids can be analyzed to determine their acidification potential in grams of H\(^+\) equivalent.

In addition to acidification another form of environmental waste that can be found when evaluating environmental impact is the smog potential of a particular process. In this work the smog potential of a process will be measured in grams of NO\(_x\) equivalent. For the purposes of this work smog is measured using the photochemical ozone creation potential (POCP) of a particular process’s byproducts. Then the POCP found from that process is converted to grams of NO\(_x\) equivalent for the same amount of POCP. The values listed in this paper are given in NO\(_x\) equivalent rather than in the photochemical ozone creation potential values because it is a more tangible quantity and is more likely to have meaning for the reader.
The final type of environmental impact that will be examined within this work is ecotoxicity. There are a variety of ways to measure ecotoxicity, but in this paper it will be measured in grams of 2,4 Dichlorophenoxyacetic acid equivalent, often called 2,4-D. 2,4-D is a pesticide and, according to a manufacturer’s website, the world’s most commonly used herbicide [2]. Due to its often used status 2,4-D has had its toxicity extensively tested and thus can be used as a good baseline for comparisons. Toxicity is often measured in LD50 and LC50. LD50 is the dosage required to kill half of a given population and LC50 is the concentration required to kill half of a given population, often referring to the air borne concentration. For 2,4-D the LD50 in rabbits, when the toxin is applied dermally is 2.2 grams per kilogram of the rabbit. The LC50 is 2.06 mg/L over four hours for rats. There is a fairly large discrepancy in the values obtained for oral LD50 in rats but the true value is likely between 1.09 grams and .764 grams per kilogram of the rat [3-4]. These toxicity values, and other comparisons, can be found in various material safety data sheets. To put this in perspective, an average person in the United States has an average mass of approximately 81 kg [5]. Assuming that humans are sufficiently similar to rats and rabbits this would mean that ingesting approximately 81 grams of 2,4-D or having approximately twice that amount applied dermally would be fatal. Of course, within the processes presented in this work there is no actual 2,4-D being synthesized, but the toxicity of the byproducts from the processes can be compared to 2,4-D and have an equivalent mass found.
4.3 Refrigeration Process

Before actually doing a life cycle analysis of the refrigeration system and parts required to make the system work, it is important to understand the actual process by which an ionic liquid / CO$_2$ co-fluid refrigeration system works. A representation of how an ionic liquid / CO$_2$ co-fluid system works is shown in Figure 4.1 below while many of the details of the thermodynamics are given in papers by Greenfield et al. and Mozurkewich et al. [6-7]

![Figure 4.1: ionic liquid / CO$_2$ co-fluid air conditioner](image)

An explanation of how this works will begin at point one. At point one there is a gas, CO$_2$, and a liquid, CO$_2$ in the ionic liquid. From one to two the mixture is compressed which increases the pressure and forces more of the CO$_2$ into the liquid solution. From step two to three the mixture passes through the resorber. As the mixture
passes through the resorber heat is rejected into the environment lowering the
temperature of the mixture, which causes an even greater amount of the CO$_2$ to be
absorbed into the mixture. From this point the mixture passes through a heat exchanger
which further cools it by giving even more heat to the fluid flowing in the opposite
direction, which ends up fully liquefying the mixture, after which it arrives at point four.
From this point the liquid passes through an expander, which drops the pressure and
cools the liquid even further. This cooling and pressure drop once again sets the system
into a state where the CO$_2$ is once again present in the gas phase where it arrives at point
five. The mixture then passes through a desorber where heat is taken from the space to
be refrigerated, which increases the temperature of the system and causes more of the
CO$_2$ to be separated out of the liquid state. In the final stage of this process the mixture
passes once again through the heat exchanger, except this time it absorbs the heat which
further increases the temperature and causes even more CO$_2$ to become gaseous.

From the perspective of completing a life cycle analysis of a system of this nature
most of the previous information is extraneous. Overall, from the perspective of a
complete life cycle analysis, input required to perform a life cycle analysis is the energy
required to run the air conditioner. Since refrigeration systems are measured in tons of
cooling, or the amount of cooling required to freeze one ton of ice (12,000 BTUs per
hour) and seldom display the amount of energy required to run them, it is more efficient
to use the tons of the cooling of a particular air conditioner and the coefficient of
performance (COP) of a system to determine the amount of energy the system will
require in order to operate. The coefficient of performance is defined for a refrigeration
system as:
\[ \text{COP} = \frac{Q_c}{W} \]  \hspace{1cm} (4.1)

Which can be rewritten as:

\[ W = \frac{Q_c}{\text{COP}} \]  \hspace{1cm} (4.2)

For a theoretical air conditioner with one ton of cooling and a coefficient of performance of one and a half the energy required to run the system is easily calculated at 8000 BTUs. From this it is clear that for a more efficient system the amount of energy required to run the system for a similar amount of cooling is less. Thus in order to improve the system an ionic liquid, or alternate co-fluid, that would increase the coefficient of performance would lower the amount of energy required to run the system.

4.4 ISO 14000

One of the major reasons that companies care about environmental impact is because of ISO 14000. ISO stands for internation organization for standardization and is ISO rather than IOS because ISO stands for the Greek word isos, meaning equal, therefore in whichever country it exists the shorthand version of the name will always be the same [8]. Many companies across the globe desire to obtain ISO certification because compliance with ISO certification ensure, at least in theory, that the products and services performed and delivered are reliable, of good quality, safe, and environmentally friendly. In practice this may not always be the case, but many companies recognize that having ISO certification can potentially open up new markets and increase clientele.
Within ISO certification ISO 14000 is the branch of ISO standardization that applies specifically to environmental management.
4.5 Works Cited


2 – http://www.24d.org/, The Industry Task Force on 2,4-D Research Data, Accessed 09-2013


8 – http://www.iso.org/iso/home/about.htm, ISO, Accessed 09-2013
5.1 Project Scope

In this project it was decided to attempt a complete life cycle analysis, meaning a cradle-to-grave analysis. In order to do a complete life cycle analysis the project was broken up into several distinct parts. The parts were the synthesis of the ionic liquid from resources that could be gathered from nature and the various energies required to form them, the creation the actual air conditioner, meaning the physical structure of the machine, the energy required to run the air conditioner during its life time, and what became of the various physical parts after its life was done. It was additionally decided that SimaPro, software designed to assist in doing life cycle assessments, would be used to assist in creating and analyzing the environmental impact of this cycle.

SimaPro was chosen both for its ease of use and for its large store of existing materials, energy forms, and chemicals and proved to be a good choice for a variety of reasons. First, it already had within its database a physical air conditioner without any sorts of working fluid, which alleviated the need to do detailed calculations of it and its various parts. While, admittedly there is a certain amount of deviation across different types of air conditioners, the basic framework and energy requirements should be similar across similar sizes and so the only difficulty was in figuring out the actual mass of an air
conditioner. Secondly, it had a wide variety of differing energy options. When deciding the environmental impact that would result from powering the air conditioner over its lifetime it became a question as to where the energy would come from. For example, if the power comes primarily from a coal fired power plant the air pollution would be significantly stronger than if the power had come from a nuclear power plant. SimaPro simplified this having within its database both regional blends across the United States, as well as other countries, and the pure energy types so that new blends could be created should the need arise. The third reason that made SimaPro a good choice for software was its chemical database. While it did not have the ionic liquids that would be required to run the air conditioner, it did have a wide variety of chemicals and raw natural materials that could be used. Therefore rather than having to trace the synthesis of the ionic liquids all the way back to the raw natural materials they could be traced back to certain chemicals within the SimaPro database, which obviated the need to do a large number of calculations and assessments.

As a final point it should be noted that for several of the compounds that needed to be modeled there were certain types of data were unavailable that was necessary for the calculation of the final environmental impacts. These values were estimated using the following methods where necessary. The first thing that was attempted was that, where possible, the compound was modeled in Aspen plus’ UNIFAC modeling system which would estimate the missing values. Many of the compounds that needed to be modeled this was not possible due to the incompleteness of Aspen Plus’ UNIFAC estimation data [1]. If this was deemed to be infeasible the various necessary properties
were predicted through the use of alternate methods determined by a variety of authors as outlined below.

If the heat capacity was needed and unavailable there were several methods that were employed. For the majority of the organic compounds there were two methods that were employed, depending on which of the methods had the available data to fit the compound [2-3], with a preference for the second should they both prove possible. Both of these methods used a group contribution method in order to find values for heat capacities and the second paper, by Ceriani et al., provided a method for predicting vapor pressure using a similar method. Unfortunately, both of these methods were for organic compounds and lacked any of the ions required to model ionic liquids. Fortunately there is a method proposed by Valderrama et al. that allows for the prediction of the heat capacities of ionic liquids [4-5]. This method uses the group contribution method and a mass connectivity index in order to find values for the heat capacity of ionic liquids.

Another set of important values were the critical values. There were two methods that were chosen to estimate the critical values of compounds, one by Joback and Reid [6] and one by Riazi et al. [7]. While both of these methods appeared viable it was determined that method employed by Riazi et al. was somewhat more generic and would allow a greater range of compounds to be modeled. This second method has also been tested against a wider variety of compounds, including polar and non-polar compounds, which make it appear somewhat more useful when modeling ionic liquids.

The final value that proved necessary was the enthalpy of formation. This value was necessary for calculating the heat of reaction, which was used to calculate the
amount of cooling water necessary or the heat duty required to keep the reaction moving forward. This value was calculated using a method proposed by Vatani et al. [8]. In this method QSPR was used to find descriptors which were of importance to the prediction of enthalpies of formation. The descriptors that were found to be of import were the number of non-hydrogen atoms, the sum of conventional bond orders (without including hydrogen bonds), the number of oxygen atoms, the number of fluorine atoms, and the number of heavy atoms. This model was trained using a large variety of differing compounds and tested against a reasonably large variety and proved to have good accuracy. Unfortunately this model went untested against ionic liquids and had none within the training set. Despite this it was decided that it would be sufficient.

5.2 Procedure

Since the energy and the actual air conditioner were primarily within the SimaPro database the major hurdle was the determination of the synthesis pathway and the energy requirements for the creation of the ionic liquid. Fortunately due to SimaPro’s database it was unnecessary to trace the creation method all the way back to natural resources. It was still necessary to trace it back to compounds within the database, however. Another complexity is the fact that most of the ionic liquid synthesis that is accomplished is done in lab scale sized quantities. For a theoretical ionic liquid / CO$_2$ co-fluid air conditioner an industrial scale synthesis route would be needed. This meant that when potential synthesis routes were evaluated only synthesis routes with the potential to be used on an industrial scale were considered. With these restrictions and values in mind it was simply
a matter of deciding what ionic liquids would need to be synthesized. The ionic liquids that were selected were [hmim][Tf$_2$N], because it is a relatively common ionic liquid and could serve as a good “base” case to which any other could be compared, and [P66614][3 triazolide], because it was, in theory, a good ionic liquid for creating this type of air conditioner. From these conditions and these ionic liquids the synthesis plans were created. The plan for the synthesis of [hmim][Tf$_2$N] is included in Figure 5.1 below while the synthesis plan for [P66614][3 triazolide] can be found in Figure 5.4.

![Diagram of synthesis of [hmim][Tf$_2$N]](image)

Figure 5.1: Synthesis of [hmim][Tf$_2$N]

The chemicals in green are inputs from SimaPro, and thus require no additional steps to synthesize and the red are chemicals that do not move onto the next step, or are waste. Note that although the chemicals in red are called waste it does not necessarily
mean that they are going to be thrown away, as in many cases the byproducts can be sold or used, but that since they are byproducts that do not go on to the next step they have no use in the main flow of things and are thus wasted products. The black chemicals in larger font are the chemicals that move onto the next process and are the most relevant to the production of the final compound. It is important to note that during this process the intermediate products will probably have to be shipped from one location to another, as different factories would work on different steps. Since many of these factories don’t actually exist and, therefore, distance between them is purely speculative, it was decided that the chemicals would have to travel a total of once across the country during its synthesis. It is difficult to know whether this is actually accurate, but it does allow for an accounting for the pollution created by the trucks as it is shipped.

Once a route had been determined and deemed viable the next step was finding the specifications of the actual reaction, namely things like the temperature, pressure, and how far towards completion the reaction goes. When a particular value was not specified, as was the case in certain reactions, the default temperature was assumed to be 15°C, the default pressure was assumed to be 1 bar, and the default reaction completion was 100%. Once all of these values had been determined the reaction was fed into Aspen with the following generic form:

![Figure 5.2: Generic chemical synthesis form](image)
Initially each of the components was given their own individual stream. From there they were mixed within the mixer to account for any heat of mixing that may exist. From there the compounds were passed through a heat-exchanger, which often ended up being a heater, in order to get the reaction up to the proper temperature for the reaction to occur. From there it went into the reactor. It should be noted that generally the reaction occurred at atmospheric pressure, and as such generally required no sort of pressure shift, but should one have been required there would have been a pump after the heater. From there the compounds flow into the reactor where the reaction occurs. The residual was then cooled to room temperature, and possibly depressurized should the scenario demand it, and was passed through a separator. It should be noted that the energy required here is simply an estimate and that, were this process actually an industrial process there would be somewhat more energy efficient methods employed, such as using a heat exchanger to both cool the final product and preheat the initial reactants, as well as having a more accurate separation process. Since this calculation was done as a preliminary way of calculating the environmental impact, especially in comparison to the environmental impact of actually running the air conditioner, it was deemed sufficiently accurate.

It is important to note that this is simply a generic template and that the individual processes could have their own deviations, based on the necessities of that process and a full list of each of the processes can be found within the appendix. That being said, some of the more unusual exceptions will be mentioned here. For potassium fluoride, since performing the reaction in Aspen resulted in unusual results, the energy was calculated by finding the heat of reaction, and then finding the energy required to remove the water from the resulting system. There was no Aspen calculation done during this process. For
the synthesis of [hmim][Cl] the reaction didn’t yield very much of the desired product, having a yield of only about 15%, so the reaction had a recycle included in it. The recycle was after the separator in order to only recycle the reactants. This resulted in a much more efficient system in which all of the reactant was eventually reacted, albeit after passing through the reactor approximately eight times. While there were other deviations aside from this, these were the two major deviations.

Another decision that needed to be made was the decision of the efficiency, lifetime, and amount of use that the air conditioner would see. It was determined that the lifetime of the air conditioner would be set at ten years before it was scrapped out with no recycling. The air conditioner was set to be a one ton air conditioner and would run for 50% of the time during its lifetime. Additionally it was determined that the coefficient of performance, the COP, was approximately 1.5 for an air conditioner that ran on a cofluid [hmim][Tf₂N] / CO₂ mixture. The COP for a straight CO₂ air conditioner was approximately 2.2. The COP for a hypothetical ionic liquid /CO₂ mixture was assumed to be 4.7 and this hypothetical ionic liquid was later determined to be [P₆₆₆₁₄][3 triazolide]. This COP is theoretical and, unfortunately, an actual determination could not be made. Additionally it was decided that the ionic liquid was more or less completely recycled upon its end of life and the CO₂ was “scrapped” meaning that it was released into the atmosphere. To summarize, the one ton air conditioner would be scrapped after running for ten years, being run for 50% of its life. The ionic liquid is assumed to be completely recycled with therefore no particular environmental impact except for transport after disposal, and the CO₂ is simply released into the atmosphere.
5.3 Results

The environmental impact results are best broken up into different categories, namely the environmental impact from the synthesis of the ionic liquids, the impact from the actual use of the air conditioner, and the impact from the synthesis of everything else. Since it is the strongest impact, and the basis to which the other impacts will be compared, the emissions from using the air conditioner will be analyzed first.

As mentioned previously this one ton air conditioner is assumed to last for ten years with a duty cycle of 50%. This hypothetical air conditioner will be analyzed for three different coefficients of performance, as mentioned previously. One for the [hmim][Tf2N] case, which will have a coefficient of performance of 1.5, one for a straight CO2 air conditioner with a coefficient of performance of 2.2, and one for the [P66614][3 triazolide] with a coefficient of performance of 4.7. The environmental impact will be analyzed for various energy cases. In other words, the impact will be analyzed for cases where the energy used to run the air conditioner comes from differing sources so that a more complete picture of the environmental impact can be determined. Three different electrical sources will be analyzed, the electricity at the grid from the eastern United States, the electricity at the grid from the western United States, and, for the purposes of extreme comparison, pure nuclear power generated in the United States.

For the eastern United States mix the blend was assumed to be approximately 57% bituminous coal, 23% nuclear, 10% natural gas, and the remaining 10% a mixture composed of six other sources, primarily lignite coal, hydropower, and biomass. For this type of ratio the global warming potential, measured in grams of carbon dioxide, comes
primarily from the bituminous coal, at 83.5% of the total equivalent mass, 9.97% from Natural gas, and the balance from the remaining sources. Note that these second, equivalent mass ratios aren’t the same necessarily as the percent of power that was supplied because not all types of power produce the same global warming potential. For example, while nuclear power produced almost 25% of the power used, the amount of global warming potential that results from a nuclear power plant is significantly smaller. This does not mean that nuclear power is necessarily safer or that the waste generated isn’t harmful, but that its atmospheric impact is less than the other methods. Overall for the ten year use of this product the following values are the equivalent grams of CO\textsubscript{2} that would be produced by running the three different types of air conditioners for an eastern power blend in the United States.

Table 5.1:

<table>
<thead>
<tr>
<th>Type of unit</th>
<th>g CO\textsubscript{2} eq. (10 year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[hmim][Tf\textsubscript{2}N]/CO\textsubscript{2}</td>
<td>8.35E+07</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>5.69E+07</td>
</tr>
<tr>
<td>[P\textsubscript{66614}][3 tria]</td>
<td>2.66E+07</td>
</tr>
</tbody>
</table>

In the case of the western United States blend the following percentages represent the approximate contribution of each of the various methods of production. Bituminous
coal represents approximately 32% of the total generation, hydropower represents approximately 27%, natural gas is approximately 23%, and nuclear represents about 11%, with the remaining 7% being a mix of 5 other generation blends. As was the case with the eastern power blend the contribution of each of these parts to global warming isn’t equal, as each of the methods of power production require generate differing amounts of atmospheric waste. In this case the approximate atmospheric waste percentages are 67.4% of the global warming percent comes from bituminous coal power generation, and 32% comes from natural gas power generation. The remaining waste comes from a combination of the others, but primarily residual fuel power production. The total grams of CO₂ equivalent generated from this method are shown in Table 5.2.

<table>
<thead>
<tr>
<th>Type of unit</th>
<th>g CO₂ eq (10 year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[hmim][Tf₂N]/CO₂</td>
<td>5.81E+07</td>
</tr>
<tr>
<td>CO₂</td>
<td>3.96E+07</td>
</tr>
<tr>
<td>[P₆₆₆₁₄][3 tria]</td>
<td>1.85E+07</td>
</tr>
</tbody>
</table>

For nuclear power generation the blend is irrelevant, as is the percent contribution to global warming as both percentages are fully from nuclear power generation. The total
global warming, once again measured in grams of CO$_2$ equivalent, from this method is shown in Table 5.3.

Table 5.3:

<table>
<thead>
<tr>
<th>Type of unit</th>
<th>g CO2 eq (10 year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[hmim][Te$_2$N]/CO$_2$</td>
<td>1.18E+06</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>8.03E+05</td>
</tr>
<tr>
<td>[P$_{66614}$][3 tria]</td>
<td>3.76E+05</td>
</tr>
</tbody>
</table>

During comparison of these three differing methods certain stark realities make themselves apparent. Of the three differing blends that were modeled here clearly the one with the greatest global warming impact was the eastern United States blend, outdoing the western blend by approximately 44%. By contrast, the global warming impact from nuclear power generation is only a few percent of the other methods of power generation. This is important because as we get to the other sources of global warming, namely the synthesis of the actual air conditioner and the various working fluids within the air conditioner, we will be comparing the results obtained primarily to the global warming generated from an eastern United States blend, but the percentages
would be higher if we were to compare it to the western blend, and significantly higher were it compared to a nuclear power blend.

For the synthesis of the working fluids the process becomes somewhat more complex. Some of the complexities lie in the fact that there are multiple pathways to achieve the desired synthesis. Within a particular synthesis route there are at times differing conditions that take the reaction to various levels of completion, and even within a particular compound there are a variety of ways to model the reaction. Whenever cooling was needed cooling water was used unless the temperature was extremely high (>200K) in which case refrigeration was used initially followed by cooling water. All heating was done using natural gas. These two conditions modified the equivalent grams of CO$_2$ values that were obtained for both the heating and the cooling as electrical cooling and heating has a greater environmental impact than cooling water or natural gas heating. The following tables summarize the results obtained for each step along the synthesis route. Note that there are two tables presented below. Table 5.4 represents the heating required for the process with the units given in gigacalories per one mole of the final product and Table 5.5 represents the amount of cooling water required to return the system to 25°C, per mole of the final product. Both of these tables are for the synthesis of [hmim][Tf$_2$N], the synthesis of [P$_{66614}$][3 triazolide] will be discussed later. Note that a value of zero means that for that particular step either heating, cooling, or both are not required and that the negative signs do not actually represent that there is a negative amount of water required, but that the water is required to take energy away. Also note that the separation energies are quite low in comparison
to the other values; this is due to the fact that the separation method employed was extremely simplistic and only accounted for the heat of demixing.

Table 5.4:
ENERGY REQUIRED FOR HEATING

<table>
<thead>
<tr>
<th>Compound</th>
<th>Glyoxal (Gcal)</th>
<th>Chlorohexane (Gcal)</th>
<th>Methylimi (Gcal)</th>
<th>Sulfuryl Cl (Gcal)</th>
<th>KF (Gcal)</th>
<th>Li3N (Gcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heater</td>
<td>0.005715</td>
<td>0.0083923</td>
<td>0.0096816</td>
<td>0.00052</td>
<td>0</td>
<td>0.0034</td>
</tr>
<tr>
<td>Reactor</td>
<td>0</td>
<td>0</td>
<td>1.19790839</td>
<td>0</td>
<td>0</td>
<td>0.3802</td>
</tr>
<tr>
<td>Separator</td>
<td>0</td>
<td>3.49E-05</td>
<td>0</td>
<td>0.000402</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>Hexanol (Gcal)</th>
<th>[hmim][Cl] (Gcal)</th>
<th>CH3SO2Cl (Gcal)</th>
<th>CH3SO2F (Gcal)</th>
<th>CF3SO2F (Gcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heater</td>
<td>0</td>
<td>0.017385</td>
<td>0.002436</td>
<td>0.007787</td>
<td>0</td>
</tr>
<tr>
<td>Reactor</td>
<td>0</td>
<td>0.007077</td>
<td>0</td>
<td>0.292293</td>
<td>0.370196</td>
</tr>
<tr>
<td>Separator</td>
<td>0.000368</td>
<td>0.030938</td>
<td>0.000158</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>LiTf2N (Gcal)</th>
<th>[hmim][Tf2N] (Gcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heater</td>
<td>.00248</td>
<td>.0087416</td>
</tr>
<tr>
<td>Reactor</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cooler</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Separator</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
## Table 5.5:
CUBIC METERS OF WATER REQUIRED FOR COOLING

<table>
<thead>
<tr>
<th>Compound</th>
<th>Glyoxal</th>
<th>Chlorohexane</th>
<th>Methylimi</th>
<th>Sulfonyl Cl</th>
<th>KF</th>
<th>Li3N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor (m³ H₂O)</td>
<td>-5.2879</td>
<td>-0.49958827</td>
<td>0</td>
<td>-2.36157</td>
<td>-0.0128</td>
<td>0</td>
</tr>
<tr>
<td>Cooler (m³ H₂O)</td>
<td>-0.6746</td>
<td>-0.41031619</td>
<td>-57.1056</td>
<td>0</td>
<td>0</td>
<td>-0.092</td>
</tr>
<tr>
<td>Separator (m³ H₂O)</td>
<td>0</td>
<td>0</td>
<td>-0.26722</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>Hexanol</th>
<th>[hmim][Cl]</th>
<th>CH₃SO₂Cl</th>
<th>CH₃SO₂F</th>
<th>CF₃SO₂F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor (m³ H₂O)</td>
<td>-4.94237</td>
<td>0</td>
<td>-12.7739</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cooler (m³ H₂O)</td>
<td>0</td>
<td>-0.98643</td>
<td>0</td>
<td>-0.41471</td>
<td>0</td>
</tr>
<tr>
<td>Separator (m³ H₂O)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-0.01039</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>LiTf₂N</th>
<th>[hmim][Tf₂N]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heater (kcal)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Reactor (kcal)</td>
<td>-8.247954073</td>
<td>-6.40088551</td>
</tr>
<tr>
<td>Cooler (kcal)</td>
<td>-0.20719531</td>
<td>-0.20570869</td>
</tr>
<tr>
<td>Separator (kcal)</td>
<td>-2.50272E-05</td>
<td>-3.83804861</td>
</tr>
</tbody>
</table>
If the results are combined for these two plots the following total resources usages, 2.34 gigacalories of heating required and 104.7 cubic meters of cooling water are left. Additionally, as mentioned previously, the overall process was determined to require a certain amount of transportation. This transportation was unknown, as the factories to produce these compounds have yet to be built on an industrial scale, but in the interest of completeness it was decided that the chemicals would cross the country at least once. Furthermore, these final values don’t actually paint the complete picture of the process, as there are chemicals that are required to synthesize the initial reactants. These can be accounted for naturally within SimaPro and so were left out of the calculations. The total global warming potential from the synthesis of one kilo-mole of [hmim][Tf₂N] can then be calculated from the program. The total global warming potential given is then approximately 4,420 grams of CO₂ equivalent. This is significantly less than one percent (approximately .005%) of our initial value of 8.35x10⁷ grams of CO₂ equivalent that it takes to run the air conditioner. From a practical standpoint, what this means is that the environmental cost to manufacture a kilogram of [hmim][Tf₂N] is virtually negligible when compared to the cost of running the air conditioner using an eastern US blend of electricity. In reality, it would probably take somewhat more than a kilogram of [hmim][Tf₂N] to actually run a small air conditioner, but the difference would likely be no more than 50% more, which is still a negligibly small value compared to the environmental impact of running the system. Frankly this value is so small that even if the power was to be obtained from strictly nuclear sources the environmental waste is negligible.
A more interesting question than the overall impact that the synthesis of these compounds makes on the environmental impact of the air conditioner is the question of which of the steps within the ionic liquid synthesis has the largest impact. The answer to this question is best summed up in Figure 5.3.
What this Figure shows is the impact of each of the steps within the synthesis of one kilogram of [hmim][Tf$_2$N] that contributes more than 8.6% to the total grams of CO$_2$ equivalent. The thickness of the line is a good visual representation of how much each step contributes, with the percentage below it showing the exact value. Note that since each step in the synthesis route contributes to the step above it each higher step is larger than the previous step. From looking at this chart one of the more unusual points worth noticing is the fact that most of the steps carry approximately the same environmental impact weight. What this means is that each of the steps carries somewhere between five to ten percent of the overall environmental impact. This is interesting because it implies that, to a certain degree it might be possible to create a model that could predict the environmental impact of step without actually performing the calculation. Additionally, this implies that, since each step currently carries a similar weight, if a single step needed to be changed it could probably be simply swapped out without too much of an impact on the overall process. Of course this assumption would be of no use should it be shown that the changed step was of a particularly high impact, but for a standard synthesis this might be a viable approach.

As the synthesis breakdown is analyzed it also becomes apparently that a number of the compounds in the sheet are not mentioned within the initial [hmim][Tf$_2$N] synthesis flowchart, such as the heating from a boiler. This is because many of the compounds and properties are taken directly from the existing SimaPro databases and thus required no particular work beyond using the values. Another point that is worth mentioning and noticing is that several of the compounds listed within the [hmim][Tf$_2$N] synthesis flowchart, as shown in Figure 5.1, aren’t mentioned. For
example, while glyoxal is given as a step within the process, nowhere within the environmental impact breakdown, Figure 5.3, is it mentioned. This is because the breakdown was given a cutoff point of eight percent. This means that any individual step that has less than an eight percent overall weight will not appear in the breakdown.

Grams of CO$_2$ equivalent are not the only environmental impacts that can be measured or that are important. There are other impacts that the air conditioner, both synthesizing and running it, can have. Another type of impact that can be measured is acidification. In an acidification test the chemicals used to create the various compounds or run the particular process are measured in terms of H$^+$ equivalent. This is an important calculation in order to see the effect that creating and running an ionic liquid / CO$_2$ co-fluid air conditioner would have on acid rain. Another method of determining environmental effects is testing the effects that a process would have on living organisms. A common method of determining this is using grams of 2,4-D equivalent. 2,4-D is 2,4-Dichlorophenoxyacetic acid and is a commonly used pesticide and herbicide. What this method of measurement does is relate the toxicity of a process to the toxicity of this pesticide. Of course, since not all organisms react the same way to a particular compound this method is not necessarily the most accurate method of determining toxicity. It is though an effective heuristic for such processes and can give a good idea as to the approximate toxicity. Another method, and the final method that will be looked at, is the smog generation of the process, measured in grams of NO$_x$ equivalent. The results for these measurements are given below for the synthesis of [hmim][Tf$_2$N].
Table 5.6:

ENVIRONMENTAL IMPACTS OF [hmim][Tf$_2$N] SYNTHESIS

<table>
<thead>
<tr>
<th>Type of Impact</th>
<th>Impact value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidification</td>
<td>$3.05 \times 10^3$</td>
<td>Moles of H$^+$ equivalent</td>
</tr>
<tr>
<td>Smog</td>
<td>13.4</td>
<td>Grams of NO$_x$ equivalent</td>
</tr>
<tr>
<td>Ecotoxicity</td>
<td>49.3</td>
<td>Grams of 2,4-D equivalent</td>
</tr>
</tbody>
</table>

In order to have a good comparison, simply having the environmental impact is not sufficient data. For comparison purposes the same values are taken and compared to running the air conditioner, assuming the same conditions above for [hmim][Tf$_2$N], using an eastern power blend.
Table 5.7: ENVIRONMENTAL IMPACTS OF RUNNING AN [hmim][Tf₂N] AIR CONDITIONER

<table>
<thead>
<tr>
<th>Type of Impact</th>
<th>Impact value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidification</td>
<td>3.75x10⁷</td>
<td>Moles of H+ equivalent</td>
</tr>
<tr>
<td>Smog</td>
<td>2.77x10⁵</td>
<td>Grams of NOₓ equivalent</td>
</tr>
<tr>
<td>Ecotoxicity</td>
<td>1.67x10⁵</td>
<td>Grams of 2,4-D equivalent</td>
</tr>
</tbody>
</table>

From these values we can learn a number of things. First, in the case of the eastern US blend of electricity, the environmental impact values seem to scale similarly to the grams of CO₂ equivalent. What this means is that if something has a high environmental impact in one of these four categories it most likely has a high impact in the others. While the smog and ecotoxicity are two orders of magnitude less than the acidification and global warming potential, they are consistently two orders of magnitude less, which makes the values obtained predicable and consistent. Another lesson that can be gathered is that if a step or process within another process is particularly large or small, it will have the tendency to be large or small when compared to the overall processes.
The final process to be analyzed is the process of actually creating the air conditioner itself, without regard for the working fluids or the energy required to run it. This was done strictly through SimaPro, as there is a process already programmed in it for air conditioning and heating equipment manufacture. A standard one ton air conditioner is estimated to weigh approximately 22kg, without any of the fluids. This is likely to vary from one manufacturer to another, but this value is a reasonable estimate. It can be assumed that all air conditioners are created relatively equally, meaning that regardless of what type of process will be running inside the air conditioner the process required to make it will be similar. From a practical standpoint what this means is that whether the air conditioner is designed to run an ionic liquid / CO\(_2\) mixture or whether it runs straight CO\(_2\), the environmental impact will be assumed to be the same. With these assumptions in place the following impact values in Table 5.8 were determined:

Table 5.8:

ENVIRONMENTAL IMPACTS OF SYNTHESIZING AN AIR CONDITIONER

<table>
<thead>
<tr>
<th>Type of Impact</th>
<th>Impact Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Global Warming</td>
<td>693</td>
<td>Grams of CO(_2) equivalent</td>
</tr>
<tr>
<td>Acidification</td>
<td>17.5</td>
<td>H(^+) moles equivalent</td>
</tr>
<tr>
<td>Smog</td>
<td>.432</td>
<td>Grams of NO(_x) equivalent</td>
</tr>
<tr>
<td>Ecotoxicity</td>
<td>2.08</td>
<td>Grams of 2,4-D equivalent</td>
</tr>
</tbody>
</table>

140
As these values are examined it becomes obvious that they are generally small, even when compared to the values of synthesizing the working fluids. When compared to the overall process, including the running of the air conditioner, the impact from synthesizing the actual air conditioner itself is negligible with values of less than .01% of the overall impact using an eastern blend of electricity.

After these results were obtained all that remained was an analysis of the entire system, including the working fluid, the CO₂ manufacture, the energy required to run the system, and the manufacture of the air conditioner itself. Among these individual processes it should be fairly apparent that the dominating process is the energy required to run the system and that is what is shown in Table 5.9:

Table 5.9:

OVERALL IMPACTS FOR [hmim][Tf₂N] / CO₂ SYSTEM

<table>
<thead>
<tr>
<th>Type of Impact</th>
<th>Impact Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Global Warming</td>
<td>8.35x10⁷</td>
<td>Grams of CO₂ equivalent</td>
</tr>
<tr>
<td>Acidification</td>
<td>3.75x10⁷</td>
<td>H+ moles equivalent</td>
</tr>
<tr>
<td>Smog</td>
<td>2.77x10⁵</td>
<td>Grams of NOₓ equivalent</td>
</tr>
<tr>
<td>Ecotoxicity</td>
<td>1.67x10⁵</td>
<td>Grams of 2,4-D equivalent</td>
</tr>
</tbody>
</table>
What this data shows is what was previously discussed, namely that the process of synthesizing and running the air conditioner is completely dominated by the energy required to run the air conditioner. However, the question arises as to what would occur should the process to involve a more efficient air conditioner. As mentioned previously, the coefficient of performance for the [hmim][Tf₂N] was determined to be 1.5, which is fairly inefficient even when compared to the performance of a straight CO₂ air conditioner, which has a coefficient of performance of 2.2. The question arises though, what if the system was even more efficient, as is the case with a chemically complexing ionic liquid such as [P₆₆₆₁₄][3 triazolide].

As mentioned previously this ionic liquid, [P₆₆₆₁₄][3 triazolide] was determined to have a coefficient of performance of 4.7. The values used to run an air conditioner under these conditions were given previously in this section at 2.66x10⁷ grams of CO₂ equivalent. This number is still very large when compared to the previous values for the air conditioner synthesis and the working fluid standpoint. Even though it is approximately one third as large as the value for running an [hmim][Tf₂N] / CO₂ air conditioner, compared to the other [hmim][Tf₂N] values it is apparent that once again the energy required to run the air conditioner would create significantly more environmental impact than either creating the working fluids or synthesizing the air conditioner. Admittedly, synthesizing the [P₆₆₆₁₄][3 triazolide] is a very different process than the previous synthesis route, but even if the environmental impact was larger by an order of magnitude it would only impact the overall process by approximately 0.1% using an eastern blend, meaning that from an overall process standpoint it is probably unnecessary to calculate. Since there may be alternate uses for the [P₆₆₆₁₄][3 triazolide], the
environmental impact for the synthesis of this compound has been included here despite its probable lack of significance to the overall environmental impact of the air conditioner unit.

Much like the case with [hmim][Tf₂N] the process for synthesizing [P₆₆₆₁₄][3 triazolide] is relatively new and not done on the large industrial scale that would be required were it to become a household air conditioning fluid. A potential and likely synthesis route has been determined and is given in Figure 5.4. Using this route an estimate for various environmental impacts, can be found as well as energy estimates and cooling required.

Figure 5.4: Synthesis of [P₆₆₆₁₄][3tria]
The energy estimates as well as the cooling values can be found in the tables below as well as the environmental impacts that would result from synthesizing this ionic liquid.

Table 5.10:

HEATING REQUIRED FOR $[\text{P}_{66614}][3\text{ triazolide}]$ SYNTHESIS

<table>
<thead>
<tr>
<th></th>
<th>Hexanol</th>
<th>1-iodohexane</th>
<th>$\text{C}<em>{14}\text{H}</em>{29}\text{Cl}$</th>
<th>$\text{P}_{666}$</th>
<th>$[\text{P}_{66614}][\text{Cl}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heater (kcal)</td>
<td>0.00</td>
<td>0.00</td>
<td>20794.52</td>
<td>0.00</td>
<td>7939.00</td>
</tr>
<tr>
<td>Reactor (kcal)</td>
<td>0.00</td>
<td>21731.23</td>
<td>0.00</td>
<td>103352.13</td>
<td>0.00</td>
</tr>
<tr>
<td>Separator (kcal)</td>
<td>386.84</td>
<td>19.51</td>
<td>0.00</td>
<td>2638.27</td>
<td>0.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$[\text{Na}][\text{N}_3]$</th>
<th>1,2,3 triazolide</th>
<th>$[\text{Na}]$</th>
<th>$[\text{P}_{66614}][3\text{ triazolide}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heater (kcal)</td>
<td>3517.13</td>
<td>7610.88</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Reactor (kcal)</td>
<td>0.00</td>
<td>21191.55</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Separator (kcal)</td>
<td>0.00</td>
<td>47.50</td>
<td>1000.00</td>
<td>40366.80</td>
</tr>
</tbody>
</table>
Table 5.11:

COOLING WATER REQUIRED FOR $[P_{66614}][3$ triazolide$]$ SYNTHESIS

<table>
<thead>
<tr>
<th></th>
<th>Hexanol</th>
<th>1-iodohexane</th>
<th>C14 Cl</th>
<th>P_{666}</th>
<th>$[P_{66614}][Cl]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor (m$^3$)</td>
<td>5.20</td>
<td>0.00</td>
<td>8.84</td>
<td>0.00</td>
<td>0.99</td>
</tr>
<tr>
<td>Cooler (m$^3$)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.35</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Separator (m$^3$)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$[Na][N_3]$</th>
<th>1,2,3 triazolide</th>
<th>$[Na]$ [3 triazolide]</th>
<th>$[P_{66614}]$ [3 triazolide]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor (m$^3$)</td>
<td>3.43</td>
<td>0.00</td>
<td>1.70</td>
<td>7.56</td>
</tr>
<tr>
<td>Cooler (m$^3$)</td>
<td>0.63</td>
<td>0.38</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Separator (m$^3$)</td>
<td>0.02</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Table 5.12:

ENVIRONMENTAL IMPACTS OF $[P_{66614}][3\text{ triazolide}]$ SYNTHESIS

<table>
<thead>
<tr>
<th>Impact</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Global warming</td>
<td>2180.00</td>
<td>g CO$_2$ eq</td>
</tr>
<tr>
<td>Acidification</td>
<td>519.00</td>
<td>H$^+$ mol eq</td>
</tr>
<tr>
<td>Smog</td>
<td>6.67</td>
<td>g NO$_x$ eq</td>
</tr>
<tr>
<td>Ecotoxicity</td>
<td>7.76</td>
<td>g 2,4-D eq</td>
</tr>
</tbody>
</table>

Looking at this data shows that the synthesis of this process is on the same order of magnitude as the synthesis of $[\text{hmim}][\text{Tf}_2\text{N}]$, but approximately half as much. This comes, in large part, from the fact that this process does not have any extremely high impact steps, as was the previous case with methylamine. The process impacts are shown in Figure 5.5.
From this plot it is clear that the high impact step in this case is the manufacture of white phosphorus and Ethylene. The synthesis of white phosphorus has such a high environmental impact value due primarily to the fact that the reaction occurs at a high temperature, with the synthesis of white phosphorus from calcium phosphate requiring temperatures of between 1,200 and 1,500 celcius. Additionally the storage and transportation of white phosphorous requires special care due to its explosive nature.
Ethylene is such a high impact step due to the fact that the process requires 16 moles of ethylene per mole of final product.

5.4 Conclusions

After analysis of the data that was presented it becomes apparent that the factor that most impacts the environment is the actual operation of the air conditioner. It is approximately four orders of magnitude larger than the impact that comes from synthesizing the ionic liquid and about five orders of magnitude larger than synthesizing the actual air conditioning unit. From a practical standpoint what this means is that the environmental cost of actually building the air conditioner and its parts is negligible when compared to the cost of running it. In order to do a relatively complete life cycle analysis one needs only look at the cost of running the air conditioner and that would account for nearly the entirety of the system. However, while the environmental impact of the running the system dominates the environmental impact; it doesn’t necessarily mean that there is no purpose in having a complete life cycle analysis of the ionic liquid. While it is true that the impact of the ionic liquid synthesis is negligible, there may well be alternate purposes which the ionic liquids have, such as their use as solvents for other processes and systems. For example, in a CO$_2$ scrubber the common working fluid is monoethanolamine [9]. This process has not been widely implemented due to the cost of both installing the facility and running it. However, it is well within the range of possibility that if an ionic liquid were used the cost to run the system could be lowered to the point where running the system becomes viable from an economic standpoint. In
such a case, where the goal is to minimize the amount of CO$_2$ released into the atmosphere a complete life cycle analysis, of both running the system and the working fluids, would be necessary in order to determine whether it is actually minimizing the amount of global warming potential being evolved or only appearing to do so.
5.5 Works Cited


CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 SAFT Conclusions

Several different SAFT models have been applied in the literature to the modeling of ionic liquids, including are the Soft SAFT model, as done by Andreu et al. [1-2], the tPC-SAFT model, as done by Economou et al. [3-6], and SAFT2, as done by Ji and Adidharma [7-10]. These models showed that the basic framework of the SAFT model is well designed for the modeling prediction of the properties of ionic liquids. However, in each of these cases there has been left some room for improvement. In fitting to the Soft SAFT model, for example, the very low vapor pressures of ionic liquids were not accounted for, which then results in the model predicting vapor pressures for the ionic liquid that are much too large. Furthermore this model, in order to make use of the association term but not increase the number of fit parameters, makes use of association parameters that were initially derived for alkanols and it is unclear whether this can be justified. The other models provided good fits and good predictive power but at the expense of greater complexity. The SAFT-based model proposed here shows that a certain degree of this complexity can be removed eliminated with little to no loss in accuracy. Furthermore this model has been tested across a wider variety of ionic liquids than the previous models and shows good fitting and predicting potential across them. Also, it has been shown that this model is capable of fitting CO$_2$ solubility data with good
accuracy using only a single binary interaction parameter, with failure only at quite high pressures (above 150 to 200).

6.2 Life Cycle Analysis Conclusions

After analysis of the data that was presented in Chapter 5 it becomes apparent that the factor that most impacts the environment is the power required to run the air conditioner. The environmental impact obtained from running the air conditioner is approximately four orders of magnitude larger than impact that comes from synthesizing the ionic liquid and about five orders of magnitude larger than manufacturing the actual air conditioner. From a practical standpoint what this means is that the environmental cost of actually building the air conditioner and its parts is negligible when compared to the cost of running it and thus in order to do a relatively complete life cycle analysis one needs only look at the cost of running the air conditioner. While this sort of analysis would not be complete without looking at the entirety of the system, it would account for majority of the impact that would result from the system. Of course, while the environmental impact of the running the system dominates the system; it doesn’t necessarily mean that there is no particular purpose in having a complete life cycle analysis of the ionic liquid. While it is true that the impact of the ionic liquid synthesis is small when compared to the overall environmental impact in the context of refrigeration, there are many other uses for ionic liquids and in such cases having a cradle-to-grave life cycle analysis would be valuable.
6.3 Recommendations for Future Work

In order to improve the performance of the CO$_2$ solubility model at very high pressure, an explicit association term is needed. To avoid introducing a large number of new fit parameters, it would be interesting to attempt to find values for the association parameters that could be used across a variety of different ionic liquids, with perhaps a different set of association parameters for different association types. Another approach that could be attempted is to model each of the ions within the ionic liquid as a separate species and then combine them using a very strong association term. This is similar to what is attempted using the SAFT2 model, but without the additional terms included within the SAFT2 model. This could result in a model with stronger predictive capabilities but without the large amount of data required, which is often unavailable for many of the ionic liquids, to perform an initial fit. The work within this paper shows that the SAFT model, in particular the PC-SAFT model, is a very good model for both the prediction and modeling of ionic liquids.

In order to improve the accuracy of the life cycle analysis one thing that could be done is to obtain more accurate heats of reaction. In this work the heats of reaction were mostly estimated as explained in Chapter 5 because there was little data available for the specific reactions and compounds of interest. While the methods used to estimate enthalpies of formation and reaction have been proven over some classes of compounds, they have had no testing on ionic liquids and, therefore, provide little more than reasonable estimates. Should the actual heats of reaction be significantly different, then the amount of energy required, or evolved, in the reactors could be quite different than the listed values. Another approach to improve the life cycle analysis would be to use
more realistic separation models. The model used in most cases was the basic component separator in Aspen Plus. This method model determines energy duties that in many cases corresponds to the minimum amount of energy that would be required. While this may be a reasonable estimate in some cases, more accurate values could be obtained by making the separation processes and models more realistic. Furthermore it appears that ionic liquid CO2 air conditioners have the potential to be viable should there be an improvement in the efficiency of the refrigeration system, in particular if a compressor could be developed that could efficiently handle both a liquid and a gas the refrigeration system could be made viable.
6.4 Works Cited


## APPENDIX A

### Table A.1

SIMPLIFIED SAFT PARAMETERS AND RATIOS

<table>
<thead>
<tr>
<th></th>
<th>[hmim]</th>
<th>[hmim]</th>
<th>[hmpy]</th>
<th>[bmim]</th>
<th>[TMG]</th>
<th>[TSILmpy]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[eFAP]</td>
<td>[gly]</td>
<td>[Tf2N]</td>
<td>[Tf2N]</td>
<td></td>
<td>[Tf2N]</td>
</tr>
<tr>
<td>m</td>
<td>1.36</td>
<td>1.46</td>
<td>1.49</td>
<td>1.34</td>
<td>1.62</td>
<td>1.51</td>
</tr>
<tr>
<td>v(^{oo})</td>
<td>189.67</td>
<td>104</td>
<td>150.1</td>
<td>143.73</td>
<td>106.69</td>
<td>124.78</td>
</tr>
<tr>
<td>u(^{o})</td>
<td>248.12</td>
<td>280.14</td>
<td>240.73</td>
<td>253.34</td>
<td>219.22</td>
<td>258.65</td>
</tr>
<tr>
<td>MW</td>
<td>612.28</td>
<td>241.33</td>
<td>460.46</td>
<td>421.38</td>
<td>398.28</td>
<td>433.39</td>
</tr>
<tr>
<td>m*v(^{oo})</td>
<td>257.59</td>
<td>152.28</td>
<td>223.14</td>
<td>192.1</td>
<td>173.07</td>
<td>188.05</td>
</tr>
<tr>
<td>tot to cat ratio</td>
<td>3.66</td>
<td>1.44</td>
<td>2.58</td>
<td>3.03</td>
<td>3.43</td>
<td>2.87</td>
</tr>
<tr>
<td>tot to an ratio</td>
<td>1.38</td>
<td>3.26</td>
<td>1.63</td>
<td>1.49</td>
<td>1.41</td>
<td>1.54</td>
</tr>
<tr>
<td>dif ratio to m</td>
<td>1.30%</td>
<td>1.50%</td>
<td>9.80%</td>
<td>11.70%</td>
<td>13.00%</td>
<td>1.90%</td>
</tr>
<tr>
<td>dif from 0</td>
<td>0.01</td>
<td>-0.01</td>
<td>0.1</td>
<td>0.12</td>
<td>-0.13</td>
<td>0.02</td>
</tr>
</tbody>
</table>
APPENDIX B

Table B.1

PC-SAFT INITIAL IONIC LIQUIDS; INITIAL ESTIMATES, PARAMETERS, AND FITS

<table>
<thead>
<tr>
<th></th>
<th>Tf2N</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>emim</td>
<td>C3mim</td>
<td>bmim</td>
<td>C5mim</td>
<td>hmim</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Initial Estimates</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m</td>
<td>13.75</td>
<td>13.75</td>
<td>13.75</td>
<td>13.75</td>
<td>13.75</td>
</tr>
<tr>
<td>uo/k</td>
<td>251.47</td>
<td>251.47</td>
<td>251.47</td>
<td>251.47</td>
<td>251.47</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fit Values</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>voo</td>
<td>11.72</td>
<td>12.0637</td>
<td>12.8317</td>
<td>12.8162</td>
<td>13.3072</td>
</tr>
<tr>
<td>uo/k</td>
<td>253.0111</td>
<td>259.7998</td>
<td>250.5477</td>
<td>237.5311</td>
<td>224.8754</td>
</tr>
<tr>
<td>fval</td>
<td>3.6336-9</td>
<td>8.80E-10</td>
<td>3.17E-10</td>
<td>1.16E-09</td>
<td>1.42E-09</td>
</tr>
<tr>
<td></td>
<td>BF4</td>
<td>PF6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>--------------</td>
<td>--------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>emim</td>
<td>bmim</td>
<td>hmim</td>
<td>omim</td>
<td></td>
</tr>
<tr>
<td>m</td>
<td>13.75</td>
<td>13.75</td>
<td>13.75</td>
<td>13.75</td>
<td></td>
</tr>
<tr>
<td>voo</td>
<td>12.19</td>
<td>12.19</td>
<td>12.19</td>
<td>12.19</td>
<td></td>
</tr>
<tr>
<td>uo/k</td>
<td>251.47</td>
<td>251.47</td>
<td>251.47</td>
<td>251.47</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Fit Values</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m</td>
<td>12.7733</td>
<td>13.2752</td>
<td>13.3856</td>
<td>14.0009</td>
<td></td>
</tr>
<tr>
<td>voo</td>
<td>7.8609</td>
<td>8.8902</td>
<td>10.245</td>
<td>11.1949</td>
<td></td>
</tr>
<tr>
<td>uo/k</td>
<td>305.484</td>
<td>297.775</td>
<td>285.178</td>
<td>268.347</td>
<td></td>
</tr>
<tr>
<td>fval</td>
<td>6.03E-09</td>
<td>6.88E-09</td>
<td>3.14E-09</td>
<td>1.67E-09</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>CO₂</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m</td>
<td>3.9323</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>voo</td>
<td>1.689</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>uo/k</td>
<td>144.5643</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

158
Table C.1

INITIAL IONIC LIQUIDS; BINARY INTERACTION PARAMETER ($k_{ij}$) TABLES

<table>
<thead>
<tr>
<th></th>
<th>[emim][BF₄]</th>
<th></th>
<th>[bmim][BF₄]</th>
<th></th>
<th>[hmim][BF₄]</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kij</td>
<td>AARD</td>
<td>T</td>
<td>kij</td>
<td>AARD</td>
<td>T</td>
</tr>
<tr>
<td>-0.0771</td>
<td>0.0487</td>
<td>303.2</td>
<td></td>
<td>-0.0587</td>
<td>0.0364</td>
<td>308.2</td>
</tr>
<tr>
<td>-0.0730</td>
<td>0.0195</td>
<td>313.2</td>
<td></td>
<td>-0.0513</td>
<td>0.0933</td>
<td>323.2</td>
</tr>
<tr>
<td>-0.0690</td>
<td>0.0298</td>
<td>323.2</td>
<td></td>
<td>-0.0507</td>
<td>0.0902</td>
<td>333.2</td>
</tr>
<tr>
<td>-0.0654</td>
<td>0.0481</td>
<td>333.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.0598</td>
<td>0.0528</td>
<td>343.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>[omim][BF₄]</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kij</td>
<td>AARD</td>
<td>T</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0000</td>
<td>0.0468</td>
<td>308.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0000</td>
<td>0.0184</td>
<td>323.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0000</td>
<td>0.0177</td>
<td>333.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[bmim][PF6]</td>
<td>[hmim][PF6]</td>
<td>[omim][PF6]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>kij</td>
<td>AARD</td>
<td>T</td>
<td>kij</td>
<td>AARD</td>
<td>T</td>
<td>kij</td>
</tr>
<tr>
<td>-0.0453</td>
<td>0.1562</td>
<td>313.2</td>
<td>0.0234</td>
<td>0.0344</td>
<td>308.4</td>
<td>0.0553</td>
</tr>
<tr>
<td>-0.0389</td>
<td>0.0276</td>
<td>323.2</td>
<td>0.0420</td>
<td>0.2139</td>
<td>323.0</td>
<td>0.0570</td>
</tr>
<tr>
<td>-0.0440</td>
<td>0.0614</td>
<td>333.2</td>
<td>0.0440</td>
<td>0.2129</td>
<td>333.2</td>
<td>0.0463</td>
</tr>
</tbody>
</table>

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[emim][Tf2N]</td>
<td>[bmim][Tf2N]</td>
<td>[hmim][Tf2N]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>kij</td>
<td>AARD</td>
<td>T</td>
<td>kij</td>
<td>AARD</td>
<td>T</td>
</tr>
<tr>
<td>0.0029</td>
<td>0.0604</td>
<td>312.1</td>
<td>0.1284</td>
<td>0.0589</td>
<td>313.6</td>
</tr>
<tr>
<td>0.0061</td>
<td>0.0563</td>
<td>322.0</td>
<td>0.1349</td>
<td>0.0477</td>
<td>323.1</td>
</tr>
<tr>
<td>0.0088</td>
<td>0.0592</td>
<td>331.9</td>
<td>0.1395</td>
<td>0.0328</td>
<td>332.7</td>
</tr>
</tbody>
</table>
### APPENDIX D

Table D.1

PC-SAFT NEWER IONIC LIQUIDS; INITIAL ESTIMATES, PARAMETERS, AND FITS

<table>
<thead>
<tr>
<th></th>
<th>Initial Estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>m</td>
<td>13.2752</td>
</tr>
<tr>
<td>voo</td>
<td>8.8902</td>
</tr>
<tr>
<td>uo</td>
<td>297.775</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>[Ohemim][TFA]</th>
<th>[emim][HSO4]</th>
<th>[emim][MeSO4]</th>
<th>[emim][MeSO3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>m</td>
<td>13.7737</td>
<td>12.9439</td>
<td>13.6005</td>
<td>3.3602</td>
</tr>
<tr>
<td>voo</td>
<td>8.1547</td>
<td>7.6153</td>
<td>8.2513</td>
<td>36.073</td>
</tr>
<tr>
<td>uo</td>
<td>315.2721</td>
<td>335.1047</td>
<td>312.3337</td>
<td>826.0939</td>
</tr>
<tr>
<td>AARD</td>
<td>1.09E-04</td>
<td>2.40E-04</td>
<td>0.0148</td>
<td>4.42E-06</td>
</tr>
<tr>
<td></td>
<td>[hmim][Otf]</td>
<td>[emim][DEP]</td>
<td>[emim][SCN]</td>
<td>[P2444][DEP]</td>
</tr>
<tr>
<td>----------------</td>
<td>-------------</td>
<td>-------------</td>
<td>-------------</td>
<td>--------------</td>
</tr>
<tr>
<td><strong>m</strong></td>
<td>3.081</td>
<td>2.725</td>
<td>12.9668</td>
<td>2.4381</td>
</tr>
<tr>
<td><strong>voo</strong></td>
<td>56.4108</td>
<td>57.0986</td>
<td>7.5755</td>
<td>101.3755</td>
</tr>
<tr>
<td><strong>uo</strong></td>
<td>576.5044</td>
<td>591.7358</td>
<td>335.3713</td>
<td>502.5612</td>
</tr>
<tr>
<td><strong>AARD</strong></td>
<td>1.16E-07</td>
<td>7.23E-09</td>
<td>1.30E-04</td>
<td>2.89E-08</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th>[P66614][Tf2N]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>m</strong></td>
<td>30</td>
<td>5.2551</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>voo</strong></td>
<td>15</td>
<td>78.098</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>uo</strong></td>
<td>100</td>
<td>454.0273</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>AARD</strong></td>
<td></td>
<td></td>
<td>6.26E-04</td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX E:

[hmim][Tf$_2$N] SYNTHESIS ASPEN PLUS PROCESS FLOW SHEETS WITH DATA

Figure E.1: Glyoxal synthesis flow sheet
Figure E.2: Chlorohexane synthesis flow sheet

<table>
<thead>
<tr>
<th>Stream ID</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature °C</td>
<td>15.0</td>
<td>15.0</td>
<td>15.8</td>
<td>100.0</td>
<td>100.0</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
</tr>
<tr>
<td>Pressure bar</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>Vapor Frac</td>
<td>0.000</td>
<td>0.000</td>
<td>0.487</td>
<td>0.563</td>
<td>0.189</td>
<td>0.049</td>
<td>0.000</td>
<td>0.073</td>
</tr>
<tr>
<td>Mol Flow kmol/hr</td>
<td>1.000</td>
<td>1.000</td>
<td>2.000</td>
<td>2.000</td>
<td>2.000</td>
<td>2.000</td>
<td>0.860</td>
<td>1.140</td>
</tr>
<tr>
<td>Mass Flow kg/hr</td>
<td>102.177</td>
<td>36.461</td>
<td>138.637</td>
<td>138.637</td>
<td>138.636</td>
<td>138.636</td>
<td>103.733</td>
<td>34.902</td>
</tr>
<tr>
<td>Volume Flow cum/hr</td>
<td>0.122</td>
<td>23.958</td>
<td>23.513</td>
<td>35.057</td>
<td>11.892</td>
<td>2.571</td>
<td>0.109</td>
<td>2.089</td>
</tr>
<tr>
<td>Enthalpy Gcal/hr</td>
<td>-0.091</td>
<td>-0.022</td>
<td>-0.114</td>
<td>-0.105</td>
<td>-0.115</td>
<td>-0.123</td>
<td>-0.049</td>
<td>-0.075</td>
</tr>
<tr>
<td>Mol Flow kmol/hr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHLHEXAN</td>
<td>0.860</td>
<td>0.860</td>
<td>0.860</td>
<td>0.860</td>
<td>0.860</td>
<td>0.860</td>
<td>0.860</td>
<td>0.860</td>
</tr>
<tr>
<td>H2O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH14-O1</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>0.140</td>
<td>0.140</td>
<td>0.140</td>
<td>0.140</td>
<td>0.140</td>
</tr>
<tr>
<td>HCL</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Heat and Material Balance Table

<table>
<thead>
<tr>
<th>Stream ID</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature °C</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>7.3</td>
<td>70.0</td>
<td>70.0</td>
<td>70.0</td>
<td>30.0</td>
<td>70.0</td>
</tr>
<tr>
<td>Pressure Bar</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>Vapor Flow kg/hr</td>
<td>1.300</td>
<td>1.300</td>
<td>1.300</td>
<td>1.300</td>
<td>4.000</td>
<td>4.000</td>
<td>4.000</td>
<td>4.000</td>
<td>0.970</td>
<td>0.970</td>
</tr>
<tr>
<td>Mass Flow kg/hr</td>
<td>58.037</td>
<td>17.031</td>
<td>30.026</td>
<td>31.057</td>
<td>136.151</td>
<td>113.151</td>
<td>136.146</td>
<td>77.995</td>
<td>77.995</td>
<td>58.151</td>
</tr>
<tr>
<td>Volume Flow m³/hr</td>
<td>0.048</td>
<td>24.789</td>
<td>24.789</td>
<td>24.789</td>
<td>70.654</td>
<td>114.122</td>
<td>42.614</td>
<td>27.104</td>
<td>23.945</td>
<td>0.048</td>
</tr>
<tr>
<td>Enthalpy kcal/hr</td>
<td>-0.038</td>
<td>-0.011</td>
<td>-0.026</td>
<td>-0.005</td>
<td>-0.101</td>
<td>-0.091</td>
<td>1.107</td>
<td>1.300</td>
<td>0.139</td>
<td>-0.190</td>
</tr>
<tr>
<td>Mole Flow kmol/hr</td>
<td>C₂H₂O₂</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>0.050</td>
<td>0.050</td>
<td>0.050</td>
<td>0.050</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>AMMONIA</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>0.050</td>
<td>0.050</td>
<td>0.050</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₂O</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>0.050</td>
<td>0.050</td>
<td>0.050</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₅N</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>0.050</td>
<td>0.050</td>
<td>0.050</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>METHIM</td>
<td>0.956</td>
<td>0.956</td>
<td>0.956</td>
<td>0.956</td>
<td>0.956</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>WATER</td>
<td>2.850</td>
<td>2.850</td>
<td>2.850</td>
<td>2.850</td>
<td>2.850</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure E.3: Methylimidazole synthesis flow sheet**
Figure E.4: Sulfuryl Chloride synthesis flow sheet
Figure E.5: Methanesulfonyl Chloride synthesis flow sheet
### Heat and Material Balance Table

<table>
<thead>
<tr>
<th>Stream ID</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
<td>170.6</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>Vapor Fraction</td>
<td>0.000</td>
<td>1.000</td>
<td>1.000</td>
<td>0.000</td>
<td>1.000</td>
<td>0.750</td>
<td>0.126</td>
<td>0.000</td>
<td>0.220</td>
</tr>
<tr>
<td>Mole Flow (kmol/hr)</td>
<td>1.000</td>
<td>1.500</td>
<td>1.500</td>
<td>1.000</td>
<td>3.000</td>
<td>8.000</td>
<td>2.300</td>
<td>0.950</td>
<td>0.950</td>
</tr>
<tr>
<td>Mass Flow (kg/hr)</td>
<td>26.982</td>
<td>3.024</td>
<td>47.998</td>
<td>18.015</td>
<td>84.161</td>
<td>180.180</td>
<td>180.180</td>
<td>97.068</td>
<td>83.112</td>
</tr>
<tr>
<td>Volume Flow (cm³/hr)</td>
<td>0.011</td>
<td>35.954</td>
<td>35.898</td>
<td>0.018</td>
<td>71.361</td>
<td>49.040</td>
<td>7.255</td>
<td>0.116</td>
<td>7.328</td>
</tr>
<tr>
<td>Enthalpy (Gcal/hr)</td>
<td>&gt; -0.001</td>
<td>&gt; -0.001</td>
<td>&gt; -0.001</td>
<td>0.077</td>
<td>0.077</td>
<td>0.077</td>
<td>&gt; -0.001</td>
<td>&gt; -0.001</td>
<td>&gt; -0.001</td>
</tr>
<tr>
<td>Mole Flow (kmol/hr)</td>
<td>AL</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>H₂</td>
<td>1.500</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>O₂</td>
<td>1.500</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>WATER</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C₂H₄</td>
<td>3.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HEXANOL</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>AL(OH)₀₁</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure E.6: Hexanol synthesis flow sheet**
Figure E.7: [hmim][Cl] synthesis flow sheet
Figure E.8: Methane sulfonyl Fluoride synthesis flow sheet
<table>
<thead>
<tr>
<th>Stream ID</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature C</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>50.0</td>
<td>50.0</td>
<td>50.0</td>
<td>25.0</td>
<td></td>
</tr>
<tr>
<td>Pressure bar</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Mass VFrac</td>
<td>0.000</td>
<td>1.000</td>
<td>0.400</td>
<td>0.400</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Mass SFrac</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td></td>
</tr>
<tr>
<td>Mass Flow kg/hr</td>
<td>41.646</td>
<td>28.013</td>
<td>69.659</td>
<td>69.659</td>
<td>69.659</td>
<td>69.659</td>
<td>69.659</td>
<td>0.000</td>
</tr>
<tr>
<td>Volume Flow cum/hr</td>
<td>0.079</td>
<td>24.789</td>
<td>24.717</td>
<td>26.812</td>
<td>53.736</td>
<td>53.736</td>
<td>49.578</td>
<td></td>
</tr>
<tr>
<td>Enthalpy Gcal/hr</td>
<td>-0.031</td>
<td>0.000</td>
<td>-0.031</td>
<td>-0.029</td>
<td>0.161</td>
<td>0.161</td>
<td>0.160</td>
<td>0.000</td>
</tr>
<tr>
<td>Density kg/cum</td>
<td>529.765</td>
<td>1.130</td>
<td>2.818</td>
<td>2.598</td>
<td>1.296</td>
<td>1.296</td>
<td>1.405</td>
<td></td>
</tr>
</tbody>
</table>

Figure E.9: Lithium Nitride synthesis flow sheet
Figure E.10: Trifluoromethanesulfonyl Fluoride synthesis flow sheet

<table>
<thead>
<tr>
<th>Stream ID</th>
<th>1</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature°C</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td></td>
</tr>
<tr>
<td>Pressure bar</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Vapor Fractions</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>0.834</td>
<td>0.815</td>
<td>1.000</td>
<td>0.815</td>
</tr>
<tr>
<td>Mole Flow kmol/hr</td>
<td>1.000</td>
<td>3.000</td>
<td>5.000</td>
<td>5.000</td>
<td>5.000</td>
<td>4.000</td>
<td>1.000</td>
<td>4.000</td>
</tr>
<tr>
<td>Mole Flow kg/hr</td>
<td>98.097</td>
<td>60.019</td>
<td>197.646</td>
<td>197.646</td>
<td>197.646</td>
<td>158.117</td>
<td>39.529</td>
<td>158.117</td>
</tr>
<tr>
<td>Volume Flow cum/hr</td>
<td>24.789</td>
<td>74.368</td>
<td>123.946</td>
<td>123.946</td>
<td>103.467</td>
<td>80.852</td>
<td>24.789</td>
<td>80.852</td>
</tr>
<tr>
<td>Enthalpy Gcal/hr</td>
<td>&lt; 0.001</td>
<td>-0.196</td>
<td>-0.245</td>
<td>-0.245</td>
<td>-0.060</td>
<td>-0.011</td>
<td>-0.049</td>
<td>-0.011</td>
</tr>
<tr>
<td>Mole Flow kmol/hr</td>
<td>1.000</td>
<td>1.250</td>
<td>1.250</td>
<td>0.250</td>
<td>0.250</td>
<td>0.250</td>
<td>0.250</td>
<td>0.250</td>
</tr>
<tr>
<td>CF3SO2F</td>
<td>3.000</td>
<td>3.750</td>
<td>3.750</td>
<td>0.750</td>
<td>0.750</td>
<td>0.750</td>
<td>0.750</td>
<td>0.750</td>
</tr>
<tr>
<td>H2</td>
<td>3.000</td>
<td>3.000</td>
<td>3.000</td>
<td>3.000</td>
<td>3.000</td>
<td>3.000</td>
<td>3.000</td>
<td>3.000</td>
</tr>
</tbody>
</table>
Figure E.11: [Li][Tf₂N] synthesis flow sheet
Figure E.12: [hmim][Tf$_2$N] synthesis flow sheet
APPENDIX F:

[\text{P_{6614}}][3 \text{ triazolide}] \text{ SYNTHESIS ASPEN PLUS PROCESS FLOW SHEETS WITH DATA}

![Hexanol synthesis flow sheet](image)

<table>
<thead>
<tr>
<th>Stream ID</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
<td>-170.6</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>Vapor Flow (kmol/hr)</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>0.000</td>
<td>1.000</td>
<td>0.750</td>
<td>0.126</td>
<td>0.000</td>
<td>0.220</td>
</tr>
<tr>
<td>Mole Flow (kmol/hr)</td>
<td>26.982</td>
<td>1.024</td>
<td>1.500</td>
<td>1.500</td>
<td>5.000</td>
<td>3.000</td>
<td>2.500</td>
<td>0.900</td>
<td>1.350</td>
</tr>
<tr>
<td>Mass Flow (kg/hr)</td>
<td>26.982</td>
<td>35.954</td>
<td>35.898</td>
<td>0.018</td>
<td>71.361</td>
<td>49.040</td>
<td>7.255</td>
<td>0.116</td>
<td>7.324</td>
</tr>
<tr>
<td>Mole Flow (kmol/hr)</td>
<td>26.982</td>
<td>1.024</td>
<td>1.500</td>
<td>1.500</td>
<td>5.000</td>
<td>3.000</td>
<td>2.500</td>
<td>0.900</td>
<td>1.350</td>
</tr>
</tbody>
</table>

Figure F.1: Hexanol synthesis flow sheet
Figure F.2: 1-iodohexane synthesis flow sheet

<table>
<thead>
<tr>
<th>Stream ID</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature °C</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
</tr>
<tr>
<td>Pressure bar</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>Vapor Frac</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.131</td>
<td>0.000</td>
<td>&lt;0.001</td>
<td>0.000</td>
<td>1.000</td>
</tr>
<tr>
<td>Mole Flow kmol/hr</td>
<td>2.000</td>
<td>1.000</td>
<td>3.000</td>
<td>3.455</td>
<td>1.820</td>
<td>1.182</td>
<td>3.002</td>
<td>0.453</td>
</tr>
<tr>
<td>Volume Flow cum/hr</td>
<td>0.245</td>
<td>0.060</td>
<td>0.319</td>
<td>11.196</td>
<td>0.300</td>
<td>0.047</td>
<td>0.331</td>
<td>10.865</td>
</tr>
<tr>
<td>Enthalpy Gcal/hr</td>
<td>-0.183</td>
<td>0.003</td>
<td>-0.180</td>
<td>-0.140</td>
<td>-0.062</td>
<td>-0.078</td>
<td>-0.140</td>
<td>&gt;-0.001</td>
</tr>
<tr>
<td>Mole Flow kmol/hr</td>
<td>HEXANOL</td>
<td>2.000</td>
<td>2.000</td>
<td>0.180</td>
<td>0.180</td>
<td>0.180</td>
<td>&lt;0.001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>IODINE</td>
<td>1.000</td>
<td>1.000</td>
<td>0.090</td>
<td>0.090</td>
<td>0.090</td>
<td>&lt;0.001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C6H13-01</td>
<td>1.820</td>
<td>1.820</td>
<td>1.820</td>
<td>1.820</td>
<td>1.820</td>
<td>&lt;0.001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>WATER</td>
<td>0.910</td>
<td>0.907</td>
<td>0.907</td>
<td>0.003</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>OXYGEN</td>
<td>0.455</td>
<td>0.004</td>
<td>0.004</td>
<td>0.455</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Heat and Material Balance Table
Figure F.3: 1-chlorotetradecane synthesis flow sheet

<table>
<thead>
<tr>
<th>Stream ID</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature °C</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
<td>233.4</td>
<td>100.0</td>
<td>100.0</td>
<td>15.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressure bar</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>40.000</td>
<td>40.000</td>
<td>1.000</td>
<td>1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vapor Frac</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mole Flow kmol/hr</td>
<td>7.000</td>
<td>1.000</td>
<td>8.000</td>
<td>8.000</td>
<td>8.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass Flow kg/hr</td>
<td>320376</td>
<td>36.461</td>
<td>232837</td>
<td>232837</td>
<td>232837</td>
<td>232837</td>
<td>232837</td>
<td>232837</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volume Flow cm³/hr</td>
<td>0.087</td>
<td>0.022</td>
<td>0.065</td>
<td>0.072</td>
<td>0.086</td>
<td>0.009</td>
<td>0.009</td>
<td>0.009</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Enthalpy Gcal/hr</td>
<td>0.087</td>
<td>0.022</td>
<td>0.065</td>
<td>0.072</td>
<td>0.086</td>
<td>0.009</td>
<td>0.009</td>
<td>0.009</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mole Flow kmol/hr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C14H29CL</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C2H4</td>
<td>7.000</td>
<td>7.000</td>
<td>7.000</td>
<td>7.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCL</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure F.3: 1-chlorotetradecane synthesis flow sheet
Figure F.4: \([\text{Na}][\text{N}_3]\) synthesis flow sheet

<table>
<thead>
<tr>
<th>Stream ID</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature °C</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
<td>27.7</td>
<td>190.0</td>
<td>190.0</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
</tr>
<tr>
<td>Pressure bar</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>Mass Flow Rate kg/hr</td>
<td>0.900</td>
<td>0.900</td>
<td>0.900</td>
<td>0.672</td>
<td>0.689</td>
<td>0.437</td>
<td>0.172</td>
<td>0.000</td>
<td>0.372</td>
</tr>
<tr>
<td>Mol Flow Rate k mole/hr</td>
<td>1.000</td>
<td>1.000</td>
<td>0.900</td>
<td>2.900</td>
<td>2.900</td>
<td>3.350</td>
<td>3.350</td>
<td>1.800</td>
<td>1.550</td>
</tr>
<tr>
<td>Mol Flow Rate kg/hr</td>
<td>17.031</td>
<td>44.013</td>
<td>20.690</td>
<td>81.734</td>
<td>81.734</td>
<td>81.734</td>
<td>81.734</td>
<td>58.509</td>
<td>23.225</td>
</tr>
<tr>
<td>Volume Flow Rate m³/hr</td>
<td>23.958</td>
<td>23.958</td>
<td>0.117</td>
<td>48.881</td>
<td>77.093</td>
<td>56.765</td>
<td>14.032</td>
<td>0.234</td>
<td>13.817</td>
</tr>
<tr>
<td>Enthalpy GJ/hr</td>
<td>-0.011</td>
<td>0.020</td>
<td>0.131</td>
<td>0.140</td>
<td>0.143</td>
<td>0.081</td>
<td>0.070</td>
<td>0.131</td>
<td>-0.062</td>
</tr>
<tr>
<td>Mol Flow Rate k mole/hr</td>
<td>0.900</td>
<td>0.900</td>
<td>0.900</td>
<td>0.900</td>
<td>0.900</td>
<td>0.900</td>
<td>0.900</td>
<td>0.900</td>
<td>0.900</td>
</tr>
<tr>
<td>Mol Flow Rate kg/hr</td>
<td>15.0</td>
<td>15.0</td>
<td>0.100</td>
<td>0.100</td>
<td>0.100</td>
<td>0.100</td>
<td>0.100</td>
<td>0.100</td>
<td>0.100</td>
</tr>
<tr>
<td>Volume Flow Rate m³/hr</td>
<td>0.900</td>
<td>0.900</td>
<td>0.900</td>
<td>0.900</td>
<td>0.900</td>
<td>0.900</td>
<td>0.900</td>
<td>0.900</td>
<td>0.900</td>
</tr>
<tr>
<td>Enthalpy GJ/hr</td>
<td>-0.000</td>
<td>-0.000</td>
<td>-0.000</td>
<td>-0.000</td>
<td>-0.000</td>
<td>-0.000</td>
<td>-0.000</td>
<td>-0.000</td>
<td>-0.000</td>
</tr>
</tbody>
</table>

Heater and Material Balance Table
### Heat and Material Balance Table

<table>
<thead>
<tr>
<th>Stream ID</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature °C</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
</tr>
<tr>
<td>Pressure bar</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>Vapor Frac</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>1.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Mole Flow kmol/hr</td>
<td>3.000</td>
<td>0.250</td>
<td>3.250</td>
<td>2.688</td>
<td>0.750</td>
<td>1.938</td>
</tr>
<tr>
<td>Mass Flow kg/hr</td>
<td>636.221</td>
<td>30.974</td>
<td>667.195</td>
<td>667.195</td>
<td>214.861</td>
<td>452.334</td>
</tr>
<tr>
<td>Volume Flow cum/hr</td>
<td>0.499</td>
<td>0.001</td>
<td>0.463</td>
<td>0.225</td>
<td>18.592</td>
<td>0.200</td>
</tr>
<tr>
<td>Enthalpy Gcal/hr</td>
<td>-0.100</td>
<td>-0.001</td>
<td>-0.101</td>
<td>-0.023</td>
<td>0.000</td>
<td>-0.021</td>
</tr>
<tr>
<td>Mole Flow kmol/hr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P666</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P4</td>
<td>0.250</td>
<td>0.250</td>
<td>0.063</td>
<td>0.063</td>
<td>0.063</td>
<td></td>
</tr>
<tr>
<td>I2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.125</td>
<td>1.125</td>
</tr>
<tr>
<td>C6H13I</td>
<td>3.000</td>
<td>3.000</td>
<td>0.750</td>
<td>0.750</td>
<td>0.750</td>
<td></td>
</tr>
</tbody>
</table>

**Figure F.5: P666 synthesis flow sheet**
Figure F.6: \([P_{66614}]\text{[Cl]}\) synthesis flow sheet
Figure F.7: 1,2,3 triazolide synthesis flow sheet
Figure F. 8: [Na][3 triazolide] synthesis flow sheet
Figure F.9: $[\text{P}_{66614}][3\text{ triazolide}]$ synthesis flow sheet

<table>
<thead>
<tr>
<th>Stream ID</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature ^oC</td>
<td>15.0</td>
<td>15.0</td>
<td>145.8</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
</tr>
<tr>
<td>Pressure bar</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>Vapor Frac</td>
<td>1.000</td>
<td>0.000</td>
<td>0.724</td>
<td>0.000</td>
<td>1.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Mole Flow kmol/hr</td>
<td>1.000</td>
<td>1.000</td>
<td>2.000</td>
<td>2.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>Mass Flow kg/hr</td>
<td>519.309</td>
<td>91.047</td>
<td>610.356</td>
<td>610.355</td>
<td>551.913</td>
<td>58.442</td>
</tr>
<tr>
<td>Volume Flow cum/hr</td>
<td>23.958</td>
<td>0.055</td>
<td>50.731</td>
<td>0.826</td>
<td>23.958</td>
<td>0.035</td>
</tr>
<tr>
<td>Enthalpy Gcal/hr</td>
<td>-0.232</td>
<td>0.040</td>
<td>-0.192</td>
<td>-0.344</td>
<td>-0.219</td>
<td>-0.084</td>
</tr>
<tr>
<td>Mole Flow kmol/hr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{P}_{66614}\text{CL}$</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$3\text{TRIAZOL}$</td>
<td></td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{P}_{63}\text{TRIA}$</td>
<td>1.000</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{NACL}$</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>