DIFFUSION COEFFICIENTS AND 1-OCTANOL-WATER PARTITION
COEFFICIENTS OF IONIC LIQUIDS

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by

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DIFFUSION COEFFICIENTS AND OCTANOL-WATER PARTITION COEFFICIENTS OF IONIC LIQUIDS

Abstract

by

Laurie Ropel

Two physical properties of ionic liquids were studied for this thesis, namely diffusion coefficients and octanol-water partition coefficients ($K_{OW}$). Diffusion coefficients of CO$_2$ into various ionic liquids (IL) were measured at atmospheric pressure because they are needed for properly designing processes. Values of the diffusion coefficients ranged between $1.8 \times 10^{-6}$ cm$^2$/s for an IL with viscosity of 603 cP and $1.2 \times 10^{-5}$ cm$^2$/s for an IL with viscosity of 14 cP. Diffusion coefficients increased in a linear fashion with the inverse of the IL’s viscosity. $K_{OWs}$ of imidazolium-based ILs were measured to help characterize ILs’ potential environmental impact prior to widespread industrial use. The effect of chemical structure on the $K_{OW}$ was measured. The $K_{OWs}$ were extremely low, ranging between 0.001 and 11.1, indicating that the ILs have extremely low bioconcentration and soil adsorption potential.
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CHAPTER 1
INTRODUCTION

1.1 Thesis Objective

The research summarized in this thesis was performed to further understand physical properties of ionic liquids, a potentially greener class of chemicals than the volatile organic compounds they may suitably replace. Further understanding of ionic liquids’ (IL) physical properties and correlations with their molecular structures are necessary so that systems using ILs are designed properly and an appropriate selection of cation and anion can be made for the application. This thesis investigates the effect of molecular structure, specifically the anion type, cation type, cation alkyl chain length, and methyl group substitution on the cation, on the mutual diffusion coefficients of CO$_2$ absorbing into ionic liquids at atmospheric pressure. The effect of temperature on the diffusion coefficient of one ionic liquid at atmospheric pressure was also studied. Various diffusion coefficient models were evaluated so that the diffusion coefficient of an ionic liquid not measured in this research could be predicted with reasonable accuracy if the viscosity is known.

This thesis also investigates octanol-water partition coefficients ($K_{OW}$) of ILs with a popular cation type, imidazolium. Correlations between $K_{OW}$ values and IL structural variations, including the anion type, cation alkyl chain length, and methyl group substitution on the cation, were evaluated.
1.2 Overview of Ionic Liquids

“Ionic liquids” (ILs) described by researchers today refer to salts comprised of organic cations and/or anions that are liquid at or around room temperature, about 25 to 100 deg C. Since discovery in 1992, ILs have become a subject of growing interest among researchers as evidenced by the number of publications increasing exponentially. Researchers are interested because ILs have numerous potential industrial applications and are “greener” than traditionally used chemicals. ILs offer promising industrial application as a replacement for volatile liquids in synthesis, catalysis, and separations. As a result of ILs’ most distinctive characteristic, low vapor pressure, replacement of currently used volatile liquids with ILs could reduce air pollution and worker exposure to harmful airborne chemicals. ILs’ physical properties, such as large liquidus range, ability to solvate polar and nonpolar molecules, and electrochemical stability, offer enhanced capabilities over some traditionally used volatile liquids. Also, their properties can be adjusted predictably by selecting an appropriate cation and anion based on published trends when changes to their structures are made.

Since potentially over one trillion ILs could be synthesized by combining various anions and cations, it is important when reporting physical properties to understand the effect caused by the ILs’ structures. Thus, structures of ILs studied for this thesis were varied systematically to understand the effect on diffusion coefficients and $K_{ow}$. Previous studies showing effect of molecular structure on CO$_2$ solubility, IL viscosity, alcohol solubility, and water solubility are reviewed to
evaluate reasonableness of the results presented in this thesis. Structural effects on diffusion coefficients of ILs’ precursors, molten salts, are reviewed as well.

1.2.1 Background

Ionic liquid research originated in the 1940s when aluminum chloride-based molten salts with melting points below room temperature were developed for the first time. Hurley and Weir used the IL containing a mixture of chloride and chloroaluminate(III) anions and n-ethylpyridinium halide cations as an electrolyte for depositing aluminum⁵⁷. In the 1960s, the Air Force applied Hurley and Weir’s findings toward assembling electrical batteries⁹⁶. In 1982, Wilkes as part of the Air Force, developed dialkylimidazolium chloroaluminate ILs with superior properties to the pyridinium ILs in terms of liquidus temperatures, electrochemical window, meaning the difference between the anodic and cathodic decomposition potentials in volts, and reactivity with aluminum⁹⁷. The electrochemical reaction was⁹⁶:

\[
\text{emim}^+ + \text{AlCl}_4^- + (x + y)C \rightleftharpoons [\text{emim}]C_x + [\text{AlCl}_4]C_y
\]

“negative” “positive”

(1.1-1)

The dialkylimidazolium cation favored by Wilkes, ethyl methyl imidazolium (emim⁺), frequently used in research today, is evaluated as part of this thesis.

Chloroaluminate ILs were found to be useful in electroplating and electrical batteries, but further applications were limited for several reasons. First, chloroaluminate ILs are either acidic or basic depending on the aluminum chloride concentration as shown by the following equilibrium equations.

\[
2[\text{AlCl}_4]^- \rightarrow [\text{Al}_2\text{Cl}_7]^- + \text{Cl}^- \tag{1.1-2}
\]
\[
2[\text{Al}_2\text{Cl}_7]^- \rightarrow [\text{Al}_3\text{Cl}_{10}]^- + [\text{AlCl}_4]^- \tag{1.1-3}
\]
These IL’s are highly reactive with oxides, and hydrolyze to form hydrochloric acid when exposed to moisture. These characteristics make handling difficult in standard industrial applications\(^9^7\).

In 1992, Zaworotko working with the Air Force developed the first air and water stable ILs by substituting water-stable anions such as tetrafluoroborate, hexafluorophosphate, nitrate, sulfate, and acetate for the aluminochlorate anions\(^9^8\).

The ILs that are popularly investigated today are air and water stable, and frequently contain anions originally used by Zaworotko. Typical cations studied include alkylpyridinium, alkyl methyl imidazolium, tetra alkylammonium and tetra alkylphosphonium. ILs with new cations and anions continue to be developed with the intent of enhancing particular physical characteristics.

### 1.2.2 Ionic Liquid Applications Relevant to This Thesis

Numerous possibilities exist for using ILs in industrial applications. This section of this thesis will focus on applications where diffusion coefficients of CO\(_2\) into ILs, and \(K_{OWs}\) would be useful. Diffusion coefficients of CO\(_2\) into ILs are necessary for properly designing systems where the rate of CO\(_2\) absorption into the IL must be known. Anthony et. al. showed that ILs may be used to separate gas mixtures by measuring and comparing solubilities of various gases in ILs. Anthony showed that CO\(_2\) and water vapor were highly soluble in ILs while methane and nitrogen were only slightly soluble. The Henry’s constants of water vapor, CO\(_2\), methane, and nitrogen in 1-butyl-3-methyl imidazolium hexafluorophosphate IL at 25 degrees Celsius were 0.17, 53.4, 1690, and greater than 20,000 bar, respectively. Gases with lower Henry’s constants have higher solubility. Comparison of these
Henry’s constants indicate that ILs have the potential to separate CO$_2$ and water from natural gas to improve product purity, or to separate CO$_2$, a greenhouse gas, from flue gas$^{14}$.

Ionic liquids have several inherent advantages over currently used aqueous amine solvents for separating gas mixtures. First, ionic liquids do not evaporate and thus, would not contaminate the gaseous product, unlike currently used volatile liquids. Also, water from the aqueous stream in current solvents adds moisture to the product, whereas ionic liquids would absorb moisture from the product.

Additional work is needed to optimize the type of ionic liquid that would make the best solvent for gas separations, and to maximize the absorption system’s efficiency with the new IL solvent. Anthony approximated, and then compared the operating energy requirements of a CO$_2$ absorption process using the most common solvent in CO$_2$ separation today, monoethanolamine (MEA), versus the IL [C$_4$mim][PF$_6$]. Anthony’s calculations assumed that existing equipment would be used, which desorbed CO$_2$ from the solvent by raising the solvent’s temperature. Since the solubility of CO$_2$ is much greater in MEA than in [C$_4$mim][PF$_6$], the amount of [C$_4$mim][PF$_6$] required per ton CO$_2$ desorbed is approximately 350 times more than MEA. Since more liquid must be heated in a system containing [C$_4$mim][PF$_6$], Anthony calculated that between 60 and 150 times more energy would be required per ton of CO$_2$ recovered. The following equation was used to determine energy requirements.

\[ Q = -\Delta h_{\text{abs}} + m \cdot Cp \cdot \Delta T \quad (1.2-1) \]
where \( Q \) is the energy needed, \( \Delta h_{\text{abs}} \) is the enthalpy of absorption for \([C_4\text{mim}][\text{PF}_6]\) or the enthalpy of reaction for MEA, \( m \) is the mass of solvent, \( C_p \) is the heat capacity of the solvent, and \( \Delta T \) is the temperature difference between the absorption and desorption step.

Anthony’s calculations suggest that an ionic liquid with higher selectivity for CO\(_2\) than \([C_4\text{mim}][\text{PF}_6]\) would make MEA replacement more feasible. Higher selectivity would reduce the amount of IL needed per ton of CO\(_2\) absorbed and energy required to heat the IL during desorption. Anthony used \([C_4\text{mim}][\text{PF}_6]\) in her calculations because it is a commonly studied IL. However, there are several other ILs already synthesized with higher CO\(_2\) solubilities than \([C_4\text{mim}][\text{PF}_6]\). Aki et. al. showed that CO\(_2\) solubility increases as the number of fluoroalkyl groups on the ionic liquid’s cation increases\(^9\). Henry’s constants of ILs with fluorinated cations or anions measured by our laboratory were 28.5 bar and 25.2 bar for \([C_6\text{F}_9\text{H}_4\text{mim}][\text{ Tf}_2\text{N}]\) and \([C_6\text{mim}][\text{P(C}_2\text{F}_5)_3\text{F}_3]\), demonstrating much greater CO\(_2\) solubility than \([C_4\text{mim}][\text{PF}_6]\) having a Henry’s constant of 53.4. Davis and coworkers developed a “task-specific ionic liquid” by adding an amine group, the same functional group in MEA that chemically binds with CO\(_2\), to the alkyl chain on the imidazolium ring. The IL chemically bound CO\(_2\) to form ammonium carbamate. He found that CO\(_2\) was absorbed into the IL at the same molar ratio as MEA\(^1^9\). One disadvantage of both our laboratory’s fluorosubstituted ILs and Davis’ ILs is high viscosities, which could cause mass transfer limitations. One possible solution is mixing \([C_8\text{F}_{13}\text{mim}][\text{Tf}_2\text{N}]\) with a lower viscosity IL to optimize the CO\(_2\) solubility and viscosity\(^1^8\). As part of this thesis, the diffusion coefficients of fluorosubstituted ionic liquids
[C₆F₅H₄mim][Tf₂N] and [C₆mim][P(C₂F₅)₃F₃] are measured. The ideal IL for gas separations would have high CO₂ solubility, low viscosity, and high diffusivity. The absorption system’s operating efficiency could be maximized by operating with a pressure-swing system or combination pressure-temperature swing system. The temperature-swing system currently used in MEA absorption systems is more efficient when MEA is used as the solvent instead of ILs because MEA chemically binds CO₂, as opposed to ILs, which bind CO₂ by physisorption. Systems employing temperature-swing are effective for overcoming the heat of reaction, which is not an issue with ILs. In a pressure-swing system, the feed gas is compressed prior to and during absorption, then expanded during desorption. Less energy would be required to compress feed gas containing ten percent CO₂ than raise the solvent’s temperature 100 degrees Celsius. Anthony calculated that if the feed gas was compressed so that CO₂ partial pressure was 1 bar instead of 0.1 bar, CO₂ solubility in [C₄mim][PF₆] increases, and energy requirements are reduced from 534 MMBtu per ton CO₂ removed to 49 MMBtu per ton CO₂ removed.

The mutual diffusion coefficient of CO₂ and ILs may also be useful in separation processes where supercritical CO₂ is used to extract organic products from ILs. Blanchard et. al. showed that supercritical CO₂ can achieve greater than 95% recovery when removing organics miscible with ILs. There are several advantages to separation using supercritical CO₂ extraction versus distillation or extraction with volatile solvents. Although organic products could be separated effectively from ILs by distillation owing to ILs’ negligible vapor pressure, separation of organics with low volatility by distillation would be energy intensive. Product extraction with
volatile organics negates the environmental benefits of using nonvolatile ILs in the industrial process. Alternatively, CO$_2$ is inexpensive, nonflammable, nontoxic and environmentally benign. Blanchard showed that ILs do not dissolve in supercritical CO$_2$, but polar and nonpolar, aromatic and aliphatic, volatile and nonvolatile organics do dissolve in supercritical CO$_2$. Thus, the organic and supercritical CO$_2$ phase and IL phase can be easily separated. Best engineering practices currently used by industry minimize energy requirements in the reuse of the CO$_2$ solvent through partial depressurization, temperature changes instead of depressurization, and cooling and liquefying the recycled CO$_2$ so it could be pumped instead of compressed. The products of this separation are of high purity and can be reused. Although ILs do not dissolve in supercritical CO$_2$, CO$_2$ is highly soluble in ILs. Thus, the mutual diffusion coefficient of ILs and CO$_2$ may be relevant in the supercritical CO$_2$ extraction process.

$K_{OWs}$ of ILs are an indicator of their hydrophilicity and bioconcentration potential at infinite dilution. Several publications cite processes where ILs could be used in aqueous systems. If these systems are constructed, it is likely that very low concentrations of ILs contained in the aqueous waste stream will be discharged to the environment. Environmental exposure to ILs may also occur inadvertently during their use in synthesis, catalysis, and separations. Since ILs do not evaporate, their avenue to potentially impact the environment would be through aqueous waste streams or spills. Rogers and coworkers suggested that hydrophobic ILs could replace volatile organic solvents in liquid-liquid extraction processes, because hydrophilic products can easily be extracted from hydrophobic ILs with water$^{56}$. The
same group showed that metal extractions could be performed in IL/aqueous biphasic systems with added chelating agents\textsuperscript{91}. Fadeev et. al suggested recovering butanol from aqueous fermentation broths, an intermediate material in forming biofuels, using hydrophobic ILs\textsuperscript{46}. It is important that $K_{\text{OW}}$ values are available when industries contemplate the type of IL to implement in their aqueous system.

1.2.3 Structures of Ionic Liquids Studied

Many different anions and cations forming ILs are available for study. Table 1.1 shows the ILs selected for measuring diffusion coefficients with structures and shorthand names. Structural effects on the diffusion coefficient of CO$_2$ into ILs were studied by varying the ILs’anion, type of cation from imidazolium to pyridinium, and alkyl chain length on an imidazolium cation. Also, hydrogens on an imidazolium’s alkyl chain were replaced by fluorines, and the hydrogen at the C-2 position on the imidazolium ring was replaced with a methyl group.
### Table 1.1

IONIC LIQUIDS SELECTED FOR DIFFUSION COEFFICIENT MEASUREMENT

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>Short-hand Name</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>([\text{C}_2\text{mim}][\text{Tf}_2\text{N}])</td>
<td><img src="image1" alt="Structure" /></td>
</tr>
<tr>
<td>1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>([\text{C}_4\text{mim}][\text{Tf}_2\text{N}])</td>
<td><img src="image2" alt="Structure" /></td>
</tr>
<tr>
<td>1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>([\text{C}_6\text{mim}][\text{Tf}_2\text{N}])</td>
<td><img src="image3" alt="Structure" /></td>
</tr>
<tr>
<td>1-hexyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>([\text{C}_6\text{mmim}][\text{Tf}_2\text{N}])</td>
<td><img src="image4" alt="Structure" /></td>
</tr>
<tr>
<td>1-hexyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide</td>
<td>([\text{C}_6\text{mPy}][\text{Tf}_2\text{N}])</td>
<td><img src="image5" alt="Structure" /></td>
</tr>
<tr>
<td>1-(1,1,2,2,3,3,4,4-nonafluorohexyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>([\text{C}_6\text{F}_9\text{H}_4\text{mim}][\text{Tf}_2\text{N}])</td>
<td><img src="image6" alt="Structure" /></td>
</tr>
<tr>
<td>1-n-butyl-3-methylimidazolium hexafluorophosphate</td>
<td>([\text{C}_4\text{mim}][\text{PF}_6])</td>
<td><img src="image7" alt="Structure" /></td>
</tr>
<tr>
<td>1-hexyl-3-methylimidazolium tri(pentafluoroethyl) trifluorophosphate</td>
<td>([\text{C}_6\text{mim}][\text{P(C}_3\text{F}_5)_3\text{F}_3])</td>
<td><img src="image8" alt="Structure" /></td>
</tr>
</tbody>
</table>

Table 1.2 shows the ILs selected for measuring $K_{OWS}$ with structures and shorthand names. Several $K_{OWS}$ were measured by a coworker, Lionel Belveze, and are marked in Table 1.2 with an asterisk (*). Belveze measured $K_{OWS}$ of ILs with the 1-butyl-3-methyl imidazolium cation and determined the effect caused by varying the ILs’ anion. The author of this thesis measured $K_{OWS}$ of ILs with the bis(trifluoromethylsulfonyl)imide anion, and determined the effect caused by varying the alkyl chain length on the imidazolium cation. Also, the effect on the $K_{OW}$ caused
by replacing the hydrogen at the C2 position on the imidazolium ring with a methyl group was measured. Additionally, the author measured the $K_{OW}$ of 1-butyl-3-methyl imidazolium chloride because the original sample analyzed by Belveze contained impurities.

**TABLE 1.2**

IONIC LIQUIDS SELECTED FOR $K_{OW}$ MEASUREMENT

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>Short-hand Name</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-(n)-butyl-3-methylimidazolium tetrafluoroborate*</td>
<td>[C(_4)mim][BF(_4)]</td>
<td><img src="image1" alt="Structure" /></td>
</tr>
<tr>
<td>1-(n)-butyl-3-methylimidazolium nitrate*</td>
<td>[C(_4)mim][NO(_3)]</td>
<td><img src="image2" alt="Structure" /></td>
</tr>
<tr>
<td>1-(n)-butyl-3-methylimidazolium hexafluorophosphate*</td>
<td>[C(_4)mim][PF(_6)]</td>
<td><img src="image3" alt="Structure" /></td>
</tr>
<tr>
<td>1-(n)-butyl-3-methylimidazolium chloride</td>
<td>[C(_4)mim][Cl]</td>
<td><img src="image4" alt="Structure" /></td>
</tr>
<tr>
<td>1-(n)-butyl-3-methylimidazolium bromide*</td>
<td>[C(_4)mim][Br]</td>
<td><img src="image5" alt="Structure" /></td>
</tr>
<tr>
<td>1-ethyl-3-methylimidizolium bis(trifluoromethylsulfonyl)imide</td>
<td>[C(_2)mim][Tf(_2)N]</td>
<td><img src="image6" alt="Structure" /></td>
</tr>
<tr>
<td>1-ethyl-2,3-dimethylimidizolium bis(trifluoromethylsulfonyl)imide</td>
<td>[C(_2)mmim][Tf(_2)N]</td>
<td><img src="image7" alt="Structure" /></td>
</tr>
<tr>
<td>1-propyl-2,3-dimethylimidizolium bis(trifluoromethylsulfonyl)imide</td>
<td>[C(_3)mmim][Tf(_2)N]</td>
<td><img src="image8" alt="Structure" /></td>
</tr>
<tr>
<td>1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>[C(_4)mim][Tf(_2)N]</td>
<td><img src="image9" alt="Structure" /></td>
</tr>
<tr>
<td>1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>[C(_6)mim][Tf(_2)N]</td>
<td><img src="image10" alt="Structure" /></td>
</tr>
<tr>
<td>1-hexyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>[C(_6)mmim][Tf(_2)N]</td>
<td><img src="image11" alt="Structure" /></td>
</tr>
<tr>
<td>1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>[C(_8)mim][Tf(_2)N]</td>
<td><img src="image12" alt="Structure" /></td>
</tr>
</tbody>
</table>

*\(K_{OW}\) values of these ILs were measured by Belveze$^{20}$. 

11
1.3 Physical Properties of Ionic Liquids

Physical properties of ILs relevant to this thesis include carbon dioxide solubility, viscosity, density, alcohol solubility and water solubility. CO$_2$ solubilities in ILs have been measured in our laboratory by an Intelligent Gravimetric Analyzer (IGA) and published. Previously measured CO$_2$ solubilities were compared with measurements taken by the diffusion apparatus to confirm that the apparatus was measuring the amount of CO$_2$ absorbed by the IL accurately. Correlations were established between ILs’ diffusion coefficients and viscosities in the Results Chapter 5. IL densities were required to calculate the diffusion coefficients. Alcohol solubilities and water solubilities were compared with $K_{OW}$s measured to qualitatively confirm $K_{OW}$ results. This section describes how IL structures affect these physical properties and reports their values.

1.3.1 Carbon Dioxide Solubility in ILs

Gas solubilities in ILs at low pressures are reported in terms of Henry’s constants (H). Henry’s law states that:

\[ P_1 = H_1(T) x_1 \]  

(1.3-1)

where $P_1$ is the gas pressure, $H_1(T)$ is the Henry’s constant of the gas dissolved in liquid, which is a function of temperature, and $x_1$ is the mole fraction of gas in the liquid phase. In accordance with Henry’s law, gas solubility increases as the Henry’s constant decreases. Several measurements have been taken of CO$_2$ solubility in ionic liquids. It has been shown that CO$_2$ solubility increases as alkyl chain length on an imidazolium cation increases $^9, ^{14}, ^{18}$. Baltus et. al. hypothesized that as the length of the carbon chain increases, steric constraints decrease the strength of the ionic
interaction between the imidazolium cation and Tf$_2$N anion. The weaker cation-anion interactions can strengthen the interaction between the cation and CO$_2$, leading to an increased CO$_2$ solubility. Addition of fluoroalkyl groups increases CO$_2$ solubility$^{9,14,18}$. The exact mechanism of this phenomenon is poorly understood$^{35,41,101}$. Aki et al. found that substituting a methyl group for the hydrogen at the C2 position on the imidazolium has little effect on solubility at low pressures, but decreases CO$_2$ solubility at higher pressures. Molecular simulations showed that in imidazolium ILs, the CO$_2$ interacts more strongly with the greater partial positive charge on the N3 atom than with the lower charge on the N3 atom of the methyl substituted imidazolium. Our laboratory has shown that the anion primarily affects CO$_2$ solubility$^{9,14}$ and that solubility increases with the number of fluoroalkyl groups on the anion. CO$_2$ solubility in ILs decreases as temperature increases$^{9,14,18,58,59}$, which is typical for CO$_2$ dissolving in liquids$^{73}$. Published Henry’s constants of CO$_2$ absorbed by ILs selected for measuring diffusion coefficients are shown in Table 1.3.

**TABLE 1.3**

HENRY’S CONSTANTS$^{12}$

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>Temperature (degrees Celsius)</th>
<th>Henry’s Constant (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C$_2$mim][Tf$_2$N]</td>
<td>25</td>
<td>35.6 ± 1.4</td>
</tr>
<tr>
<td>[C$_4$mim][Tf$_2$N]</td>
<td>10</td>
<td>25.3 ± 0.3</td>
</tr>
<tr>
<td>[C$_6$mim][Tf$_2$N]</td>
<td>25</td>
<td>33.0 ± 0.3</td>
</tr>
<tr>
<td>[C$_{10}$mim][Tf$_2$N]</td>
<td>50</td>
<td>48.7 ± 0.9</td>
</tr>
<tr>
<td>[C$_{10}$mPy][Tf$_2$N]</td>
<td>25</td>
<td>31.7 ± 0.4</td>
</tr>
<tr>
<td>[C$_{4}$F$_9$H$_4$mim][Tf$_2$N]</td>
<td>25</td>
<td>28.5 ± 0.5</td>
</tr>
<tr>
<td>[C$_{4}$mim][PF$_6$]</td>
<td>25</td>
<td>53.4 ± 0.3</td>
</tr>
<tr>
<td>[C$_{4}$mim][P(C$_2$F$_5$)$_2$F]</td>
<td>25</td>
<td>25.2 ± 0.3</td>
</tr>
</tbody>
</table>
1.3.2 Viscosities

Viscosity is a measure of a fluid’s internal friction opposing change in the fluid’s motion. It is a dynamic, nonequilibrium property dependent upon the effect of molecular motions and interaction. Although it is a nonequilibrium property, it is a function of the state of the fluid, and may be used to define the state of the material, similarly to temperature, pressure and volume \(^75\). Isaac Newton defined a coefficient, \(\eta\), now termed absolute viscosity using a model like the one shown in Figure 1.1 consisting of a fluid sandwiched between two plates separated by distance, \(dy\), moving at constant velocities, \(v_1\) and \(v_2\) \(^87\).

\[
\tau_{yx} = -\eta \frac{dv_x}{dy} \tag{1.3-2}
\]

where \(\tau_{yx}\) is the force in the \(x\) direction on a unit area perpendicular to the \(y\) direction \(^22\), and \(dv_x/dy\) is the shear rate \(^87\). Scientists typically express viscosity in units of poises or centipoises. A poise denotes a viscosity of 1 g-mass/(s*cm).
Newton’s law relates the force necessary to maintain flow along the x–axis to the area of a layer of molecules and to the velocity gradient. If the friction between layers of fluid is small (low viscosity), an applied shearing force will result in a large velocity gradient. As viscosity increases, each fluid layer exerts a larger frictional drag on adjacent layers. The shear stress can also be interpreted as the flow per unit area of x-momentum in the positive y-direction, because each fluid layer is imparting momentum to the adjacent fluid layer.

Newtonian fluids, such as water and olive oil have constant viscosities independent of shear rate. Viscosities of non-newtonian fluids, such as polymers and yogurt vary with different shear rates. The force required to move large, non-symmetric molecules, typically with molecular weights greater than 5000, past each other depends on their alignment and cohesiveness.

Much information is available on IL viscosities. Torres showed that ILs are Newtonian fluids. ILs are more viscous than common solvents, ranging between 28 cP and 603 cP at room temperature for ILs selected for diffusion coefficient measurement in this thesis, which can be compared with benzene and ethanol having viscosities of 0.601 cP and 1.786 cP, respectively. Torres showed that ILs’ viscosities decrease over small temperature ranges according to the Vogel-Tamman-Fulcher (VTF) equation:

\[
\mu = A \exp\left(\frac{k}{T - T_0}\right)
\]

(1.3-3)

where \(\mu\) is the viscosity at temperature, \(T\), and \(A\), \(k\), and \(T_0\) are empirical constants determined experimentally. It has been proposed by Angell and supported by
Torres’ data that \( T_0 \) could reasonably represent the ideal glass transition temperature.

The VTF equation is an empirical modification of the Arrhenius equation:

\[
\mu = A \exp \left( \frac{-E_\mu}{RT} \right)
\]

where \( A \) is an empirical constant determined experimentally, \( E_\mu \) is the activation energy for viscous flow, also empirical, and \( R \) is the gas constant. The Arrhenius equation is based on the premise that a minimum energy is required for a molecule to shed its neighbors so that it can move. The probability that the molecule can acquire this energy is given by the Boltzmann distribution. The Boltzmann distribution asserts that the ratio of the numbers of atoms in the states with energies \( E_i \) and \( E_j \) is:

\[
\frac{N_i}{N_j} = \exp \left( \frac{-(E_i - E_j)}{RT} \right)
\]

A molecule’s mobility and viscosity are proportional. Thus, the viscosity is proportional with the Boltzmann distribution\(^{17}\).

IL viscosities are affected by many types of molecular interactions including hydrogen bonding, van der Waals interactions, side chain mobility, molecular weight, and symmetry of the cation \(^{24, 70, 87}\). Viscosities increase as alkyl chain length on an imidazolium cation increases. As the alkyl chain increases, the molar mass increases and van der Waals attractions increase between the aliphatic alkyl chains \(^{24, 44, 87}\).

Alkyl dimethyl imidazolium ILs have higher viscosities than their analogous alkyl methyl imidazolium ILs (ie. \([\text{C}_6\text{mmim}][\text{Tf}_2\text{N}]\) vs. \([\text{C}_6\text{mim}][\text{Tf}_2\text{N}]\)) \(^{24, 87}\), possibly because the additional methyl group adds symmetry to the cation allowing the crystals to pack more tightly \(^{87}\). Bonhote et. al found that fluorinating the alkyl chain on an imidazolium cation increases viscosity dramatically due to increased van der
Waals attractions. Torres found that changing the cation from imidazolium to the more symmetric pyridinium increases viscosity, probably because the pyridinium cation packs more efficiently. Anion viscosity for the ILs studied decreased in the order: PF$_6$ > P(C$_2$F$_5$)$_3$F$_3$ > Tf$_2$N. Okoturo et. al. found that the viscosity of radially symmetric anions, including PF$_6$, is generally greater than the viscosity of anions with diffuse charges, such as Tf$_2$N. They speculated that even charge distribution allowed the PF$_6$ anion to interact with more surrounding ions$^{70}$.

Chapter 5 of this thesis shows how diffusion coefficients correlate with viscosity. Viscosities of ILs selected for measuring diffusion coefficients are shown in Table 1.4. The average of the reported viscosities were used in the correlations with diffusion coefficients in Chapter 5. The uncertainty in the viscosity was estimated as the standard deviation of the reported viscosities. For viscosities measured by our laboratory and when other viscosities were not reported, the uncertainty in the viscosity was estimated as ± 5% based on the rheometer’s precision.
TABLE 1.4
VISCOSITIES OF ILs SELECTED FOR MEASURING DIFFUSION COEFFICIENTS

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>Temperature (degrees Celsius)</th>
<th>Viscosity (cP)</th>
<th>Reference</th>
<th>Average Viscosity (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C₄mim][Tf₂N]</td>
<td>25</td>
<td>31</td>
<td>69</td>
<td>28 ± 3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>44*</td>
<td></td>
</tr>
<tr>
<td>[C₄mim][Tf₂N]</td>
<td>10</td>
<td>84</td>
<td>70</td>
<td>84 ± 4</td>
</tr>
<tr>
<td>[C₄mim][Tf₂N]</td>
<td>25</td>
<td>47</td>
<td>70</td>
<td>48 ± 4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>44</td>
<td>44*</td>
<td></td>
</tr>
<tr>
<td>[C₄mim][Tf₂N]</td>
<td>25</td>
<td>58</td>
<td>44</td>
<td>63.5 ± 8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>69</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>[C₆mmim][Tf₂N]</td>
<td>25</td>
<td>131</td>
<td>67</td>
<td>131 ± 7</td>
</tr>
<tr>
<td>[C₆mPy][Tf₂N]</td>
<td>25</td>
<td>71</td>
<td>67</td>
<td>71 ± 4</td>
</tr>
<tr>
<td>[C₆F₅H₄mim][Tf₂N]</td>
<td>25</td>
<td>603</td>
<td>67</td>
<td>603 ± 30</td>
</tr>
<tr>
<td>[C₄mim][PF₆]</td>
<td>25</td>
<td>272</td>
<td>87</td>
<td>234 ± 53</td>
</tr>
<tr>
<td></td>
<td></td>
<td>257</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>173</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>[C₄mim][P(C₃F₃)F₆]</td>
<td>25</td>
<td>87</td>
<td>72</td>
<td>87 ± 4</td>
</tr>
</tbody>
</table>

*Viscosity value was read from publication’s graph

It is important that the ILs are dried thoroughly for obtaining accurate viscosities. Even very low water concentrations can significantly reduce IL viscosities. Torres reported that increasing the water content of [C₄mim][BF₄] from 1.1 weight % to 2.2% reduces the viscosity from 96.5 cP to 57.1 cP, respectively.

Our laboratory has found through experience that ILs in Table 1.4 can be dried sufficiently by drawing a vacuum several hours on the heated, stirring, sample.

Okoturo⁷⁰, McLean⁶⁴ and Dzyuba⁴⁴ did not report water content of their samples, but
did report drying each IL several hours under vacuum at around or above 70 degrees Celsius. Noda reported drying the ILs under vacuum and storing them in an argon atmosphere. Torres reported 76 ppm water in the [C₄mim][PF₆] sample.

1.3.3 Densities

Densities of ILs were necessary for determining the buoyancy force on the IL sample while measuring diffusion coefficients. IL densities used in the diffusion coefficient calculations were interpolated from reported data and are shown in Table 1.5. Densities of ILs decrease as the length of the alkyl chain on the cation increases. For a given cation, the density increases as the molecular weight of the anion increases.⁴⁷


### Table 1.5

Densities of ILS Selected for Measuring Diffusion Coefficients

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>Temperature (deg C)</th>
<th>Density (g/cm³)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C₂mim][Tf₂N]</td>
<td>25</td>
<td>1.5212</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.4495</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>1.4374</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>1.4143</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>1.3931</td>
<td></td>
</tr>
<tr>
<td>[C₄mim][Tf₂N]</td>
<td>25</td>
<td>1.3759</td>
<td>12</td>
</tr>
<tr>
<td>[C₆mmim][Tf₂N]</td>
<td>25</td>
<td>1.3630</td>
<td>8</td>
</tr>
<tr>
<td>[C₆mPy][Tf₂N]</td>
<td>25</td>
<td>1.3489</td>
<td>12</td>
</tr>
<tr>
<td>[C₆F₉H₄mim][Tf₂N]</td>
<td>25</td>
<td>1.6910</td>
<td>12</td>
</tr>
<tr>
<td>[C₆mim][PF₆]</td>
<td>25</td>
<td>1.3603</td>
<td>49</td>
</tr>
<tr>
<td>[C₆mim][PF(C₂F₅)₃F]</td>
<td>25</td>
<td>1.5573</td>
<td>12</td>
</tr>
</tbody>
</table>

### 1.3.4 Solubility of Imidazolium-Based ILs in Alcohols

Understanding imidazolium-based IL solubilities in alcohols was important for predicting how the IL would dissolve in 1-octanol when measuring $K_{OW}$, and understanding the reasonableness of $K_{OW}$ results measured. Mutual solubilities of ILs and alcohols have been measured by starting at a temperature where the two liquids are immiscible, then raising the temperature until the cloud point, the temperature where the two liquids form one phase, is reached. The cloud points are plotted on a temperature – composition phase diagram in Figure 1.2. The highest cloud point temperature on the phase diagram is referred to as the upper critical solution temperature (UCST). A high UCST indicates low mutual solubility.
concentrations of ILs in 1-octanol at 25 degrees Celsius were not available for most of the ILs measured. Thus, the T-x diagrams of ILs and alcohols were reviewed to qualitatively estimate $K_{OW}$. 

![T-x Diagram](image)

**Figure 1.2** T-x Diagram for $[\text{C}_4\text{mim}][\text{triflate}]$ with 1-dodecanol$^{38}$

Alcohol/IL mutual solubilities have been measured by our group and the groups of Marsh and Heintz. It has been shown that increasing the length of the alkyl chain length on the imidazolium cation increases mutual solubility with alcohols$^{38,100}$. Most likely the cation’s longer alkyl chain experiences greater van der Waals attractions with the alkyl chain on the alcohol$^{38}$. Crosthwaite et. al. found that replacing the hydrogen at the C2 position on the imidazolium cation of $[\text{C}_3\text{mim}][\text{Tf}_2\text{N}]$ with a methyl group forming $[\text{C}_3\text{mmim}][\text{Tf}_2\text{N}]$ reduces mutual solubility with 1-butanol. He explained that replacing the hydrogen with a methyl group eliminates a hydrogen-bonding site where the cation could have interacted with the alcohol. The reduced hydrogen bonding causes an increase in UCST and lowers mutual solubility. Alcohol affinity of anions reported by Crosthwaite and selected for measuring $K_{OW}$s increases in the order $\text{Tf}_2\text{N}>\text{BF}_4>\text{PF}_6$. Crosthwaite concluded that since this trend is the same as the trend observed for strength of hydrogen bonding
between these and additional anions and water, that increasing the hydrogen bond
strength between the anion and the alcohol leads to higher mutual solubilities.
Available solubilities of ILs in 1-octanol are shown in Table 1.6.

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>Solubility in 1-octanol, mol %</th>
<th>Temperature (°K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C₄mim][Cl]</td>
<td>35.07</td>
<td>299.64</td>
<td>42</td>
</tr>
<tr>
<td>[C₂mim][Tf₂N]</td>
<td>1.98</td>
<td>298</td>
<td>37</td>
</tr>
<tr>
<td>[C₆mim][Tf₂N]</td>
<td>1.06</td>
<td>298</td>
<td>37</td>
</tr>
</tbody>
</table>

1.3.5 Solubility of Imidazolium-based ILs in Water

Like alcohol solubility data, water-solubility of imidazolium-based ILs was
important for checking the reasonableness of $K_{ow}$ results measured for this thesis.
Available water solubilities of ILs selected for $K_{ow}$ measurement are shown in Table
1.7. IL solubility in water decreases as alkyl chain length on the cation increases. This phenomenon is similar to organic molecules, which have reduced water
solubility as the nonpolar portion of the structure becomes larger. As the surface area
of the molecule or ion increases, more energy is required to break apart the water
molecules from each other and insert the solute ion or molecule. Crosthwaite et. al.
found that IL solubility in water decreased when a methyl group was substituted for
hydrogen in the C2 position on the imidazolium cation. He explained that
replacement of the acidic hydrogen at the C2 position reduced hydrogen bonding
between the imidazolium cation and water. Anion solubility increases in the order
[Tf₂N] < [PF₆] < [BF₄] following the same trend as increasing charge density. It is
thought that the anions with greater charge density exhibit stronger coulombic and hydrogen bonding interactions with water\textsuperscript{15,38}. ILs with chloride, bromide and nitrate anions tend to be completely miscible with water at room temperature\textsuperscript{38}.

**TABLE 1.7**

**PUBLISHED SOLUBILITIES IN WATER**

**OF ILS SELECTED FOR** $K_{ow}$ **MEASUREMENT**

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>Solubility of IL in water (mol %)</th>
<th>Temperature (deg K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C\textsubscript{4}mim][Cl]</td>
<td>54.40</td>
<td>296</td>
<td>42</td>
</tr>
<tr>
<td>[C\textsubscript{4}mim][PF\textsubscript{6}]</td>
<td>0.13 0.16 0.15</td>
<td>298 303 296</td>
<td>38 99 46</td>
</tr>
<tr>
<td>[C\textsubscript{3}mim][Tf\textsubscript{2}N]</td>
<td>0.08</td>
<td>298</td>
<td>38</td>
</tr>
<tr>
<td>[C\textsubscript{4}mim][Tf\textsubscript{2}N]</td>
<td>0.032</td>
<td>298</td>
<td>38</td>
</tr>
<tr>
<td>[C\textsubscript{2}mmim][Tf\textsubscript{2}N]</td>
<td>0.052</td>
<td>298</td>
<td>38</td>
</tr>
<tr>
<td>[C\textsubscript{3}mmim][Tf\textsubscript{2}N]</td>
<td>0.033</td>
<td>298</td>
<td>38</td>
</tr>
</tbody>
</table>

### 1.4 Diffusion Overview

There are several types of diffusion including ordinary diffusion, pressure diffusion, forced diffusion due to an external force field, or thermal diffusion\textsuperscript{53}. This thesis focuses on ordinary transport diffusion at constant temperature, pressure and without external force fields. Ordinary transport diffusion is the process where matter is transported from one part of a system to another by random molecular motions\textsuperscript{36}. This phenomenon can be observed when a red dye is slowly added without causing convection currents to a still glass of water. Soon after adding the dye, the color is very red toward the top of the water and becomes fainter toward the bottom. After sufficient time, the whole glass becomes uniformly colored. Evidently, the red dye
molecules transferred from the top of the glass to the bottom without the presence of
convective currents. The dye is said to have diffused throughout the water.

1.4.1 Types of Ordinary Diffusion

There are two types of ordinary diffusion, namely transport diffusion and self-
diffusion. Transport diffusion occurs under nonequilibrium conditions where there is
a gradient in chemical potential, which typically corresponds with a gradient in
concentration. Molecules of higher chemical potential diffuse to the location of lower
chemical potential until the chemical potential throughout the substance is uniform\textsuperscript{60}.
Prausnitz defines chemical potential, $\mu$, according to the following relation:

$$
\mu_i \equiv \left( \frac{\partial U}{\partial n_i} \right)_{s,p,n_j}
$$

(1.4-1)

where $U$ is internal energy, $n_i$ refers to all mole numbers, and $n_j$ refers to all mole
numbers other than the $i$th\textsuperscript{73}. Self-diffusion is the random movement of molecules or
Brownian motion occurring under equilibrium conditions\textsuperscript{60}. Both transport diffusion
and self-diffusion can be quantified by diffusion coefficients.

1.4.2 Fick’s Laws

The transport diffusion coefficient was defined by Adolf Fick who found that
diffusing matter obeys laws in the same general form as heat conduction proposed by
Fourier. Fourier’s Laws of heat conduction and Fick’s laws for unidirectional
diffusion are compared in Table 1.8. In these equations, $q$ is the heat flux, $k$ is the
heat transfer coefficient, $z$ is distance, $J$ is the diffusive flux, $D$ is the binary diffusion
coefficient, and $C$ is the solute concentration.
Fick’s laws can be verified conceptually using a model of hydrogen diffusing into metal shown in Figure 1.3. We first define a hydrogen flux as:

\[
\text{hydrogen flux} = \frac{\text{amount of hydrogen penetrating surface}}{\text{time} \times \text{area of metal's surface}} \quad [\text{m}^*\text{t}^{-1}\text{d}^{-2}] \quad (1.4-6)
\]

An approximation of the hydrogen flux at steady state can be made by:

\[
\left( \text{hydrogen flux} \right) = D \left( \frac{\text{hydrogen concentration at } z = 0}{\text{thickness at } z = 0} \right) - \left( \frac{\text{hydrogen concentration at } z = \Delta z}{\text{thickness at } z = \Delta z} \right) \quad (1.4-7)
\]

where \( \Delta z \) is the distance over which diffusion occurs. Symbolically, this equation can be written as:

\[
J = D \frac{C\big|_{z=0} - C\big|_{z=d}}{l - 0} \quad [\text{m}^*\text{t}^{-1}\text{d}^{-2}] \quad (1.4-8)
\]

where \( C \) refers to the concentration of hydrogen. The units are shown in brackets with \( m \) equal to mass, \( t \) equal to time, and \( d \) equal to distance. When the distance \( \Delta z \) is infinitesimally small, then the equation is written as Fick’s first law:

\[
J = D \lim_{{\Delta z \to 0}} \frac{C\big|_{z=0} - C\big|_{z=\Delta z}}{z\big|_{\Delta z} - z\big|_{0}} = -D \frac{\partial C}{\partial z} \quad [\text{m}^*\text{t}^{-1}\text{d}^{-2}] \quad (1.4-9)
\]
Fick’s second law for unidirectional diffusion can be derived by performing a mass balance on the hydrogen diffusing across the metal in the z direction:

\[
\left( \text{hydrogen accumulation} \right) = \left( \text{rate of diffusion into the metal at } z \right) - \left( \text{rate of diffusion out of the metal at } z + \Delta z \right) \quad (1.4-10)
\]

\[
\frac{d}{dt} (\Delta V C) = \Delta V \frac{dC}{dt} = a_z J_z (0) - a_z J_z (\Delta z) \quad [m^3 t^{-1}]. \quad (1.4-11)
\]

Where \( V \) is the volume, \( a_z \) is the metal’s surface area perpendicular to the z direction, and \( J_z \) refers to the flux in the z direction. Division by \( \Delta V (\Delta V = a_z \Delta z) \) yields:

\[
\frac{dC}{dt} = \frac{a_z}{\Delta V} [J_z (0) - J_z (\Delta z)] = \frac{1}{\Delta z} [J_z (0) - J_z (\Delta z)] \quad [m^3 d^3 t^{-1}]. \quad (1.4-12)
\]

Then, taking the limit as \( \Delta z \) goes to zero yields:

\[
\frac{\partial C}{\partial t} \bigg|_{z} = \frac{\partial J_z}{\partial z} \bigg|_{t} \quad [m^3 d^3 t^{-1}]. \quad (1.4-13)
\]

Substituting Fick’s first law for the flux yields Fick’s second law:

\[
\frac{\partial C}{\partial t} = -\frac{\partial}{\partial z} \left( -D \frac{\partial C}{\partial z} \right) = D \frac{\partial^2 C}{\partial z^2} \quad [m^3 d^3 t^{-1}]. \quad (1.4-14)
\]
1.4.3 Driving Force for Diffusion

Earlier in this thesis it was stated that chemical potential was the driving force for diffusion contrary to Fick’s laws, which imply that concentration gradient drives diffusion. Fick’s laws are models for predicting diffusion that correlate well with experimental data for many substances. However, it has been shown experimentally by Haase and Siry that transport diffusion depends on a gradient in chemical potential\textsuperscript{60, 88}. Haase and Siry measured diffusion coefficients of solvent mixtures around their critical solution temperatures, where chemical potential is independent of composition. It will be shown in section 2.1 that a diffusion coefficient expression thermodynamically derived based on chemical potential as the driving force can be written as:

\[
D = D_0 \frac{d \ln p}{d \ln C} \quad [d^2 t^{-1}]
\]  

(1.4-15)

According to equation 1.4-15, the diffusion coefficient should equal zero when the partial pressure is independent of composition. Haase and Siry found that indeed around the critical solution temperature, the diffusion coefficient approached zero\textsuperscript{50}.

1.5 Octanol-Water Partition Coefficients ($K_{OW}$)

Partitioning is the process occurring when a solute, IL in this thesis, is added to two liquids, octanol and water in this thesis, contacting each other and forming two phases. The solute distributes between the two phases until equilibrium is reached at concentrations dependent upon molecular interactions between the solute and the two liquids. The $K_{OW}$ is defined by the following equation\textsuperscript{82}:

\[
\]
\[
K_{\text{OW}} = \frac{C_{\text{IL}}^O}{C_{\text{IL}}^W}
\]  \quad (1.5-1)

where \(C_{\text{IL}}^O\) is the molar concentration of the solute, \(IL\), dissolved in the octanol-rich phase, and \(C_{\text{IL}}^W\) is the molar concentration of the \(IL\) dissolved in the water-rich phase.

Ideally, concentrations of the same solute species are measured in the two liquid phases when determining \(K_{\text{OW}}\) values. This measurement can be difficult for species such as acids or salts, where the solute may dissociate more in the aqueous phase than in the octanol-rich phase. As shown in Figure 1.4, it is anticipated that \(IL\)s ([\(M_{u^+}X_{u^-}\)]) will have a greater tendency to dissociate in the water-rich phase.

![Figure 1.4 Partitioning of an organic salt between octanol and water.](image)

When solute dissociation is expected, the \(K_{\text{OW}}\) commonly reported is the concentration of both undissociated and dissociated (if any) salt in the octanol-rich phase divided by the total concentration (both dissociated and undissociated) in the water-rich phase\(^{79}\). For this thesis, concentrations were measured in each phase using UV-vis spectroscopy, which detects the imidazolium ring on the cation (whether dissociated or undissociated). Therefore, the \(K_{\text{OW}}\) values reported in section 6.2 are:

\[
K_{\text{OW}} = \frac{[M_{u^+}X_{u^-}]_{\text{octanol}} + [M_{u^+}]_{\text{octanol}}}{[M_{u^+}X_{u^-}]_{\text{water}} + [M_{u^+}]_{\text{water}}}. \quad (1.5-2)
\]
It is important to recognize that octanol and water are not completely
immiscible. At 25 °C, the solubility of water in octanol is quite large, approximately
0.275 mole fraction\textsuperscript{16}, but the solubility of octanol in water is just 7.5 x 10\textsuperscript{-5} mole
fraction\textsuperscript{63}. Since the solubility of water in octanol is high, the $K_{OW}$ cannot be
represented simply as the ratio of saturation concentrations of a solute dissolved in
separate solutions of octanol and water. The mutually saturated octanol and water
phases affect the partitioning of the solute between the two solvents.

1.6 Application of Measured Diffusion Coefficients and $K_{OW}$

One reason diffusion coefficients of CO\textsubscript{2} into ILs were measured was because
they are needed for designing systems to separate CO\textsubscript{2} from gas mixtures.
Information on diffusion coefficients would be especially important when ILs are
used as the solvent because the ILs’ high viscosities may result in mass transfer
limitations by diffusion into the IL. Potential methods for separating CO\textsubscript{2} from gas
mixtures include IL supported membranes and absorbers.

$K_{OW}$ values are important for predicting a chemical’s potential impact on the
aqueous environment. Since ILs do not evaporate and most are highly soluble in
water, the most likely route of environmental exposure is through aqueous waste
streams or accidental spills. Several correlations use $K_{OW}$ values to estimate
ecosystem impact parameters such as concentrations of chemical that would adsorb to
soil, and accumulate in fish or higher levels in the food chain. Understanding the way
that ILs would impact the ecosystem will be helpful for regulatory agencies setting
standards, such as maximum contaminant levels in aqueous waste streams. $K_{OW}$
values of various ILs would also be of interest to a person selecting an IL with minimal environmental impact prior to bulk, industrial implementation.

1.6.1 Application of Diffusion Coefficients in IL Supported Membrane Design

The diffusion coefficient can be used to calculate the separation factor between components separated by the IL supported membrane. Figure 1.5 shows the concentration and partial pressure profiles for solute transport through a dense membrane.

\[
\alpha_{A,B} = \frac{y_A / x_A}{y_B / x_B}
\]

where \(y_i\) is the mole fraction in the permeate leaving the membrane and \(x_i\) is the mole fraction in the retentate on the feed side of the membrane. The flux of solute \(i\) across the membrane can be written as:

\[
N_i = \frac{D_i}{l_m} (c_{i0} - c_{iL})
\]
where $D_i$ is the diffusion coefficient in cm$^2$/s, $l_m$ is the length across the membrane in cm, $c_{i0}$ is the concentration in the membrane on the feed side of the membrane, $c_{il}$ is the concentration within the membrane on the permeate side of the membrane. The membrane separation is strongly influenced by the partition of the solute between the membrane and the adjacent solution. A partition coefficient or solubility constant, $H_m$, can be defined as:

$$c_i = H_m C_i$$  \hspace{1cm} (1.6-3)$$

and the flux equation written as:

$$N_i = \frac{DH_m}{l_m} (C_{i0} - C_{il})$$  \hspace{1cm} (1.6-4)$$

where $C_{i0}$ is the concentration in the fluid adjacent to the feed surface of the membrane and $C_{il}$ is the concentration in the fluid adjacent to the permeate surface of the membrane. Assuming that the gas mixture follows the ideal gas law, the flux can be described in terms of partial pressures.

$$N_i = \frac{DH_m n_i}{l_m PV} (x_{i0} P - x_{il} P) = \frac{DH_m n_i}{l_m PV} (p_{i0} - p_{il}) = \frac{DH_m}{l_m RT} (p_{i0} - p_{il})$$  \hspace{1cm} (1.6-5)$$

where $P$ is the total pressure, $V$ is the gas volume, $n_i$ is the number of moles of component $i$, $R$ is the gas constant, $p_i$ is the partial pressure$^{39}$. 

When external mass-transfer resistances are neglected, $p_{iF} = p_{i0}$ and $p_{iL} = p_{iP}$ and the flux across the membrane can be approximated by:

$$N_i = \frac{H_m D}{l_m RT} (p_{iF} - p_{iP}).$$  \hspace{1cm} (1.6-6)$$
For the separation of a binary gas mixture of species A and B in the absence of boundary layer or film mass-transfer resistances, the ratio of the transport fluxes is the ratio of $y_A$ and $y_B$ and can be expressed as:

$$\frac{N_A}{N_B} = \frac{y_A}{y_B} = \frac{H_{mA} D_A (x_A P_F - y_A P_P)}{H_{mA} D_A (x_A P_F - y_A P_P)}.$$

(1.6-7)

where $P_F$ and $P_P$ are pressures on the feed and permeate sides of the membrane, respectively. If the pressure on the permeate side is negligible compared to the pressure on the feed side, then a relation for the ideal separation factor, $\alpha^*_{A,B}$ holds.

$$\alpha^*_{A,B} = \frac{H_{mA} D_A}{H_{mA} D_B}$$

(1.6-8)

When the downstream pressure is not negligible, equation (1.6-7) can be rearranged to yield an expression for the separation factor, $\alpha_{A,B}$.

$$\alpha_{A,B} = \frac{\alpha^*_{A,B}}{(x_B / y_B)^r - r}$$

(1.6-9)

where $r = P_P / P_F$

Assuming perfect mixing, the required membrane area, $A_M$, normal to flow through the membrane can be calculated by performing a mass balance on the membrane.

$$y_p n_p = \frac{A_M H_{mb} D_B}{l_m} (x_{R_p} P_R - y_{p_p} P_P)$$

(1.6-10)

where $n_p$ is the molar flow rate of the permeate.

### 1.6.2 Application of Diffusion Coefficients in Absorber Design

In absorbers, turbulent flow facilitates mass transfer so that mass transfer rates are greater than by diffusion, or simply molecular motions. Turbulent or convective mass transfer rates are described by a mass transfer coefficient, $k$, specific to the
absorber’s configuration. Mass transfer coefficients can be approximated from empirical correlations with diffusion coefficients based on experimental data. These correlations are useful for the design of small pilot plants, typically displaying accuracy within thirty percent\textsuperscript{39}. Examples of some correlations are shown in Table 1.9.

### TABLE 1.9

**EQUATIONS RELATING DIFFUSION COEFFICIENTS WITH MASS TRANSFER COEFFICIENTS FOR ABSORBERS**

<table>
<thead>
<tr>
<th>Physical Situation</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid in a packed tower\textsuperscript{39}</td>
<td>[ k_i \left( \frac{1}{v_i g} \right) = 0.0051 \left( U_{av_i} \right)^{0.67} \left( \frac{D}{v_i} \right)^{0.5} (ad)^{0.4} ] (1.6-11)</td>
</tr>
<tr>
<td>Gas in a packed tower\textsuperscript{39}</td>
<td>[ \frac{k_g}{aD} = 3.6 \left( U_{av} \right)^{0.7} \left( \frac{v_i}{D} \right)^{1/3} (ad)^{-2.0} ] (1.6-12)</td>
</tr>
<tr>
<td>Liquid in a sieve tray absorber\textsuperscript{31}</td>
<td>[ k_i a_s = 78.8 D^{0.5} \left( U_{av} \rho_g \right)^{0.5} + 0.425 ] (1.6-13)</td>
</tr>
<tr>
<td>Gas in a sieve tray absorber\textsuperscript{31}</td>
<td>[ k_g a_s = \frac{1030 D^{0.5} \left( f - 0.842 f^2 \right)}{(h_i)^{0.5}} ] (1.6-14)</td>
</tr>
<tr>
<td>Liquid in a valve tray absorber\textsuperscript{81}</td>
<td>[ Sh_i = 125 Re_g^{0.684} Re_i^{0.087} W^{0.051} Sc_i^{0.5} ] (1.6-15)</td>
</tr>
<tr>
<td>Gas in a valve tray absorber\textsuperscript{81}</td>
<td>[ Sh_g = 9.93 Re_g^{0.865} Re_i^{0.130} W^{0.389} Sc_i^{0.5} ] (1.6-17)</td>
</tr>
</tbody>
</table>

Definitions of variables and their units in Table 1.9 follow.

- \(a\) is the packing area per bed volume, (m\(^2\))
- \(a_s\) is interfacial area for mass transfer, (m\(^2\)/m\(^3\))
- \(a_r = 0.270 Re_g^{0.375} Re_i^{0.247} W^{0.515}\), interfacial area per unit tray area
- \(d\) is the nominal packing diameter, (m)
**d**, is the characteristic length, taken as 1 meter

**D** is the molecular diffusion coefficient of the solute being transferred, (cm\(^2\)/s)

\( f = \frac{U_a}{U_f} \) fractional approach to the active area gas velocity at flooding, (dimensionless)

**G** is the superficial gas mass velocity, (kg*m\(^{-2}\)*s\(^{-1}\))

\( k_l \) and \( k_g \) are the mass transfer coefficients in the liquid and vapor, respectively, (m/s)

\( k_s a_t, k_g a_t \) are the liquid-phase and gas-phase mass-transfer coefficients based on mole fraction driving force, (kg*mol*m\(^{-2}\)*s\(^{-1}\))

**L** is the superficial liquid mass velocity, (kg*m\(^{-2}\)*s\(^{-1}\))

\( \rho_g, \rho_l \) are the density of the gas and liquid, respectively, (kg*mol/m\(^3\))

**Re** \(_g\) = \( Gd / \mu_g \), gas-phase Reynolds number, (dimensionless)

**Re** \(_l\) = \( LD / \mu_l \), liquid-phase Reynolds number, (dimensionless)

**Sc** \(_g\) = \( v_g / D \), gas-phase Schmidt number, (dimensionless)

**Sc** \(_l\) = \( v_l / D \), liquid-phase Schmidt number, (dimensionless)

\( Sh_g = \frac{k_s a_t d_l}{\rho_g D} \), gas-phase Sherwood number, (dimensionless)

\( Sh_l = \frac{k_s a_t d_l}{\rho_l D} \), liquid-phase Sherwood number, (dimensionless)

**U**\(_f\) is the active area gas velocity at flooding, (m/s)

\( v_g, v_l \) are the kinematic viscosities of the gas and liquid respectively, kg/(m*s)

**U**\(_a\) is the superficial fluid velocity, (m/s)

**W** is the weir height, (m)

\( W' = W/d_l \), dimensionless weir height
The following parameters included in equation (1.6-14) were developed by Bennett et. al.\textsuperscript{21} based on a broad range of sieve tray holdup data.

\[
h_L = \phi_e h_w + 1533\phi_e C \left(\frac{q_L}{\phi_e}\right)^{\frac{2}{3}}, \text{ liquid holdup on tray, (cm)} \tag{1.6-18}
\]

\[
\phi_e = \exp(-12.55K_s^{0.91}), \text{ effective relative froth density} \tag{1.6-19}
\]

\[
C = 0.0327 + 0.0286e^{-1.378b_s} \tag{1.6-20}
\]

\[
K_s = U_a \left(\frac{\rho_y}{\rho_L + \rho_y}\right)^{\frac{1}{2}} \tag{1.6-21}
\]

Mass transfer coefficients are necessary for calculating the number of trays or in the case of a packed tower absorber, the packed height required to perform the desired separation\textsuperscript{83}. Using equations (1.6-13) and (1.6-14) as an example to calculate the number of trays required in an absorber, we start by calculating the number of gas and liquid phase transfer units, \(N_G\) and \(N_L\), respectively. Chan and Fair showed that for a sieve tray absorber:

\[
N_G = k_g a_h t_g \tag{1.6-22} \quad \text{and} \quad N_L = k_l a_h t_l \tag{1.6-23}
\]

where

\[
t_l = \frac{h_L A_a}{q_l} \quad \text{and} \tag{1.6-24}
\]

\[
t_g = \frac{(1 - \phi_e) h_L}{\phi_e U_a} \quad \text{are the average liquid and gas resistance times} \tag{1.6-25}
\]

\(A_a\) is the active, or bubbling, area of the tray, (m\textsuperscript{2})

\(q_l\) is the liquid flow rate per unit length of overflow weir, (m\textsuperscript{2}/s)

Next, the number of overall gas-phase mass transfer units, \(N_{OG}\), is calculated.
\[ \frac{1}{N_{OG}} = \frac{1}{N_G} + \frac{(KG/L)}{N_L} \quad (1.6-26) \]

where \( K \) is the equilibrium ratio for vapor-liquid equilibria. Once \( N_{OG} \) is known, the Murphree vapor-point efficiency, \( E_{OV} \), can be estimated.

\[ N_{OG} = -\ln(1-E_{OV}) \quad (1.6-27) \]

The Murphree vapor efficiency, \( E_{MV} \), is related to the Murphree vapor-point efficiency by:

\[ \frac{E_{MV}}{E_{OV}} = \frac{1 - e^{-(\eta+N_{Pe})}}{(\eta+N_{Pe})(1+[(\eta+N_{Pe})/\eta])} + \frac{e^{\eta} - 1}{\eta(1+[(\eta/N_{Pe})])} \quad (1.6-28) \]

\[ \eta = \frac{N_{Pe}}{2} \left( \left(1 + \frac{4\lambda E_{OV}}{N_{Pe}} \right)^{\frac{1}{2}} - 1 \right) \quad (1.6-29) \]

The dimensionless Peclet number, \( N_{Pe} \), serves as a partial mixing parameter and is defined by:

\[ N_{Pe} = Z_L u / D_E \quad (1.6-30) \]

where \( Z_L \) is the length of the liquid flow path across the tray, \( D_E \) is the eddy diffusion coefficient in the direction of liquid flow, \( u \) is the mean liquid velocity across the tray and \( \lambda = KG/L \). When equilibrium and operating lines are straight, the overall stage efficiency, \( E_o \), is related to \( E_{MV} \) by the following equation.

\[ E_o = \frac{\log[1 + E_{MV} (\lambda - 1)]}{\log \lambda} \quad (1.6-31) \]

Finally, the actual number of contacting trays, \( N_a \), is related to the number of theoretical trays, \( N_t \), by:

\[ E_0 = N_t / N_a \quad (1.6-32) \]
1.6.3 Application of $K_{OW}$ Values

$K_{OW}$ values are useful for estimating ecosystem risk factors because partition coefficients in octanol-water systems display similarities to partition effects with natural organic substances and biological components in water. Correlations between natural systems and $K_{OW}$s have been successful because octanol and lipids exhibit similar molecular structures and physical properties. Both octanol and lipids contain a polar, hydrophilic oxygen at the end of a long hydrophobic alkyl chain\textsuperscript{33}. Comparison of 1-octanol’s structure with a lipid’s structure is made in Figure 1.6.

![Lipid Tristearin and Octanol structure comparison](image)

Figure 1.6 Comparison of a lipid’s structure with 1-octanol’s structure

Numerous empirical correlations connect $K_{OW}$ with bioconcentration ($BCF$) and bioaccumulation ($BAF$) factors, soil sorption coefficients ($K_{OC}$), and toxicity. Bioconcentration is the process that causes an increased chemical concentration in an aquatic organism compared to that in water, due to the uptake of chemical by absorption\textsuperscript{92}. The bioconcentration factor is the equilibrium ratio of the chemical’s
concentration in the organism, \( v_w \) in \( \mu g/kg \) lipid, to the concentration in the water, \( c_w \) in \( \mu g/L \), where exposure is only to the chemical in the water\(^{86}\).

\[
BCF = \frac{v_w}{c_w}
\]  

(1.6-33)

Pollutants also enter into biota along the food chain through dietary uptake, which is referred to as biomagnification. The sum of bioconcentration and biomagnification is referred to as bioaccumulation\(^{92}\). The bioaccumulation factor is the equilibrium ratio of the organism chemical concentration, \( v \), resulting from the water and food routes to the water concentration\(^{86}, c_w \).

\[
BAF = \frac{v}{c_w}
\]  

(1.6-34)

Soil sorption coefficients, \( K_{OC} \), describe soil-water partitioning. The \( K_{OC} \) is the ratio of the mass of a chemical adsorbed per unit weight of organic carbon in a soil, \( c_s \) in \( \mu g/g \) organic carbon, to the concentration of the chemical in a liquid phase, \( c_{ls} \), in \( \mu g/mL \).

\[
K_{OC} = \frac{c_s}{c_{ls}}
\]  

(1.6-35)

Toxicity is typically reported in terms of mortality to various species quantified by the \( LC_{50} \) in \( \mu mol/L \), which is the lethal concentration to half of the species population over a 14-day exposure\(^{10}\). Examples of equations based on experimental data relating \( K_{OW} \) with \( BCF \), \( K_{OC} \) and \( LC_{50} \) are shown in Table 1.10.
TABLE 1.10

CORRELATIONS OF $K_{OW}$ WITH ECOSYSTEM RISK PARAMETERS

| Equation |  
|----------|---|
| Log (BCF) = 0.79log ($K_{OW}$) – 0.40 |  
| Log ($K_{OC}$) = 0.544log($K_{OW}$) + 1.377 |  
| Log (1/LC$_{50}$) = 0.871log($K_{OW}$) – 4.87 | (for guppies)  

1.7 Previous Ionic Liquid Diffusion Coefficient and $K_{OW}$ Publications

1.7.1 Previous Ionic Liquid Diffusion Coefficient Publications

Previous publications have reported ionic liquid self-diffusion coefficients, mutual diffusion coefficients of [C$_4$mim][PF$_6$] with methanol, transport diffusion coefficients of oxygen into ILs and the transport diffusion coefficient of carbon dioxide into one IL. Noda et. al. $^{69}$ measured self-diffusion coefficients of the anions and cations in [C$_2$mim][BF$_4$], [C$_4$mim][BF$_4$], [C$_2$mim][Tf$_2$N], and [C$_4$mim][Tf$_2$N] at various temperatures by pulsed-gradient spin-echo NMR. The temperature dependencies of the self-diffusion coefficient, viscosity and ionic conductivities obeyed the VTF equation. Summation of the anionic and cationic self-diffusion coefficients correlated well with the inverse of the viscosity. At room temperature, the sum of the anion and cation self-diffusion coefficients ranged between 1 x $10^{-6}$ cm$^2$/s and 2.3 x $10^{-7}$ cm$^2$/s. Every et. al. $^{45}$ measured self-diffusion coefficients of C$_n$mim cations and bromide, iodide triflate or Tf$_2$N anions using pulsed field gradient and fringe field gradient NMR. The self-diffusion coefficients were strongly linked to viscosity and also varied with ionic radius of the cation. The diffusion coefficients followed the VTF model for various temperatures.
Richter et al. measured mutual diffusion coefficients of methanol with [C₄mim][PF₆] at various concentrations using digital image holography. The diffusion coefficients decreased hyperbolically as IL concentration increased. Diffusion coefficients ranged between $1.4 \times 10^{-5}$ cm$^2$/s at 0.05 mol/L [C₄mim][PF₆] concentration to $1 \times 10^{-6}$ cm$^2$/s at 4.5 mol/L [C₄mim][PF₆] concentration.

Diffusion coefficients and solubilities of oxygen into various ILs and carbon dioxide into hexyltriethylammonium bis(trifluoromethylsulfonyl)imide, [N₆22][Tf₂N], have been measured by a chronoamperometric technique. Percent error was not reported for any of the diffusion coefficients. However, two different values, $2.5 \times 10^{-6}$ cm$^2$/s$^{27}$ and $7.3 \times 10^{-6}$ cm$^2$/s$^{29}$, for the diffusion coefficient for oxygen diffusing into [C₂mim][Tf₂N] at 20 degrees Celsius were reported by the same authors in separate papers. No explanation was given for the discrepancy. Diffusion coefficients into ILs having published viscosities measured using this chronoamperometric technique are shown in Table 1.10. Solubility of oxygen in [C₄mim][PF₆] measured using the chronoamperometric technique was similar to the solubility measured gravimetrically by Anthony et al., 3.6 mM versus 1.3 mM, respectively. Our laboratory has not measured oxygen solubilities for the other ILs in Table 1.11.
TABLE 1.11
DIFFUSION COEFFICIENTS OF OXYGEN IN IONIC LIQUIDS

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>Temperature (deg C)</th>
<th>Viscosity (cP)</th>
<th>Diffusion Coefficient $x 10^6$ (cm$^2$/s)</th>
<th>Solubility (mM)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C$_2$ mim][Tf$_2$N]</td>
<td>20</td>
<td>35</td>
<td>2.5 (7.3)</td>
<td>10.8 (3.9)</td>
<td>27/29</td>
</tr>
<tr>
<td>[C$_4$ mim][Tf$_2$N]</td>
<td>20</td>
<td>105</td>
<td>2.1</td>
<td>7.2</td>
<td>27</td>
</tr>
<tr>
<td>[N$_6$222][Tf$_2$N]</td>
<td>20</td>
<td>220</td>
<td>1.5</td>
<td>11.6</td>
<td>29</td>
</tr>
<tr>
<td>[C$_4$ mim][PF$_6$]</td>
<td>25</td>
<td>234</td>
<td>2.2</td>
<td>3.6</td>
<td>11</td>
</tr>
</tbody>
</table>

1.7.2 Previous Ionic Liquid $K_{OW}$ Publications

Two previous publications measure or compute octanol/water partition coefficients for some ionic liquids$^{34,42}$. Domańska et al.$^{42}$ measured binary liquid-liquid equilibrium (LLE) for several alkylmethylimidazolium chlorides ([C$_n$mim][Cl], for n = 4, 8, 10 and 12) with both water and octanol. They used the solubility data of [C$_4$mim][Cl] in each solvent to estimate $K_{OW}$ values ($K_{OW} \approx$ solubility of IL in pure octanol/solubility of IL in pure water). However, the concentration of the IL was rather high in each phase and the authors could not take into account the mutual saturation of the solvents (i.e., they measured the solubility in each of the pure solvents). Domanska’s $K_{OW}$ for [C$_4$mim][Cl] at room temperature was 0.48, which was much higher than the value of 0.004 measured in this study. Chou et al.$^{34}$ measured the $K_{OW}$ of [C$_2$mim][PF$_6$] and [C$_4$mim][PF$_6$] by using a shake-flask method but did not centrifuge their samples to eliminate the emulsion created by the shaking process. Although the ILs were present at low concentrations, the value of $K_{OW}$ for [C$_4$mim][PF$_6$] did not match the value measured by our laboratory$^{20}$. Chou et. al measured a $K_{OW}$ value of 0.005 and our laboratory measured a value of 0.022. Also,
the trend observed with increasing alkyl chain length is opposite the trend measured in this study.
2.1 Thermodynamics of Diffusion

During diffusion, more than one chemical species with chemical potential varying spatially in a system is approaching equilibrium. Figure 2.1 illustrates an isolated, nonequilibrium system where diffusion is occurring.

![Diagram of an isolated, nonequilibrium system](Image)

Figure 2.1 An isolated, nonequilibrium system

It can be shown that chemical potential is the driving force for diffusion based on the second law of thermodynamics. The second law of thermodynamics states that the rate of internal generation of entropy within the system is greater than zero until equilibrium is reached and that entropy does not change with time at equilibrium. The entropy balance of an open system is:

\[
\frac{dS}{dt} = \sum_{k=1}^{K} M_k \dot{S}_k + \frac{\dot{Q}}{T} + \dot{S}_{gen} \tag{2.1-1}
\]
where $S$ is entropy, $\sum_{k=1}^{K} M_k \tilde{S}_k$ is the net rate of entropy flow due to the flow of mass into and out of the system, $\dot{S}_k$ is the entropy per unit mass, $\dot{Q}/T$ is the rate of entropy flow due to the flow of heat across the system boundary, and $\dot{S}_{\text{gen}}$ is the rate of internal generation of entropy within the system. For the closed, isothermal system represented in Figure 2.1, the entropy balance reduces to:

$$\frac{dS}{dt} = \dot{S}_{\text{gen}} \geq 0.$$  \hspace{1cm} (2.1-2)

From the second law, entropy must increase during the approach to equilibrium. Thus, the entropy is a maximum at equilibrium. Considering the entropy as a function of internal energy, volume, and moles, the change in entropy of subsystem I is:

$$dS^I = \left(\frac{\partial S^I}{\partial U^I}\right)_{v^I,N^I} dU^I + \left(\frac{\partial S^I}{\partial V^I}\right)_{U^I,N^I} dV^I + \left(\frac{\partial S^I}{\partial N^I}\right)_{U^I,V^I} dN^I$$ \hspace{1cm} (2.1-3)

$$dS^I = \frac{1}{T^I} dU^I + \frac{P^I}{T^I} dV^I - \frac{1}{T^I} \sum_i \overline{G}_i^I dN_i^I$$ \hspace{1cm} (2.1-4)

where $\overline{G}$ is the partial molar free energy. An analogous equation can be written for subsystem II. The total internal energy, volume, and moles are constant for this closed system. Thus, the equation for $dS$ of the system, which is the sum of $dS^I$ and $dS^{II}$ becomes:

$$dS = \left(\frac{1}{T^I} - \frac{1}{T^{II}}\right) dU^I + \left(\frac{P^I}{T^I} - \frac{P^{II}}{T^{II}}\right) dV^I - \sum_i \left(\frac{\overline{G}_i^I}{T^I} - \frac{\overline{G}_i^{II}}{T^{II}}\right) dN_i^I$$ \hspace{1cm} (2.1-5)
When entropy is at its maximum, \( dS \) equals zero. Thus, at equilibrium \( T^I = T^{II} \), \( P^I = P^{II} \), and \( \bar{G}_i^I = \bar{G}_i^{II} \), \( \mu_i^I = \mu_i^{II} \) for each species \( i \). During diffusion in a constant temperature, constant pressure system, the system is approaching the uniform chemical potential equilibrium position.

The gradient in chemical potential can be envisioned as the driving force for diffusion using a physical analogy. When 1 mol of solute is shifted from a region where its chemical potential is \( \mu(1) \) to where it is \( \mu(2) \) the amount of work required is 
\[
w = \mu(2) - \mu(1).
\]
If the chemical potential depends on the position \( x \) in the system, then the amount of work involved in transferring 1 mol of material from \( x \) to \( x + dx \) is:
\[
dw = \mu(x + dx) - \mu(x) = \left[ \mu(x) + (d\mu / dx)dx \right] - \mu(x) = (d\mu / dx)dx
\]
(2.1-6)
The amount of work required to shift an object through a distance \( dx \) against a force \( F \) is:
\[
dw = -Fdx
\]
(2.1-7)
Comparing equations (2.1-6) and (2.1-7), it can be seen that the gradient of chemical potential acts like a force. Although there is not an actual force pushing molecules, the second law of thermodynamics verifies that molecules will proceed toward maximum entropy and uniform chemical potential.

An alternative diffusion coefficient based on gradient in chemical potential may describe diffusion more accurately than Fick’s Laws, which indicate that the flux of a diffusing component is proportional to the concentration gradient. If the gradient in chemical potential drives the diffusive flux corresponding with molecular flow, it is expected that the molecular velocity, \( u_i \), will be proportional to the gradient in chemical potential.
\[
\mu_i = -\frac{d\mu_i}{dz}
\]  \hspace{1cm} (2.1-8)

where \(f\) is a friction coefficient. From the definition of fugacity, \(f_u\), the chemical potential of an ideal gas species \(i\) at a pressure and composition different than the standard state, defined as composition \(x_i^0\) and 1 bar pressure, can be expressed as:

\[
\mu_i(T, P, x) = \mu_i^0(T, P = 1\text{bar}, x_i^0) + \left[\mu_i(T, P, x) - \mu_i^0(T, P = 1\text{bar}, x_i^0)\right]
\]  \hspace{1cm} (2.1-9)

\[
\mu_i(T, P, x) = \mu_i^0(T, P = 1\text{bar}, x_i^0) + RT \ln \left(\frac{f_u(T, P, x)}{f_u^0(T, P = 1\text{bar}, x_i^0)}\right)
\]  \hspace{1cm} (2.1-10)

\[
\mu_i = \mu_i^0 + RT \ln a_i
\]  \hspace{1cm} (2.1-11)

where \(a\) is the activity. Taking the derivative of equation (2.1-11) with respect to \(z\) yields:

\[
\frac{d\mu_i}{dz} = \frac{RT \ln a_i}{dz}
\]  \hspace{1cm} (2.1-12)

Since

\[
c_i = \frac{dc_i}{d \ln c_i},
\]

and by combining equation (2.1-12) with equation (2.1-8), the expression for the flux becomes:

\[
J_i = u_i c_i = -\frac{RT}{f} \frac{d \ln a_i}{d \ln c_i}\left(\frac{dc_i}{dz}\right)
\]  \hspace{1cm} (2.1-13)

Comparison of equation (2.1-13) with Fick’s first law (1.4-3) results in an effective diffusion coefficient, \(D_0\), based on a chemical potential gradient.

\[
D_i = \frac{RT}{f} \frac{d \ln a_i}{d \ln c_i} = D_0 \frac{d \ln a_i}{d \ln c_i}
\]  \hspace{1cm} (2.1-14)

If the system is thermodynamically ideal as in the Henry’s law region, \(d \ln a_i/d \ln c_i\) equals one. Then, the Fickian and effective diffusion coefficients are equal.
Measurements taken for this thesis were performed at atmospheric pressure in the Henry’s law region. Therefore, the effective diffusivity equals the Fickian diffusivity for results reported in this thesis.

2.2 Theoretical Basis of Diffusion Coefficient Correlations

Several theoretical models describing diffusion correlate fundamental physical properties, such as viscosity, with diffusion coefficients. Hydrodynamic theory describes a molecule moving with very low Reynolds number at constant velocity through a continuous liquid. This theory states that the diffusion coefficient is proportional to a friction factor dependent on viscosity and solute molecular diameter. Eyring’s theory of absolute reaction rates describes a minimum potential energy equal to the solvent’s heat of vaporization required for a solvent molecule to form a vacant hole where the solute can enter. Eyring’s theory leads to an equation for the diffusion coefficient similar to hydrodynamic theory, which can be related to results reported in this thesis. Since ILs do not evaporate, the form of Eyring’s equation, which includes the heat of vaporization will not be evaluated. Kinetic theory describes diffusion through statistical mechanics. Equations based on diffusion theory, which predict diffusion coefficients include Stokes-Einstein and Eyring’s equation.

2.2.1 Hydrodynamic theories

Hydrodynamic theories can adequately describe a molecule moving through a fluid. A mass balance on fluid moving through a control volume having fixed position and shape produces the continuity equation (2.2-3), which can be applied to the fluid that the molecule moves through.
Accumulation in Rate of mass change
\[ \left( \text{control volume} \right) = \left( \text{mass change} \right) \] (2.2-1)

\[ \int_{V} \frac{\partial \rho'}{\partial t'} dV' = -\int_{S} \rho' u' ndS' = -\int_{V} \nabla' (\rho' u') dV' \] (2.2-2)

where \( \rho \) is the fluid density, \( t \) is time, \( V \) is volume, \( u \) is the fluid velocity, \( n \) is the unit vector normal to the surface, \( S \), \( \nabla \) is the differential operator, and the (') symbol denotes dimensional variables. Rearranging yields:

\[ \frac{\partial \rho'}{\partial t'} + \nabla' (\rho' u') = 0 \] (2.2-3)

For an incompressible fluid, the continuity equation reduces to:

\[ \nabla' u' = 0 \] (2.2-4)

An energy and momentum balance on a Newtonian, incompressible, isothermal fluid leads to the Navier-Stokes equation.

\[ \rho \left( \frac{\partial u'}{\partial t} + u' \nabla' u' \right) = -\nabla' p' + \eta \nabla'' u' \] (2.2-5)

where \( \nabla' p' \) is the gradient of the dynamic pressure and \( \eta \) is the fluid viscosity. The Navier-Stokes equation is most simply evaluated in dimensionless form using the following dimensionless variables.

\[ u = \frac{u'}{u_c}, \quad t = \frac{t'}{t_c}, \quad \nabla = \nabla' l_c, \quad p = \frac{p'}{\eta u_c l_c}, \quad R_e = \frac{\rho u_c l_c}{\eta}, \quad S = \frac{t_c}{l_c / u_c} \]

where the subscript, \( c \), denotes the critical dimension, \( R_e \) is the Reynolds number, and \( S \) is the Strouhal number. When the dimensionless variables are substituted into (2.2-4) and (2.2-5), the dimensionless equations become:

\[ \nabla \cdot u = 0 \] (2.2-6)
The hydrodynamic theories that predict diffusion coefficients assume steady motion of a molecule in a fluid, so that $S$ equals one. The Reynolds number is assumed to be much less than one, which means that the velocity or length scales are very small or the kinematic viscosity is very large. When the Reynolds number is very small, the acceleration or inertial terms on the left side of (2.2-5) are negligible compared to the pressure gradient and viscous terms on the right side. The reduced equations are called creeping flow equations (2.2-8) and (2.2-9).

\[ \nabla \cdot u = 0 \]  \hspace{1cm} (2.2-8)

\[ \nabla^2 u = \nabla p \]  \hspace{1cm} (2.2-9)

The Stokes-Einstein equation, the most commonly used correlation for estimating diffusion coefficients in liquids and the basis of many semi-empirical correlations, is partially derived from the creeping flow equations. The Stokes-Einstein equation is:

\[ D = \frac{k_B T}{6 \pi \eta a} \]  \hspace{1cm} (2.2-10)

where $D$ is the diffusion coefficient (cm$^2$/s), $k_B$ is the Boltzmann constant equal to $1.38 \times 10^{-16}$ g*cm$^2$/((s*°K)), $\eta$ is the solvent viscosity (g/(cm*s)), and $a$ is the solute radius (cm). Equation (2.2-10) is representative of a rigid, spherical solute molecule moving slowly through a continuum of solvent, because the mass, energy, and momentum balances in the creeping flow equations are identical whether the molecule is moving through a still fluid or the fluid is moving past a still molecule.
The model applied to solving the creeping flow equations leading to the Stokes-Einstein equation is shown in Figure 2.2.

Figure 2.2 Steady solvent flow past spherical molecule

The critical variables are:

\[ u_c = u_\infty, \quad l_c = a, \quad p_c = \frac{\eta u_c}{a} \]

The continuity equation written in terms of spherical coordinates is:

\[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 u_r \right) + \frac{1}{r \sin \Theta} \frac{\partial}{\partial \Theta} \left( \sin \Theta u_\Theta \right) = 0 \]  \hspace{1cm} (2.2-11)

The radial Navier-Stokes equation is:

\[ \frac{1}{r^2} \left[ \frac{\partial}{\partial r} \left( r^2 \frac{\partial u_r}{\partial r} \right) + \frac{1}{\sin \Theta} \frac{\partial}{\partial \Theta} \left( \sin \Theta \frac{\partial u_\Theta}{\partial \Theta} \right) - 2u_r - 2 \frac{\partial u_\Theta}{\partial \Theta} - 2u_\Theta \cot \Theta \right] - \frac{\partial p}{\partial r} = 0 \]  \hspace{1cm} (2.2-12)

The angular Navier-Stokes equation is:

\[ \frac{1}{r^2} \left[ \frac{\partial}{\partial r} \left( r^2 \frac{\partial u_\Theta}{\partial r} \right) + \frac{1}{\sin \Theta} \frac{\partial}{\partial \Theta} \left( \sin \Theta \frac{\partial u_\Theta}{\partial \Theta} \right) + 2 \frac{\partial u_r}{\partial \Theta} - \frac{u_\Theta}{\sin^2 \Theta} \right] - \frac{1}{r} \frac{\partial p}{\partial \Theta} = 0 \]  \hspace{1cm} (2.2-13)

The Stokes-Einstein equation assumes no slip at the sphere’s surface, and the boundary conditions are:

\[ u_r \big|_{r=1} = u_\Theta \big|_{r=1} = 0, \quad u_r \big|_{r=\infty} = \cos \Theta, \quad u_\Theta \big|_{r=\infty} = -\sin \Theta \]
When these equations are evaluated to solve for the drag force on the sphere, the result is $6\pi\eta a u_\infty$, which is Stoke’s Law. The derivation of Stoke’s Law is provided in Appendix A. Since these equations model flow of a sphere through fluid, Stokes law is more accurate for systems where large solute molecules, typically greater than five times the radius of the solvent molecules, diffuse into small solvent molecules. Errors are especially large in highly viscous and highly dense solvents\(^{39}\).

The Stokes-Einstein equation is further derived by assuming that the drag force, $F$, on an object moving through a fluid is proportional to a friction coefficient, $f$, and the object’s velocity.

$$F = fu_i$$  \hspace{1cm} (2.2-14)

where $f$ is the friction factor equivalent to $6\pi\eta a$. Einstein estimated that the drag force on the molecule is the negative of its chemical potential gradient.

$$\frac{-d\mu_i}{dz} = 6\pi\eta a u_i$$  \hspace{1cm} (2.2-15)

If the concentration of solute $i$ is dilute, the activity is essentially the concentration, $c_i$, and equation (2.1-12) becomes:

$$\frac{d\mu_i}{dz} = \frac{RT}{c_i} \frac{dc_i}{dz}$$  \hspace{1cm} (2.2-16)

Divide equation (2.2-16) by Avogadro’s number, $A_n$, to determine the chemical potential gradient for one molecule or ion, where $R/A_n$ equals Boltzmann’s constant, $k_B$.

$$\frac{d\mu_i}{dz} = k_B T \frac{dc_i}{c_i} \frac{dz}{dz}$$  \hspace{1cm} (2.2-17)

Combining equations (2.2-17) and (2.2-15) yields:
\[ u_i = -\frac{k_b T}{c_i 6\pi \eta a} \frac{dc_i}{dz} \]  

(2.2-18)

Then, the flux can be approximated by:

\[ J_i = c_i u_i = -\frac{k_b T}{6\pi \eta a} \frac{dc}{dz} \]  

(2.2-19)

Comparison of equation (2.2-19) with Fick’s first law (1.4-3) yields the Stokes-Einstein equation (2.2-10).

Several adaptations have been made to the Stokes-Einstein equation to account for different solute shapes and smaller solute molecules. Diffusion coefficients of macromolecules, such as proteins diffusing in aqueous solutions, more accurately follow a modified Stokes-Einstein equation where the radius term, \( a \), is replaced with a more geometrically accurate term for a prolate (football shaped) ellipsoid or oblate (disk-shaped) ellipsoid. Specifically, the term for the radius, \( a \), is replaced with \( \frac{7}{6} \):

For a prolate ellipsoid:

\[ \frac{\left( b^2 - c^2 \right)^{\frac{1}{2}}}{\ln \left[ \frac{b}{c} + \left( b^2 - c^2 \right)^{\frac{1}{2}} \right]} \]  

(2.2-20)

For an oblate ellipsoid:

\[ \tan^{-1} \left[ \frac{\left( b^2 - c^2 \right)^{\frac{1}{2}}}{c^2} \right] \]  

(2.2-21)

where \( b \) and \( c \) are the major and minor axes of the ellipsoid, respectively. Another modification of the Stokes-Einstein equation assumes that molecules slip past each other as may be the case where the solute and solvent molecules have similar size. The resulting drag force on a smaller spherical molecule was determined to be \( 4\pi \eta u_c \) rather than \( 6\pi \eta u_c \)[Cussler, 1997 #45].
2.2.2 Theory of Absolute Reaction Rates

Eyring’s theory of absolute reaction rates is based on statistical mechanics and the theory that an activation energy is required for molecules to react, slide past each other when applied to viscosity, or move around each other when applied to diffusion. The viscosity model shown in Figure 2.3 is comprised of two layers of molecules in a liquid, at a distance $\lambda_1$ apart.

![Figure 2.3 Distances between molecules]

One layer slides past the other under the influence of an applied force, $f$, per square centimeter. The viscosity can be defined as:

$$\eta = \frac{f\lambda_1}{\Delta u} \quad [\text{mass distance}^{-1} \text{ time}^{-1}]$$

(2.2-22)

where $\Delta u$ is the difference in the velocity of the two layers. When one molecule jumps from one equilibrium position to the next, it must pass over a potential energy barrier. It is assumed that the number of times a molecule passes over the potential energy barrier per second when one layer of molecules is moving past another follows an equation having the same form as from Eyring’s reaction rate theory. Eyring’s reaction rate theory states that the specific reaction rate constant, $k_r$, is equal to:
\[ \frac{k_r}{F} = \frac{k_B T}{h} \cdot \frac{F_a}{F_A F_B} e^{-E_0 / RT} \quad [\text{time}^{-1}] \]  

(2.2-23)

where \( k_B \) is Boltzmann’s constant, \( T \) is absolute temperature, \( h \) is Planck’s constant, \( F_a \) is the statistical mechanic partition function per unit volume for the activated complex without the contribution due to translational motion of the molecule, \( F_A \) and \( F_B \) are the partition functions per unit volume of the reactants, and \( E_0 \) is the activation energy required for a mole of molecules to pass the barrier. The number of times a molecule passes over the potential energy barrier per second in viscous flow is:

\[ \frac{k_n}{F} = \frac{k_B T}{h} \cdot \frac{F_a}{F} e^{-E_0 / k_B T} \quad [\text{time}^{-1}] \]  

(2.2-24)

where \( F_a \) and \( F \) are the partition functions per unit volume of the molecule in the activated and initial states, respectively, and \( E_0 \) is the activation energy of the molecule. \( F_a \) excludes the contribution of the degree of translational freedom normal to the barrier. It is assumed that the potential-energy barrier is symmetrical as shown in Figure 2.4, so the distance between the initial equilibrium position and activated state is \( 0.5\lambda \), i.e. half the distance between the initial and final positions of the molecule.
The applied force acting on a single molecule in the direction of motion is $f \lambda_2 \lambda_3$ because $\lambda_2 \lambda_3$ is the effective area per molecule. Thus, the energy that the moving molecule acquires when it has reached the top of the potential energy barrier is $f \lambda_2 \lambda_3 \times 0.5 \lambda$. Also, the force causing the liquid to flow reduces the height of the energy barrier in the forward direction by $0.5 f \lambda_2 \lambda_3$. Since the height of the barrier is altered by $0.5 f \lambda_2 \lambda_3$ when the force causing the liquid to flow is applied, the specific rate of flow in the forward direction is:

$$k_{eff} = \frac{kT}{h} \cdot \frac{F}{F} \cdot e^{\frac{(e_0 - 0.5 f \lambda_2 \lambda_3)}{kT}} \quad [\text{second}^{-1}]$$

(2.2-25) can be simplified by expressing the first part as one variable, $c_T$.

$$k_{eff} = c_T e^{\frac{0.5 f \lambda_2 \lambda_3}{kT}} \quad [\text{second}^{-1}]$$

(2.2-26)

Likewise, the specific rate in the backward direction is:

$$k_{ebp} = c_T e^{\frac{0.5 f \lambda_2 \lambda_3}{kT}} \quad [\text{second}^{-1}]$$

(2.2-27)
The net rate of molecular flow, $\Delta u$, in the forward direction as a result of the force is equal to $(k_f - k_b) \lambda$.

$$\Delta u = \lambda c_f \left( e^{0.5 f / \lambda^2 \lambda_3 / kT} - e^{-0.5 f / \lambda^2 \lambda_3 / kT} \right) \text{[cm s}^{-1}] \quad (2.2-28)$$

Combining (2.2-28) and (2.2-22) yields:

$$\eta = \frac{\lambda_f f}{\lambda c_f \left( e^{0.5 f / \lambda^2 \lambda_3 / kT} - e^{-0.5 f / \lambda^2 \lambda_3 / kT} \right)} \text{[g cm}^{-1} \text{s}^{-1}] \quad (2.2-29)$$

It is assumed that viscosity is not very high, so $f$ must be small. Also when the molecular distances are small, $k_b T$ is much greater than $f / \lambda^2 \lambda_3$. Therefore, when the exponentials are expanded in series, only the first terms are significant. The resulting equation is:

$$\eta = \frac{\lambda_f k_b T}{\lambda^2 \lambda_2 \lambda_3 c_f} \text{[g cm}^{-1} \text{s}^{-1}] \quad (2.2-30)$$

Eyring’s theory of absolute reaction rates for diffusion is based on a model of one solute molecule “jumping” around a solvent molecule into the open position of a solute molecule that moved previously. The theory is only applicable to dilute, ideal solutions. Eyring postulated that the concentrations in moles per cubic centimeter of solute molecules in initial and final states of diffusion are $c$ and $c + \lambda dc/dz$, where $\lambda$ is the distance between successive equilibrium positions. Since the concentration decreases in the direction of diffusion, $dc/dz$ is negative and $c + \lambda dc/dz$ is less than $c$.

The number of molecules moving in the forward direction through a cross section of 1 square centimeter is:

$$v_f = A_n c \lambda k_d \text{[molecules cm}^{-2} \text{s}^{-1}] \quad (2.2-31)$$
where \( A_n \) is Avogadro’s number and \( k_d \) is the specific reaction rate for diffusion, i.e., the number of times a molecule moves from one position to the next per second.

Similarly, the rate of movement in the backward direction is:

\[
v_b = A_n \left( c + \lambda \frac{dc}{dz} \right) \lambda k_d \quad \text{[molecules cm}\textsuperscript{-2}s\textsuperscript{-1}] \quad (2.2-32)
\]

The resultant flow, \( v_b - v_f \) is:

\[
v = A_n \lambda^2 k_d \frac{dc}{dz} \quad \text{[molecules cm}\textsuperscript{-2}s\textsuperscript{-1}] \quad (2.2-33)
\]

Fick’s first law can be rearranged, so that the resultant flow per square centimeter per second is:

\[
v = -DA_n \frac{dc}{dz} \quad \text{[molecules cm}\textsuperscript{-2}s\textsuperscript{-1}] \quad (2.2-34)
\]

By comparing (2.2-33) and (2.2-34), it can be seen that

\[
D = \frac{\lambda \lambda_2}{\lambda_3 \eta} k_T \quad \text{[molecules cm}\textsuperscript{-2}s\textsuperscript{-1}] \quad (2.2-35)
\]

Eyring’s diffusion coefficient correlation is comparable to the diffusion coefficient calculated using the Stokes-Einstein equation if it is assumed that large solute molecules diffuse in small solvent molecules as shown in Figure 2.5. When a large molecule diffuses into a solvent consisting of small molecules, it is likely that movement of the solvent molecules will be the rate-determining step, because a large amount of work is necessary to make space for the large solute molecule. Thus, the movement of solvent molecules determines the rate of the solute’s diffusion. Eyring stated in his description of the model:
It is evident, therefore, that the solvent molecule must move through a distance of at least $\pi r$, where $r$ is the radius of the large diffusing molecule in order that the latter may move from right to left a distance of approximately $\lambda$, where $\lambda$ is the distance between successive equilibrium positions of the solvent molecule. If the solute molecule were small, however, e.g., $B'$, it would move from the right to left a distance of approximately $\lambda$ in each jump of the solvent molecule and so it follows that:

$$D_l = D_s \frac{\lambda}{\alpha \pi r} \quad \text{[cm}^2 \text{s}^{-1}]$$

(2.2-36)

where $D_l$ and $D_s$ are the diffusion coefficients of the large and small solute molecules, respectively, and $\alpha$ is a factor to allow for the solvent molecule traveling a distance of at least $\pi r$.

![Diagram of diffusion](image)

Figure 2.5 Diffusion of large molecule (B) due to movement of small solvent molecule (A)

The interpretation of this theory by the author of this thesis is that Eyring assumes the rate of diffusion is inversely proportional to approximately half of the circumference of the solute molecule, which he calls the distance traveled by the solvent. Then, the radius of the small solute named $B'$ must be $\lambda/\pi$. The model is questionable, but the resulting equations are frequently cited and adopted in other diffusion coefficient equations. The value of $D_s$ from (2.2-35) may be put in the form of:
\[ D_1 = \frac{kT}{\lambda \eta} \quad [\text{cm}^2 \text{ s}^{-1}] \quad (2.2-37) \]

Then, (2.2-36) becomes:

\[ D_i = \frac{kT}{a \pi \eta} \quad [\text{cm}^2 \text{ s}^{-1}] \quad (2.2-38) \]

Eyring explains that the factor of \( a \) would equal 6 in Stokes-Einstein, which appears probable for diffusion of large molecules in a solvent of small molecules. Eyring estimated that:

\[ \lambda = x_1 \left( \frac{V_1}{A_n} \right)^{1/3} + x_2 \left( \frac{V_2}{A_n} \right)^{1/3} \quad [\text{cm}] \quad (2.2-39) \]

where \( V \) is the molar volume and \( x \) is the equilibrium mole fraction of each component. Eyring continued to develop an expression for the diffusion coefficient by substituting a correlation including \( c_T \) for the viscosity, which is dependent upon temperature and the heat of vaporization. The correlation which uses heat of vaporization will not be evaluated as part of this thesis, because it cannot be directly used to calculate diffusion coefficients, unlike other correlations. Since ionic liquids do not evaporate, they do not have a heat of vaporization according to the normal definition.

### 2.2.3 Kinetic Theory

Early kinetic theories described low pressure, gaseous systems having molecules with mean free paths much larger than their diameters. Kinetic theory is based on classical mechanics with symmetrically spherical molecules “encountering” each other, not quite colliding, then repelling away from each other. Examples of kinetic theory potential energy models include the Lennard-Jones 12,6 model, the
Sutherland model, and the Exp-6 potential\textsuperscript{32}. Diffusion coefficient correlations derived from these models are well-developed for gaseous systems\textsuperscript{39,89}. Semi-empirical modifications of the original, gaseous, kinetic theory diffusion coefficient models have been used to calculate diffusion coefficients of gases into liquids\textsuperscript{89}. However, not enough data on ionic liquids is available to determine the model parameters, such as collision integrals. One of the criteria for selecting an appropriate model to predict diffusion coefficients of gases into ionic liquids was that the model parameters be readily available and easier to measure than diffusion coefficients. Therefore, other available models for predicting diffusion coefficients (i.e. Stokes-Einstein and empirical models) were evaluated in more detail for this thesis than kinetic theory models.

2.3 Empirical Correlations

Hildebrand\textsuperscript{52} explained the difference between transport theory in liquids and reality when he wrote:

\textit{The fact that a liquid can be so fluid although expanded so little over its intrinsic volume is evidence of the unreality of some of the concepts that have been used by writers on transport theory; concepts such as “trajectories” between separable “collisions,” some of which are “hard” and others “soft,” and “cages” in which a molecule is “oscillating” with a definite frequency while awaiting an access of “activation energy” sufficient to enable it to break through a “barrier” into a “hole” awaiting it at a distance of exactly one diameter.}

Several of the assumptions made in the theoretical models do not match physical properties of the system for gases diffusing into liquids. Assumptions in Stokes-Einstein do not accurately depict systems of gaseous solutes in dense liquids because the molecular diameter of the solute is much smaller than the solvent. When the solute is smaller than the solvent, Eyring’s theory suggests that the diffusion
coefficient would be higher than predicted by Stokes-Einstein because less energy is required for the solvent to vacate spaces that would fit smaller solute molecules. Also, the assumption of very low Reynolds number made in the Stokes-Einstein equation is less accurate for high-density solvents, such as ionic liquids. Assumptions made in Eyring’s theory of reaction rates may be valid for predicting self-diffusion coefficients, but are presumptuous for application to mutual diffusion coefficients. The model of the liquefied state also appears oversimplified.

Numerous empirical correlations have been developed for predicting diffusion coefficients of gases into various types of liquids with improved accuracy over theoretical models\textsuperscript{39, 53}. A very basic empirical correlation\textsuperscript{51} was applied to data measured as part of this thesis:

\[ D = A\eta^B \]  

(2.3-1)

where \( A \) and \( B \) are empirical coefficients dependent on the solute composition, \( D \) is the binary diffusion coefficient and \( \eta \) is the solvent viscosity. This correlation was developed from a set of eleven solutes diffusing into various solvents. This correlation was selected for comparison with experimental data because data for both parameters, experimental diffusion coefficients and viscosities, were available. Also, Hayduk and Cheng suggested that their correlation may be more accurate for predicting diffusion coefficients in viscous solvents because previously published empirical diffusion coefficient correlations tended to be inaccurate for viscous liquids\textsuperscript{51, 54}. Alternatively to the majority of empirical correlations developed from low viscosity solvents, (2.3-1) does not require that the intercept on a graph of \( D \) versus \( 1/\eta \) be equal to zero. Therefore, this correlation fits the data reported for
diffusion of CO$_2$ into the viscous ILs better than other empirical correlations. It is expected that the intercept previously mentioned would not equal zero exactly, but would equal a smaller diffusion coefficient. It is expected that as the viscosity increases, the liquid becomes more solid-like and consequently the diffusion coefficient would approach a more solid-like value. It is known that diffusion coefficients of gases into solids have values greater than zero.

Hiss and Cussler$^{54}$ applied (2.3-1) to diffusion coefficients measured in viscous liquids with moderate molecular weight. They reported that the average $B$ value was $-2/3$ for “electrolyte and nonelectrolyte solutes” diffusing into solvents, including water, alcohols and hydrocarbons, having viscosities of 5 to greater than 5000 cP. They set their $A$ values for each solute-solvent system equal to the intercept of the $D$ vs. $\eta$ graph when each solute-solvent system was measured at various temperatures. Gas solutes were not reported as being included in the solutes evaluated. For diffusion of large solutes into small solvents having viscosity less than or equal to 1 cP, the value for $B$ reported was about $-1$. Hiss and Cussler admit that there is a large amount of scatter in the data, and no quantitative information is given regarding the wellness of the fit. They state that the $-2/3$ value should not be applied to polymers or gels.

The results section of this thesis will compare Hayduk and Cheng’s$^{51}$ reported diffusion coefficients of CO$_2$ into various solvents with data measured as part of this thesis. Hayduk and Cheng found that the slope for CO$_2$ diffusing into various solvents with viscosities between 0.3 and 4 cP was $B = -0.44$. It appears from their
The graph of log $D$ vs. log $\eta$ for CO$_2$ diffusing into various solvents that the diffusion coefficient equals $3.5 \times 10^{-5}$ cm$^2$/s when the viscosity is 1 cP.

The data reported for this thesis was also compared to the empirical Wilke-Chang$^{95}$ correlation:

$$D = 7.4 \times 10^{-8} \frac{(xM)^{1/2}T}{\eta V^{0.6}}$$

(2.3-2)

where $x$ is an empirical association factor, $M$ is the molecular weight of the solvent, $T$ is the absolute temperature, $\eta$ is the viscosity of the solvent, $V$ is the solute molar volume at the boiling point estimated by the atomic contributions of LeBas. Wilke and Chang compared their correlation with the Stokes-Einstein equation. On the assumption that molecules are spherical with a radius equal to $(3V/4\pi A_n)^{1/3}$, the Stokes-Einstein equation was rewritten as:

$$\frac{T}{D \eta} = 1.004 \times 10^7 V^{1/3}$$

They designated the term $T/D\eta$ as $F$, and found that over the middle range of molar volumes $F$ was proportional to $V^{0.6}$ rather than the $1/3$ power as indicated by Stokes-Einstein. They found that for large solute molar volumes, around 400 cm$^3$/gmol, the $1/3$ power term intersected with $V^{0.6}$. Wilke and Cheng found that molecular weight correlated with the data most successfully when compared with other variables such as heat of vaporization. They found an association parameter was necessary for hydrogen-bonding solvents. The association parameters for nonassociating solvents such as heptane equals one, while the association parameter for solvents such as water, methanol, and ethanol equal 2.6, 1.9, and 1.5, respectively. Analysis of their
data of 155 points among 123 solute-solvent systems showed that (2.3-2) has an average deviation of about 6%.

2.4 Thermodynamics of Octanol-Water Partitioning

The following sections describe thermodynamic theory of the second property measured in this study, which is the octanol-water partition coefficient ($K_{OW}$). The $K_{OW}$ was derived from the fundamental equilibrium relationship, and enthalpic and entropic contributions to the $K_{OW}$ were evaluated.

2.4.1 $K_{OW}$ Derived from Equilibrium Relationship

The difference in chemical potential drives the partitioning process so that the IL molecules originally in the octanol-rich phase, as will be explained in the experimental method section, move to the water-rich phase having lower chemical potential until the IL’s fugacities in the octanol-rich phase and water-rich phase are equal. The equilibrium distribution of the IL between the octanol-rich phase and the water-rich phase is determined from the equilibrium equation:

\[
\overline{f}_{il}^O(T, P, x^O) = \overline{f}_{iw}^w(T, P, x^W)
\]

(2.4-1)

where $\overline{f}$ is the partial molar fugacity in the ($O$) octanol-rich phase and the ($W$) water-rich phase. From the definition of the activity coefficient, $\gamma$, the partial molar fugacity is written:

\[
\overline{f}_{il}^O(T, P, x) = x_{il}^O \gamma_{il}^O(T, P, x) f_{il}^O(T, P)
\]

(2.4-2)

Since temperature and pressure are equal in both phases, the pure component fugacities are equal in both phases.

\[
f_{il}^O(T, P) = f_{il}^w(T, P)
\]

(2.4-3)
Substitution into (2.4-1) yields:

\[ x_{ii}^O,\gamma_{il}^O(T, P, \chi^O) = x_{ii}^W,\gamma_{il}^W(T, P, \chi^W) \]  \hspace{1cm} (2.4-4)

Rearranging yields:

\[ \frac{x_{ii}^O}{x_{ii}^W} = \frac{\gamma_{il}^W(T, P, \chi^W)}{\gamma_{il}^O(T, P, \chi^O)} \]  \hspace{1cm} (2.4-5)

The \( K_{OW} \) is defined as the equilibrium ratio of the molar concentrations of solute present at infinite dilution, which has partitioned into the octanol and water phases.

\[ K_{OW} = \frac{C_{il}^O}{C_{il}^W} \]  \hspace{1cm} (1.5-1)

The octanol-rich phase contains approximately 2.3 mol/L octanol, 6.07 mol/L water and a relatively small concentration of IL. Thus, the molar concentration of IL in the octanol-rich phase is approximately 8.37 \( x_{ii}^O \). A negligible amount of octanol dissolves in the water-rich phase, so the molar density of the water-rich phase is approximately equal to the molar density of water, which is 55.5 mol/L. Therefore, the expression for the \( K_{OW} \) in terms of mole fractions or infinite dilution activity coefficients, \( \gamma^\infty \), is:

\[ K_{OW} = \frac{8.37x_{ii}^O}{55.5x_{ii}^W} = 0.151 \frac{\gamma_{il}^W}{\gamma_{il}^O} \]  \hspace{1cm} (2.4-6)

The activity coefficient is a measure of the additional free energy that the IL is carrying in a nonideal mixture as compared with the reference state, which is considered to be the pure liquid compound. Thus, the \( K_{OW} \) indicates the energy difference due to the nonideality of the solutions of IL in the octanol and water phases. The difference in the partial molar excess free energies of IL dissolving in the octanol-rich phase and the water-rich phase is:
\[
\Delta g_{IL}^{ex,OW} = RT \ln \gamma_{IL}^{ex} - RT \ln \gamma_{IL}^{exW} \tag{2.4-7}
\]

Therefore, by comparing (2.4-6) and (2.4-7) it can be seen that:

\[
K_{OW} = \exp\left(\frac{-\Delta g_{IL}^{ex,OW}}{RT}\right) \tag{2.4-8}
\]

### 2.4.2 Enthalpic and Entropic Contributions to Solvation

Excess free energy, and in this case the difference in excess free energy, contains both enthalpic and entropic contributions.

\[
\Delta g_{IL}^{ex,OW} = \Delta h_{IL}^{ex,OW} - T \Delta s_{IL}^{ex,OW} \tag{2.4-9}
\]

Enthalpic contributions to excess free energy of solution reflect the changes in interactions between solute-solute, solute-solvent, and solvent-solvent molecules when the solute dissolves. The excess enthalpy of solution can be illustrated as a sum of enthalpic contributions\textsuperscript{82}:

\[
h_{IL}^{ex,OW} = \Delta h_1 + \Delta h_2 + \Delta h_3 \tag{2.4-10}
\]

\(\Delta h_1\), which is greater than zero, can be pictured as the energy required to overcome the solute-solute interactions and separate a solute molecule from the bulk phase so that it can be inserted into the solvent. \(\Delta h_2\), also greater than zero, is the energy required to overcome solvent-solvent interactions, so that a cavity is created in the solvent molecules that can accommodate the solute. \(\Delta h_3\) is less than zero because it is the energy dissipated when the solute molecule interacts with the solvent molecules. As depicted by this illustration, molecular size of the solute and strength of molecular interactions affects the enthalpic contribution to the excess free energy of solution.

The total excess entropy change can be considered a sum of two types of contributions\textsuperscript{82}. The first contribution is an entropy of cavity formation. The second
is an enhanced randomness due to mixing dissimilar molecules. Thus, for larger differences in the size between the solute and solvent molecules the excess entropy of solution will be more negative. Also, when molecules with long, nonpolar chains dissolve in water it is expected that the water molecules surrounding the nonpolar structural parts would cause the solute to lose translational and flexing freedoms. For these nonpolar molecules, the entropy of solution would be less negative. The entropic contribution explains why a large amount of water dissolves in octanol, but only a small amount of octanol dissolves in water. The free energy of solution for octanol dissolving into water is 23.1 kJ/mol. The enthalpic contribution is 0.5 kJ/mol, and the entropic contribution (-TΔs) is 22.6 kJ/mol.⁸²
CHAPTER 3

EXPERIMENTAL METHOD FOR DIFFUSION COEFFICIENT MEASUREMENT

3.1 Methods of Measuring Diffusion Coefficients of Gases into Liquids

The most widely used techniques to determine the diffusion coefficients of gases into liquids measure the mass of gas transferred into or out of the liquid phase, or the concentration gradients in a diffusing system. Buzzeo et. al. measured the diffusion coefficient of CO$_2$ into [N$_{6222}$][Tf$_2$N] using cyclic voltammetry at a gold microdisk electrode capable of detecting CO$_2$. Mixtures of CO$_2$, oxygen and nitrogen were introduced to an electrochemical cell in increasing ratios of CO$_2$ approximately every 30 minutes when equilibrium was approached. Each time equilibrium was approached, the cell was scanned at a rate of approximately 1 volt/second while the current was recorded. The cell consisted of a temperature-controlled enclosure around the gold electrode with a glass piece placed around the gold electrode’s circumference, which retained about 20 micrograms of IL on the electrode. A silver wire secured around the glass acted as a counter/reference electrode. The experimental cyclic voltammagrams, plots of current versus electrode potential, at each CO$_2$ concentration were fitted to theoretical voltammagrams by varying the diffusion coefficient. Theoretical voltammagrams followed an equation (3.1-1) derived from Fick’s second law and the Nernst equation:

\[ i = 4nF r_c D_0 c_0 f(\tau) \]  

(3.1-1)
At short times, $\tau < 1.44$

$$f(\tau) = 1 + 0.71835\tau^{-1/2} + 0.05626\tau^{-3/2} + 0.00646\tau^{-5/2}$$  \hspace{1cm} (3.1-2)$$

$$\tau = \frac{4D_0 t}{r_c^2}$$  \hspace{1cm} (3.1-3)$$

where $i$ is the time-dependent current, $n$ is the number of electrons transferred, $F$ is the Faraday constant, $r_c$ is the radius of the microdisk, $D_0$ is the diffusion coefficient of the electroactive species (CO$_2$), and $c_0$ is the bulk concentration of CO$_2$. The diffusion coefficient that resulted in the best fit to these equations was the diffusion coefficient reported. This method is advantageous for measuring diffusion coefficients quickly, within several hours, but the variability appears large. Diffusion coefficients for oxygen diffusing into [C$_2$ mim][Tf$_2$ N] measured by the same authors reported in separate papers$^{27, 28}$ differed by a factor of about three (2.5 x 10$^{-6}$ cm$^2$/s and 7.3 x 10$^{-6}$ cm$^2$/s).

The diaphragm cell technique uses a porous glass or metal diaphragm sealed horizontally in a cylinder separating a gaseous upper chamber from liquid solvent in the lower chamber. The gas diffuses through the diaphragm’s pores from the area of high concentration to low concentration. When the volume of gas and liquid on either side of the diaphragm is sufficiently large and is stirred by magnetic bars at the proper rate to keep the concentrations uniform, the transfer conditions across the diaphragm are steady state. In 1992, Littel et. al.$^{62}$ determined the diffusion coefficient of several gases, such as propene and CO$_2$ into low viscosity liquids, such as water and toluene, using a diaphragm cell by measuring the change in gas pressure with time during diffusion. Their reported diffusion coefficients corresponded well with diffusion coefficients measured using other techniques for diffusion of CO$_2$ into
toluene \((4.14 \times 10^{-9} \text{ m}^2/\text{s})\) using Littel's method vs. \(4.61 \times 10^{-9}, 4.6 \times 10^{-9}, 4.33 \times 10^{-9}\) and \(3.44 \times 10^{-9}\) by other methods) and diffusion of propene into water \((1.16 \times 10^{-9}\) using Littel’s method vs. \(1.1\) and \(0.68\) by other methods). The diaphragm cell technique requires calibration using a solute-solvent system with a known diffusion coefficient, so that a proportion factor dependent on the individual diaphragm properties, such as diffusion area and tortuosity of the pores, can be determined. Since the proportionality factor is also dependent on solvent viscosity, the calibration must be performed in a solvent with similar viscosity. Also, surface effects within the pores of the diaphragm may affect the rate of mass transfer. Data for diffusion coefficients of gases into viscous liquids similar to ILs is scarce\(^{54, 76}\). Consequently, the accuracy of reported diffusion coefficients using this method would be dependent upon the accuracy of the scarce data for highly viscous fluids from other laboratories.

Laminar liquid jets are commonly used to measure absorption of gases into liquids because they are simple in design, are stable and rapid\(^{53}\). Gas saturated with the liquid is added to a chamber that contains the vertically flowing laminar liquid jet. The diffusion coefficient can be calculated using the following equation:

\[
\nu_s \frac{\partial c}{\partial z} = \frac{\partial}{\partial x} \left( D_p \frac{\partial c}{\partial x} \right) \tag{3.1-4}
\]

with boundary conditions:

\[
c = c_{\text{sat}} \quad \text{at } x = 0, z > 0
\]

\[
c = c_0 \quad \text{at } x \to \infty
\]

\[
c = c_0 \quad \text{at } z = 0, x > 0
\]

The solution for the diffusion coefficient is:
\[ D = \frac{N^2}{16(c_{\text{sat}} - c_0)^2 qH} \]  

(3.1-5)

where \( c_0 \) is the starting concentration of gas in the liquid, \( c_{\text{sat}} \) is the saturation concentration of gas in the liquid, \( N \) is the total gas absorbed, \( q \) is the liquid flow rate, and \( H \) is the jet length. A typical flow rate is 300 to 470 grams/minute\(^4\). With care, data of 1% precision can be obtained for gaseous diffusion into liquids using this technique. This method was infeasible for measuring diffusion into ILs because a large amount of expensive IL would be required for each experiment.

Interferometric techniques typically use monochromatic light to illuminate a fine slit, which is focused by a lens through the diffusion boundary into a photographic plate. The measurements take place in an unsteady-state absorption process during which the concentration gradient is evaluated as a function of time. Interferometry is a delicate technique requiring expensive equipment and has not been widely used for gases dissolved in liquids, but can achieve high precision\(^5\).

It was determined that diffusion of gases into ionic liquids could most reliably be measured using a gravimetric technique. Gravimetric methods are commonly used for measuring diffusion of gases into solids\(^6,8\). This method can be implemented more accurately with ionic liquids than other liquids, because weight change caused by liquid evaporation does not occur with ILs unlike another type of liquid sample. In the gravimetric method, the weight of gas absorbed into the liquid is recorded over time to determine the diffusion coefficient. There are several advantages of the gravimetric method over techniques previously mentioned. This method produces diffusion coefficients with more precision than electrolytic techniques. The accuracy of measurements using the gravimetric technique does not rely on data from other
laboratories as with the diaphragm cell technique. The method is well established, unlike the pressure change method reported for the diaphragm cell technique in 1992, and interferometric techniques. The gravimetric technique uses a small sample, approximately 100 mg, compared with the laminar jet technique, an important factor because ILs are expensive. It is beneficial that measurement of gaseous concentration in the ILs are not required because accurate concentration measurement would be difficult. Gas chromatography, a common method used for measuring gaseous concentrations could not be used because ILs do not evaporate.

3.2 Materials

Bone dry carbon dioxide from Mittler Supply Inc. was used as the absorption gas. Ionic liquids selected for diffusion coefficient measurement were listed with their structures in Table 1.1. All the ILs were dried immediately prior to measuring the first diffusion coefficient of each IL according to standard protocol at greater than 50 degrees Celsius under vacuum for at least two days. Samples were stored in containers sealed with parafilm in a dry, enclosed atmosphere between sampling events.

\([\text{C}_4\text{mim}]\)[PF$_6$]: The 1-butyl-3-methyl imidazolium hexafluorophosphate was purchased from Sachem, Inc. and was purified by washing with water to remove any residual acid and by mixing with activated carbon to remove colored compounds. The \([\text{C}_4\text{mim}]\)[PF$_6$] from Sachem is reported to contain less than 3 ppm chloride. Measurements by our laboratory confirmed that the sample contained less than 10 ppm chloride. Immediately prior to the first diffusion measurements, the
[C₄mim][PF₆] sample was washed with water ten times to remove any degradation products.  

\[C₂mim][Tf₂N]\: 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C₂mim][Tf₂N]) was obtained from Covalent Associates, Inc. and was electrochemical grade (>99% purity). The sample was used as received. The [C₂mim][Tf₂N] contained approximately 50 ppm chloride.

\[C₆mim][P(C₂F₅)₃F₃]\: 1-Hexyl-3-methylimidazolium tri(pentafluoroethyl)trifluorophosphate was purchased from Merck KgaA and was received with a yellow tint. NMR analysis performed by our laboratory showed that impurity concentrations were less than the one percent detection limit of the NMR.

Other ionic liquids were synthesized in our laboratory.

\[C₄mim][Tf₂N]\: This sample was synthesized by Sudhir N.V.K Aki in our laboratory. The sample was not purchased from Covalent Associates because a previous study by our laboratory indicated that Covalent’s [C₄mim][Tf₂N] contained impurities. The bromide content of this sample was less than 10 ppm.

\[C₆mim][Tf₂N]\: This sample was synthesized by Jacob Crosthwaite and contained less than 20 ppm bromide.

\[C₆mmim][Tf₂N]\: This sample was synthesized by Berlyn Mellein and contained less than 18 ppm bromide.

\[C₆mPy][Tf₂N]\: This sample was synthesized by Mark Muldoon and contained less than 10 ppm chloride.
\([C_6F_9H_2mim][Tf_2N]\): Mark Muldoon synthesized this sample. Impurities in the sample were removed using standard techniques, by reacting with silver nitrate to remove halides and water washing. NMR analysis did not detect any impurities.

### 3.3 Apparatus

Absorption of carbon dioxide into ILs was measured using a ThermoCahn D200 microbalance. A diagram of the apparatus is shown in Figure 3.1.

The balance capacity in the balance’s A loop, the loop used during diffusion measurements, is 1.5 g with 0.1 microgram resolution. The balance consists of a balance beam mounted to and pivoting about a piece connected to a torque motor coil located in a permanent magnetic field. A photoelectric eye detects the beam position. When a force is produced around the axis of rotation caused by the sample weight, an electric current flowing through the torque motor produces an equal and opposite force about the axis of rotation, so that the beam is held at a constant reference position determined by the photoelectric eye. The electric current required to balance the force caused by the sample is proportional to the weight. A control unit processes the signals from the balance, amplifies the signal, digitizes the signal, filters noise, compensates slightly for temperature, then converts the signals into a format that can be read by a computer.
Platinum/10% nickel alloy wires approximately two inches long soldered to either end of the balance beam had loops at the end for attaching extension wires, which hold the sample baskets. The extension wires were purchased from Alfa-Aesar, consisted of nickel chromium (Ni:Cr; 80:20 wt%), and were 0.25 mm diameter. The fused quartz sample bucket and counterweight bucket were approximately 0.5 cm diameter and 0.5 cm deep. Approximately 100 mg of nickel chromium counterweights supplied by ThermoCahn were used to counterbalance the sample weight of approximately 100 mg at ThermoCahn’s suggestion for improved balance accuracy. Glass hang-down tubes enclosed the extension wires and baskets so that the sample and counterweight baskets could be viewed during experiments. A half-spherically shaped stainless steel cover encapsulated the balance components. The pressure inside the balance chamber was measured by a BOC Edwards active strain gauge and maintained at 0.990 ± 0.005 bar by two Asco series 8262 solenoid valves and BOC Edwards Active Digital Display with control relays model D395-57-000. The sample and counterweight temperatures were measured by a K-type
thermocouple and controlled within ± 1 degree Celsius by water jackets and a VWR Scientific 1140A refrigerated circulator. Temperature signals were input to the computer using an Omega CN8500 series temperature controller and ThermoCahn software. Temperature, sample weight and the corresponding time were recorded on a Dell Optiplex GX1P computer using ThermoCahn’s Microscan Acquisition software. Welch Chemstarr 1400N and Fisher Scientific Maxima C Plus vacuum pumps were alternately used to evacuate gases from the balance chamber. An adsorption tube containing activated alumina was contained in the vacuum line between the vacuum pump and the balance to prevent significant amounts of vacuum pump oil from back streaming into the balance chamber.

3.4 Balance Calibration Procedure

While the balance held an empty sample bucket and 100 mg of counterweights in the counterweight bucket, a vacuum with pressure lower than 0.05 mbar was drawn on the balance chamber originally filled with CO₂. Once the weight readings asymptotically approached a minimum value, the balance was tared through the Microscan Acquisition software. Next, a 100 ± 0.005 mg Troemner ultra class stainless steel calibration weight was placed in the sample bucket. The balance was flushed with CO₂ four times and a vacuum was drawn on the balance chamber. Once the weight asymptotically reached a minimum value, the weight reading was set to 100.0000 mg in the calibration screen of the Microscan Acquisition software. Next, the calibration weight was removed, the balance was flushed four times with CO₂, and a vacuum was drawn on the balance chamber. It was checked that the weight reading returned to 0.000 ± 0.003 mg while the balance was under vacuum. The
balance was calibrated prior to measuring the initial diffusion coefficients. The
calibration was checked and found to be accurate about two months after the initial
calibration.

3.5 Experimental Procedure

The diffusion coefficient of three samples was calculated for each IL reported
from the mass of CO$_2$ absorbed with time. The mass of CO$_2$ absorbed in the IL was
measured using the following procedure. A clean sample bucket was connected to
the sample side extension wire using metal tweezers. The sample side, glass hang-
down tube was then connected to the balance, the thermocouple reattached to the
bottom of the hang-down tube, and the quick-connects on the water jacket lines
reattached. After flushing the balance with CO$_2$ four times to ensure high purity gas
inside the balance, vacuum was drawn on the balance chamber until gases and
residual cleaning solvent desorbed from the empty bucket and the weight
asymptotically reached a minimum. Then, the balance was tared through the
Microscan Acquisition software.

Next, the weight of the sample was measured under vacuum, so that the
sample mass could be determined. The balance was opened and a previously dried IL
sample was added to the sample bucket using a syringe. A new data collection run
was started in the Microscan Acquisition software. The balance was flushed with
CO$_2$ four times. Vacuum was drawn on the sample between 10 and 30 hours
depending on sample viscosity as gases and moisture that may have been acquired
during sample transfer to the balance were desorbed until the weight asymptotically
reached a minimum. The minimum weight was considered the sample mass.
Once the weight reached a minimum, the vacuum line ball valve was manually closed and CO₂ inlet ball valve manually opened allowing CO₂ to fill the balance chamber. Initially, the sample weight decreased because the buoyancy force on the sample was greater than the buoyancy force on the counterweights. Then, the sample weight increased as CO₂ absorbed to the sample. The weight was recorded over a time period of at least two hours after the start of absorption to measure each diffusion coefficient. When the CO₂ saturation concentration was measured, data collection continued at least eight hours until the weight reached a maximum value. Once a run was completed, data collected by the Microscan Acquisition Software was viewed in the Microscan Analysis software. A typical graph produced by the Microscan Analysis software is shown in Figure 3.2. The weight and time values shown in parenthesis on the chart were selected by the author of this thesis as the sample weight under vacuum and sample weight when saturated with CO₂. It can be seen that the balance weight drifted slightly from 106.8290 to 106.8319 micrograms after drawing vacuum and reaching a minimum. When the weight drifted, an average value was used.
3.6 Calculating the Diffusion Coefficient

The mass of CO$_2$ absorbed with time was calculated by performing a force balance on the balance beam. The diffusion coefficient was calculated by fitting the data of mass absorbed with time to either the semi-infinite medium equation or the equation for diffusion into a plane sheet depending upon the absorption rate.

3.6.1 Calculating the Mass of CO$_2$ Absorbed

The balance reports mass readings in milligrams corresponding with the time of the reading. A force balance on the balance beam must be performed to calculate the mass of CO$_2$ absorbed, because the mass read by the balance includes a theoretical mass attributable to buoyancy forces and CO$_2$ absorbed to the balance components. The mass recorded by the balance, $M$, is equal to:

$$ \frac{W}{g} = M = m_{adlt} + m_{sb} + m_s - m_{cw} - m_{cw} + \rho_g(V_{cw} - V_{ss} - V_s) + m_{adb} \quad (3.6-1) $$
where $W/g$ is the weight measured by the balance divided by the gravitational constant, $m_{adIL}$ is the mass of CO$_2$ absorbed by the IL, $m_{sb}$, $m_s$, $m_{cwb}$, and $m_{cw}$ are the masses of the sample bucket, sample, counterweight bucket, and counterweights, respectively. $\rho_g$ is the density of CO$_2$ and is a function of temperature and pressure. $V_{cws}$, $V_{ss}$, and $V_s$ are the volumes of the counterweight side of the balance, the sample side of the balance, and the sample, respectively. When the balance holding an empty sample bucket and counterweights was tared under vacuum, the following quantity was set equal to zero.

$$0 = m_{sb} - m_{cwb} - m_{cw}$$ (3.6-2)

The mass attributable to the buoyancy forces on the counterweight side and sample side of the balance, and the mass of CO$_2$ absorbed to the balance components were measured at each temperature that the diffusion coefficient was measured. The mass reading was recorded when the balance contained an empty sample bucket, counterweights in the counterweight bucket, and CO$_2$ at 0.99 bar pressure. The reading became stable approximately ten minutes after the balance was filled with CO$_2$. The mass reading attributable to buoyancy and adsorption to balance components can be expressed as $m_{b&a}$.

$$m_{b&a} = \rho_g(V_{cws} - V_{ss}) + m_{adb}$$ (3.6-3)

The density of CO$_2$ at 0.99 bar was calculated using the Span and Wagner equation of state. The sample volume was determined by dividing the sample mass measured using the microbalance under vacuum by the sample density. Substituting (3.6-2) and (3.6-3) into (3.6-1) and rearranging gives the mass of CO$_2$ absorbed by the IL.

$$m_{adIL} = M - m_{b&a} - m_s + \rho_g(V_s)$$ (3.6-4)
3.6.2 Calculating the $D$ from the Semi-Infinite Medium Equation

During short times, diffusion of gas into the IL fits the boundary conditions for diffusion into a semi-infinite medium. The semi-infinite medium equation can be derived from Fick’s Second Law.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial y^2}$$  \hspace{1cm} (1.4-5)

with boundary conditions:

$C = C^0$ at $t \leq 0$

$C = C^S$ at $y = 0$

$C = C^0$ as $y \to \infty$

Where $C^0$ is the starting concentration of CO$_2$ in the IL, $C^S$ is the saturation concentration of CO$_2$ in the IL and $y$ is the depth of the IL. The equation is evaluated using the dimensionless concentration variable:

$$Y = \frac{C - C^S}{C^0 - C^S}$$  \hspace{1cm} (3.6-5)

$$\frac{\partial Y}{\partial t} = D \frac{\partial^2 Y}{\partial y^2}$$  \hspace{1cm} (3.6-6)

with boundary conditions:

$Y = 1$ at $t \leq 0$

$Y = 0$ at $y = 0$

$Y = 1$ as $y \to \infty$

Since the equation is unbounded in $y$ direction, we do not define a dimensionless length variable. Instead, a new variable is defined, $\eta$, which is a combination of the
two independent variables \( y \) and \( t \). When \( \eta \) is substituted, the partial differential equation becomes an ordinary differential equation. \( \eta \) is defined as:

\[
\eta = \frac{y}{2\sqrt{D_t}} \tag{3.6-7}
\]

The following mathematical manipulations are used to substitute \( \eta \) into (3.6-6).

\[
\frac{\partial Y}{\partial t} = \frac{\partial Y}{\partial \eta} \frac{\partial \eta}{\partial t} \tag{3.6-8}
\]

\[
\frac{\partial^2 Y}{\partial y^2} = \frac{\partial}{\partial \eta} \left( \frac{\partial Y}{\partial \eta} \frac{\partial \eta}{\partial y} \right) \tag{3.6-9}
\]

The new ordinary differential equation is:

\[
\frac{d^2 Y}{d\eta^2} + 2\eta \frac{dY}{d\eta} = 0 \tag{3.6-10}
\]

With the boundary conditions:

\( Y = 0 \) at \( \eta = 0 \)

\( Y = 1 \) at \( \eta \to \infty \)

To solve (3.6-10), a new variable is defined, which converts the equation into a first order differential equation.

\[
\omega = \frac{dY}{d\eta} \tag{3.6-11}
\]

Substitution yields:

\[
\frac{d\omega}{d\eta} + 2\eta \omega = 0 \tag{3.6-12}
\]

Separating variables and integrating yields:

\[
\ln \omega = -\eta^2 + c_1 \quad \text{or} \quad \ln \omega = -\eta^2 + \ln c_1 \tag{3.6-13}
\]

Rearranging yields:
\[ \frac{\omega}{c_i} = e^{-\eta^2} \]  
(3.6-14)

Substituting (3.6-14) into (3.6-11) yields:

\[ dY = c_i e^{-\eta^2} d\eta \]  
(3.6-15)

Solve for the constant, \( c_1 \), by integrating over the boundary conditions.

\[ \int_{0}^{1} dY = c_1 \int_{0}^{1} e^{-\eta^2} d\eta \]  
(3.6-16)

\[ 1 = c_1 \frac{\sqrt{\pi}}{2} \quad \rightarrow \quad c_1 = \frac{2}{\sqrt{\pi}} \]  
(3.6-17)

The resulting equation is:

\[ Y = \frac{2}{\sqrt{\pi}} \int_{0}^{\eta} e^{-\eta^2} d\eta \]  
(3.6-18)

where the right hand side of (3.6-18) is called the error function, \( \text{erf}(\eta) \). Substituting (3.6-5) and (3.6-7) into (3.6-18) yields an expression for the concentration distribution of \( \text{CO}_2 \) in the bucket.

\[ \frac{C - C^S}{C^0 - C^S} = \text{erf}\left( \frac{y}{2\sqrt{Dt}} \right) \]  
(3.6-19)

\[ C = \text{erf}\left( \frac{y}{2\sqrt{Dt}} \right) \left( C^0 - C^S \right) + C^S \]  
(3.6-20)

Recalling from Fick’s first law that the mass flux equals the mass diffusing per area per time, it is logical that the mass, \( M \), of \( \text{CO}_2 \) that diffuses across the IL’s surface can be found by integrating Fick’s first law with respect to \( t \).

\[ m_{\text{adIL}} = A \int_{0}^{t} D \left( \frac{\partial C}{\partial y} \right)_{y=0} dt \]  
(3.6-21)
where \( A \) is the IL’s surface area. To solve (3.6-21), it is helpful to write the concentration in the form.

\[
C = C^s + (C^0 - C^s) \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-\eta^2} d\eta
\]  
\( \text{(3.6-22)} \)

The Leibniz rule is used to differentiate the integral in (3.6-22) with respect to \( y \).

\[
\frac{\partial}{\partial y} \int_0^\infty f(\eta) d\eta = \int_0^\infty \frac{\partial f(\eta)}{\partial y} d\eta + f(\eta) \frac{\partial}{\partial y}\eta
\]  
\( \text{(3.6-23)} \)

where \( f(\eta) \) is:

\[
f(\eta) = \frac{2}{\sqrt{\pi}} e^{-\eta^2}
\]  
\( \text{(3.6-24)} \)

The first part of the integrand in (3.6-23) is evaluated by using the expression:

\[
\frac{\partial f(\eta)}{\partial y} = \frac{\partial f(\eta)}{\partial \eta} \frac{\partial \eta}{\partial y}
\]  
\( \text{(3.6-25)} \)

Differentiation yields:

\[
\frac{\partial \eta}{\partial y} = \frac{1}{2\sqrt{Dt}} \quad \text{and} \quad \frac{\partial f(\eta)}{\partial \eta} = -\frac{4}{\sqrt{\pi}} \eta e^{-\eta^2}
\]  
\( \text{(3.6-26)} \)

The product of the equations in (3.6-26) is:

\[
\frac{\partial f(\eta)}{\partial y} = -\frac{2\eta}{\sqrt{\piDt}} e^{-\eta^2}
\]  
\( \text{(3.6-27)} \)

Substituting (3.6-24) through (3.6-27) into (3.6-23) yields:

\[
\int_0^\eta -\frac{2\eta}{\sqrt{\piDt}} e^{-\eta^2} d\eta + \frac{1}{\sqrt{\piDt}} e^{-\eta^2}
\]  
\( \text{(3.6-28)} \)
Since this expression is being evaluated at the IL’s surface where \( y \) equals zero, \( \eta \) must also equal zero. Therefore, the solution of (3.6-28) is \( \frac{1}{\sqrt{\pi Dt}} \) and (3.6-21) becomes:

\[
m_{\text{adIL}} = AD(C^0 - C^S) \int_0^t \frac{1}{\sqrt{\pi Dt}} dt = -2A(C^0 - C^S) \left( \frac{Dt}{\pi} \right)^{1/2}
\]

(3.6-29)

Parameters determining the diffusion coefficient using (3.6-29) were measured or calculated. Section 3.6.1 explains how the mass of CO\(_2\) absorbed to the IL was measured. For the experiments performed in this thesis, \( C^0 \) is negligible. The saturation concentration, \( C^S \), of each IL except \([\text{C}_6\text{mmim}][\text{Tf}_2\text{N}]\), was calculated by rearranging Henry’s law (1.3-1).

\[
C^S = \frac{P \cdot MW \cdot \rho_{IL}}{H}
\]

(3.6-30)

where \( P \) is pressure, \( MW \) is the IL’s molecular weight, \( \rho_{IL} \) is the density of the ionic liquid, and \( H \) is the Henry’s constant. Since the Henry’s constant of \([\text{C}_6\text{mmim}][\text{Tf}_2\text{N}]\) has not been measured, the saturation concentration of \([\text{C}_6\text{mmim}][\text{Tf}_2\text{N}]\) was measured using the ThermoCahn microbalance. The area of the sample perpendicular to the direction of diffusion, \( A \), was measured using digital calipers.

An expression can be written for the diffusion coefficient by rearranging (3.6-29).

\[
D^{1/2} = \left( \frac{\pi}{t} \right)^{1/2} \frac{m_{\text{adIL}}}{2AC^S}
\]

(3.6-31)

Since the equation is linear, the diffusion coefficient was calculated by squaring the slope on a graph of \( \frac{\pi^{1/2} m_{\text{adIL}}}{2AC^S} \) versus \( t^{1/2} \). Mass measurements included in the
calculation of the diffusion coefficient ranged between mass absorbed corresponding
with 10 minutes time when the balance became stable after adding CO₂, and the
maximum time that the semi-infinite medium approximation is valid.

\( C^0 \) is negligible for these experiments, because a vacuum was drawn on the IL
prior to measuring diffusion. The minimum Henry’s constant (maximum CO₂
solubility) of all of the ILs measured was 25.2 bar for \([\text{C}_6\text{mim}][\text{P(C}_2\text{F}_5)_3\text{F}_3]\). The
ultimate vacuum drawn was about 0.2 mbar measured on a BOC Edwards pirani
gauge. Therefore, the maximum mole fraction of CO₂ contained in any sample prior
to starting the diffusion experiment was \(2 \times 10^{-4} \text{ bar}/25.2 \text{ bar} = 7.94 \times 10^{-6}\), which is
equivalent to \(2.02 \times 10^{-8} \text{ mg CO}_2/\text{mL of } [\text{C}_6\text{mim}][\text{P(C}_2\text{F}_5)_3\text{F}_3]\). In comparison, the
CO₂ concentration at saturation at 0.99 bar is about 4.6 mg/mL. The minimum
saturation concentration for all of the ILs was about 2.5 mg/mL for \([\text{C}_4\text{mim}][\text{Tf}_2\text{N}]\) at
70 degrees Celsius.

Several guidelines are available for estimating the parameters, \( t, y, \) and \( D \) so
that the semi-infinite medium approximation inherent to equation (3.6-31) is valid.
Since (3.6-31) models the solvent as a semi-infinite medium, the maximum diffusion
time or minimum diffusion distance for the experimental system must be calculated to
ensure that (3.6-31) is valid. Welty, Wicks and Wilson⁹⁴ estimated the maximum
value of \( \eta \) that the semi-infinite medium approximation could be used “with little or
no error.” It is reasonable that the semi-infinite medium equation would be valid
when the change in \( Y \) defined in (3.6-5) is less than or equal to 0.5 percent. Then, the
right hand side of (3.6-19) changes from 1 to 0.995 when \( \text{erf}(\eta) \) is equal to about two.
Substituting (3.6-7) for \( \eta \) yields:
Middleman\textsuperscript{65} states that the semi-infinite medium approximation can be accurately applied to a system when \( Y \) is less than or equal to one percent. Cussler states that when the Fourier number, \( \frac{y^2}{D_t} \), is much greater than one, a semi-infinite medium can be assumed. Welty, Wicks and Wilson’s approximation is the most conservative of these three approximations, and was used to calculate the maximum diffusion time allowable for accurately determining the diffusion coefficient using the semi-infinite medium equation \((3.6-31)\). The maximum diffusion time fitting the semi-infinite medium equation shown in Table 3.1 was calculated for each sample so that the maximum number of data points could be fitted in the graph used for calculating the diffusion coefficient of each sample. The sample depth was calculated based on the sample mass and density. A maximum diffusion coefficient was estimated as 1.5 times the diffusion coefficient calculated from a graph of \( \frac{\pi^{1/2} m_{aHt}}{2 AC^5} \) versus \( t^{1/2} \) where the diffusion time was 100 minutes shown in Appendix C. Although, the time to reach saturation was between about 9.5 hours for \([\text{C}_4\text{mim}][\text{Tf}_2\text{N}]\) at 70 degrees Celsius and 30 hours for \([\text{C}_6\text{F}_9\text{H}_4\text{mim}][\text{Tf}_2\text{N}]\), it can be seen from Table 3.1 that \([\text{C}_4\text{mim}][\text{Tf}_2\text{N}]\) at 50 and 70 degrees Celsius had maximum diffusion times calculated from \((3.6-32)\) less than 14 minutes. For these systems, it was determined that the equation for diffusion into a plane sheet was more appropriate for calculating the diffusion coefficient.
### TABLE 3.1
MAXIMUM TIME FOR APPLICABILITY OF EQUATION 3.6-31

<table>
<thead>
<tr>
<th>IL</th>
<th>Temp (deg C)</th>
<th>Volume (mL)</th>
<th>Depth (cm)</th>
<th>D at 100 min (cm²/s)</th>
<th>Max D (cm²/s)</th>
<th>Max t (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C₄mim][Tf₂N]</td>
<td>25</td>
<td>0.084</td>
<td>0.429</td>
<td>4.99E-06</td>
<td>7.48E-06</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.068</td>
<td>0.345</td>
<td>4.48E-06</td>
<td>6.72E-06</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.079</td>
<td>0.403</td>
<td>4.82E-06</td>
<td>7.23E-06</td>
<td>23</td>
</tr>
<tr>
<td>[C₄mim][Tf₂N]</td>
<td>10</td>
<td>0.068</td>
<td>0.346</td>
<td>2.67E-06</td>
<td>4.00E-06</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.063</td>
<td>0.319</td>
<td>2.90E-06</td>
<td>4.35E-06</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.068</td>
<td>0.347</td>
<td>2.62E-06</td>
<td>3.93E-06</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.063</td>
<td>0.323</td>
<td>3.75E-06</td>
<td>5.63E-06</td>
<td>19</td>
</tr>
<tr>
<td>[C₆mim][Tf₂N]</td>
<td>50</td>
<td>0.067</td>
<td>0.284</td>
<td>3.95E-06</td>
<td>5.93E-06</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.070</td>
<td>0.358</td>
<td>6.30E-06</td>
<td>9.45E-06</td>
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<tr>
<td></td>
<td>50</td>
<td>0.062</td>
<td>0.315</td>
<td>5.58E-06</td>
<td>8.76E-06</td>
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</tr>
<tr>
<td></td>
<td>70</td>
<td>0.074</td>
<td>0.379</td>
<td>8.51E-06</td>
<td>1.28E-05</td>
<td>12</td>
</tr>
<tr>
<td>[C₆mim][Tf₂N]</td>
<td>70</td>
<td>0.069</td>
<td>0.349</td>
<td>6.87E-06</td>
<td>1.03E-05</td>
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<tr>
<td></td>
<td>70</td>
<td>0.067</td>
<td>0.339</td>
<td>7.23E-06</td>
<td>1.08E-05</td>
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<td>[C₆mmim][Tf₂N]</td>
<td>25</td>
<td>0.078</td>
<td>0.395</td>
<td>3.70E-06</td>
<td>5.55E-06</td>
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</tr>
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<td></td>
<td>25</td>
<td>0.079</td>
<td>0.402</td>
<td>4.14E-06</td>
<td>6.21E-06</td>
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</tr>
<tr>
<td>[C₆mPy][Tf₂N]</td>
<td>25</td>
<td>0.072</td>
<td>0.367</td>
<td>3.80E-06</td>
<td>5.70E-06</td>
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<tr>
<td>[C₆F₆H₄mim][Tf₂N]</td>
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<td>0.076</td>
<td>0.387</td>
<td>2.22E-06</td>
<td>4.83E-06</td>
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</tr>
<tr>
<td></td>
<td>25</td>
<td>0.076</td>
<td>0.389</td>
<td>2.95E-06</td>
<td>4.42E-06</td>
<td>36</td>
</tr>
<tr>
<td>[C₆mim][PF₆]</td>
<td>25</td>
<td>0.075</td>
<td>0.382</td>
<td>3.80E-06</td>
<td>5.70E-06</td>
<td>27</td>
</tr>
<tr>
<td>[C₆mim][P(C₂F₅)₃F₃]</td>
<td>25</td>
<td>0.076</td>
<td>0.389</td>
<td>3.60E-06</td>
<td>5.40E-06</td>
<td>29</td>
</tr>
<tr>
<td>[C₆mim][CF₃SO₂N]</td>
<td>25</td>
<td>0.070</td>
<td>0.357</td>
<td>1.73E-06</td>
<td>2.60E-06</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.047</td>
<td>0.240</td>
<td>1.87E-06</td>
<td>2.81E-06</td>
<td>21</td>
</tr>
<tr>
<td>[C₆mim][P(C₂F₅)₃F₃]</td>
<td>25</td>
<td>0.072</td>
<td>0.365</td>
<td>1.77E-06</td>
<td>2.65E-06</td>
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<tr>
<td>[C₆mim][PF₆]</td>
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<td>0.363</td>
<td>1.91E-06</td>
<td>2.86E-06</td>
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<td>4.11E-06</td>
<td>6.16E-06</td>
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<td>0.389</td>
<td>4.21E-06</td>
<td>6.32E-06</td>
<td>24</td>
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</table>
3.6.3 Calculating the Diffusion Coefficient from the Plane Sheet Equation

For ILs with high diffusion coefficients and consequently shorter saturation times, namely [C₄mim][Tf₂N] at 50 and 70 degrees Celsius, the equation for diffusion into a plane sheet described the diffusing system more accurately than the semi-infinite medium equation. The equation for diffusion into a plane sheet is derived from Fick’s second law.

\[
\frac{\partial Y}{\partial t} = D \frac{\partial^2 Y}{\partial y^2} \tag{3.6-6}
\]

The initial condition is:

\( Y = 1 \) for \( 0 \leq y \leq h \) at \( t = 0 \).

The boundary conditions are:

\( Y = 0 \) for \( y = 0 \) at \( t > 0 \)

\( Y = 1 \) for \( y = h \) at \( t > 0 \)

where \( h \) is the depth of the sample. The equation can be solved by separating the variables so that

\[ Y = F(y)G(t) \tag{3.6-33} \]

Substitute (3.6-33) into (3.6-6) and rearrange.

\[ \frac{G''}{G} = D \frac{F''}{F} \tag{3.6-34} \]

The ' symbol denotes the derivative with respect to the corresponding variable. The expressions on both sides of (3.6-34) can be equal only if both are equal to the same constant independent of \( y \) and \( t \), which for convenience will be selected as equal to \(-\lambda^2 D\).
\[
\frac{G'}{G} = -\lambda^2 D
\]  \hspace{1cm} (3.6-35)

\[
\frac{F'''}{F} = -\lambda^2
\]  \hspace{1cm} (3.6-36)

Integration of (3.6-35) and (3.6-36) yields:

\[
G = \exp(-\lambda^2 D t)
\]  \hspace{1cm} (3.6-37)

\[
F = A \sin(\lambda y) + B \cos(\lambda y)
\]  \hspace{1cm} (3.6-38)

Substituting (3.6-37) and (3.6-38) into (3.6-33) yields:

\[
Y = [A \sin(\lambda y) + B \cos(\lambda y)] \exp(-\lambda^2 D t)
\]  \hspace{1cm} (3.6-39)

It can be seen by substituting the first boundary condition into (3.6-39) that \(B\) must equal 0. After substituting the second boundary condition, and knowing that \(A\) cannot equal zero for a finite solution, it can be seen that \(\lambda = (2n + 1) \frac{\pi}{2h}\). Therefore, the most general solution to (3.6-39) is

\[
Y = \sum_{n=0}^{\infty} A_n \exp\left[-(2n + 1)^2 \frac{\pi^2 D t}{4h^2}\right] \sin\left(\frac{(2n + 1)\pi y}{2h}\right)
\]  \hspace{1cm} (3.6-40)

The constants \(A_n\) must conform with the initial condition.

\[
1 = \sum_{n=0}^{\infty} A_n \sin\left(\frac{(2n + 1)\pi y}{2h}\right) \quad \text{for } 0 \leq y \leq h \quad \text{at } t = 0
\]  \hspace{1cm} (3.6-41)

Multiplying both sides of (3.6-41) by \(\sin\left(\frac{(2m + 1)\pi y}{2h}\right)\) and integrating yields:

\[
\sum_{n=0}^{\infty} \int_0^h \sin\left(\frac{(2m + 1)\pi y}{2h}\right) dy = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} A_n \int_0^h \sin\left(\frac{(2n + 1)\pi y}{2h}\right) \sin\left(\frac{(2m + 1)\pi y}{2h}\right) dy
\]  \hspace{1cm} (3.6-42)

When \(n\) is not equal to \(m\), the right hand side of (3.6-42) equals zero. However, when \(n\) equals \(m\), the equation becomes
\[- \frac{\cos[(2n+1)\pi h/2h]}{(2n+1)\pi /2h} + \frac{\cos(0)}{(2n+1)\pi /2h} = \frac{2h}{(2n+1)\pi} = A_n h \]  
\[ (3.6-43) \]

Rearrange to solve for $A_n$.

$$A_n = \frac{4}{(2n+1)\pi} \quad (3.6-44)$$

Substituting (3.6-44) into (3.6-40) and putting nondimensional $Y$ into dimensional terms yields:

$$C = C^* + (C^0 - C^*) \left[ \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{(2n+1)} \sin \left[ \frac{(2n+1)\pi y}{2h} \right] \exp \left[ -\frac{(2n+1)^2 \pi^2}{4h^2} Dt \right] \right] \quad (3.6-45)$$

Since $C^0$ is negligible under the experimental conditions for this thesis, the equation can be written as

$$C = C^* \left[ 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{(2n+1)} \sin \left[ \frac{(2n+1)\pi y}{2h} \right] \exp \left[ -\frac{(2n+1)^2 \pi^2}{4h^2} Dt \right] \right] \quad (3.6-46)$$

The average concentration, $C^{\text{ave}}$, in the slab is found by integrating over $y$ and dividing by the depth of the liquid.

$$C^{\text{ave}} = \frac{1}{h} \int_0^h C dy \quad (3.6-47)$$

The ratio of the average concentration to the saturation concentration is the same as the ratio of the mass of CO$_2$ absorbed to the mass of CO$_2$ absorbed at saturation. So the equation for diffusion into a plane sheet is written:

$$M = M^{\text{sat}} \left[ 1 - \frac{4}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[ -\frac{(2n+1)^2 \pi^2}{4h^2} Dt \right] \right] \quad (3.6-48)$$
The diffusion coefficient was calculated by fitting the data of the mass fraction of CO$_2$ saturation and the corresponding time to equation (3.6-48) using SigmaPlot. The equation entered into SigmaPlot was equivalent to:

$$M/M^{sat} = 1-0.810569469*(\exp(-a*t/4)+1/9*\exp(-9*a*t/4) +1/25*\exp(-25*a*t/4)+1/49*\exp(-49*a*t/4)+1/81*\exp(-81*a*t/4) +1/121*\exp(-121*a*t/4)+1/169*\exp(-169*a*t/4) +1/225*\exp(-225*a*t/4)+1/289*\exp(-289*a*t/4) +1/361*\exp(-361*a*t/4))$$ (3.6-49)

where $a$ is equal to $\frac{D\pi^2}{h^2}$. Since the measured saturation concentration was more than five percent lower than the saturation concentration calculated from the Henry’s constant at 50 degrees Celsius, using the measured saturation concentration in (3.6-49) resulted in a better fit to the experimental data. Thus, a diffusion coefficient was calculated using the experimental saturation mass fraction for each sample of [C$_4$mim][Tf$_2$N] at 50 degrees Celsius. A diffusion coefficient was also determined using the saturation mass fraction based on the Henry’s constant. An average value is reported in the results section of this thesis. Average values of the diffusion coefficients determined using the measured saturation mass fraction and the estimated Henry’s constant was also reported for [C$_4$mim][Tf$_2$N] at 70 degrees Celsius. Data included in the analysis spanned from 10 minutes, where the balance became stable after filling with gas, to 95 percent saturation when the measured saturation mass fraction was used. Data spanned between 10 minutes and 90 percent saturation when the solubility calculated from the Henry’s constant was used to improve the fit. A Henry’s constant of 65.7 bar was used in the calculation at 70 degrees Celsius, which was extrapolated from the data in Figure 3.3.
Figure 3.3  Extrapolated Henry’s constant at 70 °C from IGA data

3.7 Error Analysis

The reported uncertainties in the diffusion coefficients are greater than the uncertainties estimated by propagation of error. In addition to error caused by uncertainties including IL density and balance readings, further error could be attributable to convective currents within the balance chamber caused by different temperatures at the top of the balance than at the sample or water jackets. The convective currents caused noise in the weight readings when the temperature at the water jackets was different than room temperature. Also, the liquid density may decrease as CO₂ is absorbed affecting the buoyancy force on the sample and change in concentration. Water flowing through the water jackets may have caused vibration of the sample bucket, although no motion was observed through the glass hangdown tubes. These possible sources of error were considered to be accounted for in the error analysis calculations.
The uncertainties of diffusion coefficients for all ILs were determined first by calculating the standard deviation of the three samples measured per IL. Next, for the systems fitting the semi-infinite medium approximation, the 95% confidence limit of the slope equal to the diffusion coefficient was calculated using Excel’s statistical analysis tool. The upper and lower 95% confidence limit of each sample was compared with the upper and lower limit about the average based on the standard deviation. The upper limit of the reported diffusion coefficient was the higher value of the standard deviation’s and 95% confidence interval’s upper limit. The lower limit of the reported diffusion coefficient was the lesser value.

For diffusion coefficients not calculated using the semi-infinite medium equation, namely [C$_4$ mim][Tf$_2$ N] at 50 and 70 degrees Celsius, the standard deviation about the average was compared with the highest and lowest diffusion coefficients calculated. The standard deviation was taken of all six calculated diffusion coefficients at each temperature, three diffusion coefficients calculated using the saturation mass fraction measured by the ThermoCahn microbalance and three diffusion coefficients calculated using Henry’s constants. The upper limit of the reported diffusion coefficient was equal to the sum of the average diffusion coefficient and the standard deviation for both temperatures. The lower limit of the diffusion coefficient at 50 degrees Celsius was equal to the difference between the average diffusion coefficient and the standard deviation. The lower limit of the diffusion coefficient at 70 degrees Celsius was equal to the lowest diffusion coefficient measured at 70 degrees Celsius.
CHAPTER 4
EXPERIMENTAL METHOD FOR OCTANOL-WATER
PARTITION COEFFICIENT MEASUREMENT

4.1 $K_{OW}$ Measurement Methods

Methods available for measuring octanol/water partition coefficients include the shake-flask method, estimation by high performance liquid chromatography (HPLC), the generator column method, and the slow-stirring method. In the shake-flask method, octanol and water are mutually saturated, then shaken with the test chemical in a container, such as a centrifuge tube, for about five minutes. The octanol and water phases are separated by centrifugation, and the concentrations of the test chemical are measured in each phase\(^6\). This method can result in erroneous $K_{OW}$ values even after centrifugation since microdroplets of octanol may remain in the water phase. The presence of the octanol in the water phase causes inaccurately high measurements of hydrophobic chemicals in the water phase\(^1\). $K_{OW}$ estimation by HPLC is performed by comparing the retention time of a test chemical with the retention times of several reference chemicals. The column packing is hydrophobic (e.g., hydrocarbons chemically bonded to silica) while the mobile phase is hydrophilic (e.g., an aqueous solution) so water-soluble chemicals are eluted first and oil soluble chemicals last. A correlation established between the reference chemicals’ retention times and previously measured $K_{OWs}$ is used to calculate the $K_{OW}$ values\(^4\). Estimation by liquid chromatography is only recommended for test chemicals with
$K_{OW}$ values greater than one$^{1, 4}$ In the generator column method, water presaturated with octanol is slowly passed through a column, which is packed with a solid support that has been coated with octanol containing a small amount of the test chemical. The aqueous solution leaving the column is assumed to be in equilibrium with the octanol phase on the packing so analysis of the aqueous phase concentration yields the $K_{OW}^5$. Care must be taken to ensure that measurements taken using the generator column method do not include errors caused by interaction between the test chemical and the column packing. In the slow-stirring method$^{26}$, a small amount of the test chemical is mixed with either octanol saturated with water or water saturated with octanol. Then, the presaturated octanol and water, one of which contains the test chemical, are stirred slowly in a flask to minimize the stagnant diffusion layer between the phases while preventing emulsification. Once the concentrations in each phase have stabilized, the test chemical concentrations are measured in each phase to determine the $K_{OW}$.

4.2 Method Selected for Measuring $K_{OW}$

In this study, the slow-stirring method$^{26}$ was used because it is a direct method for measuring $K_{OWS}$ with accurate results over a wide range of values without the need for complex equipment$^{40}$. The apparatus consisted of a 40 mL, 27.75 mm diameter, 98 mm tall, clear, glass vial containing a 1 cm Teflon coated magnetic stir bar. The glass vial’s lid was an open-top screw cap sealed with a septum made of 90 mil silicone covering 10 mil Teflon. 12 gauge Teflon tubing with a Kel-F® hub by Hamilton Company protruded through the septum into the vial so that the hub sat above the septum and the tubing’s end hung approximately 85 mm below the septum.
A white rubber septum was fit inside the tubing’s hub to seal the tubing. A diagram of the experimental apparatus is shown in Figure 4.1.

Figure 4.1. Apparatus used for the slow-stirring method.

Approximately 15 mL of distilled, deionized water that had been presaturated with 1-octanol was added to a vial containing a magnetic stir bar. The vial’s lid was set loosely on the vial so that one end of the Teflon tubing was located below the water’s surface. Approximately 15 mL of octanol/IL “stock” solution, consisting of 1-octanol, which was presaturated with water and contained a known amount of IL, was carefully added to the vial so that the solution did not emulsify. Once the octanol “stock” solution was added, the lids were tightened on the vials to prevent octanol evaporation.

The vials were stirred slowly to prevent emulsification and were maintained at room temperature (24 ± 2 °C). Samples were taken from the octanol-rich phase by penetrating the silicone septum with a syringe. Samples were withdrawn from the water-rich phase using a syringe with four-inch stainless steel needle inserted through the tubing directly into the aqueous phase to prevent octanol contamination. Samples of each phase were taken from all vials during at least three sampling events.
occurring over a 10 to 43 day period. Sampling ceased when the concentrations in
both phases stabilized. Concentrations of IL in each phase were measured using UV-
vis spectroscopy (Cary 3, Varian), which has a sensitivity of ± 0.01 absorbance units.
Samples taken from the vials were diluted if necessary so that the measured
absorbance was less than 1. Pure deionized water or octanol saturated with water was
used in the reference cell. When samples from the octanol-rich phase were diluted
with pure octanol, the reference cell contained octanol saturated with water diluted at
the same ratio.

To best represent the concentrations of IL that may be found in ecological
systems if IL was released to the environment, the $K_{OW}$ were measured at very dilute
concentrations. The starting concentration of IL in the octanol phase was less than 2
$\times 10^{-2}$ mol/L, just enough to ensure that the IL could be measured accurately in both
phases. The final concentrations of IL in the octanol phase were between $6.43 \times 10^{-6}$
mol/L and $1.47 \times 10^{-4}$ mol/L and in the water phase were between $1.47 \times 10^{-4}$ and
$1.18 \times 10^{-2}$ mol/L.

The ILs for which $K_{OW}$ were measured by the author of this thesis are listed
in Table 1.2. For [C$_4$ mim][Cl], five stock solutions of varying dilute concentrations
were prepared with one vial tested per stock solution. The values obtained were
consistent within ± 10.3%. For this IL and ILs measured by Belveze$^{20}$, concentrations in the water phase were less than 0.014 mol/L and $K_{OW}$ values were
essentially independent of concentration (as they should be in the dilute limit). Thus,
the uncertainty is adequately represented by the standard deviation of replicates from
separate stock solutions. Unfortunately, for the Tf$_2$N ILs, $K_{OW}$ were slightly
concentration dependent, even at total concentrations less than $10^{-3}$ mol/L. Thus, for ILs with the Tf$_2$N anion, $K_{OWs}$ of five stock solutions at various dilute concentrations were measured to determine the variability more accurately. Specifically, [C$_4$mim][Tf$_2$N], [C$_6$mim][Tf$_2$N], [C$_6$mmim][Tf$_2$N], and [C$_8$mim][Tf$_2$N] $K_{OWs}$ were measured using five stock solutions with one vial per stock solution. For a different sample of [C$_4$mim][Tf$_2$N], as well as [C$_2$mim][Tf$_2$N], [C$_2$mmim][Tf$_2$N] and [C$_3$mmim][Tf$_2$N] (all samples obtained from Covalent Associates, as described below) initially the $K_{OW}$ values of five replicates from the same stock solution were measured. Later we repeated measurements for [C$_4$mim][Tf$_2$N], [C$_2$mmim][Tf$_2$N] and [C$_3$mmim][Tf$_2$N] with multiple samples from one or more different stock solutions in order to better understand the concentration dependence of the $K_{OW}$ values and the resulting uncertainties in the reported values.

4.3 Materials

Solvents used to measure $K_{OWs}$ were distilled, deionized water from a Millipore purification unit and Sigma-Aldrich, 99+%, HPLC grade 1-octanol.

[C$_2$mim][Tf$_2$N], [C$_2$mmim][Tf$_2$N], and [C$_3$mmim][Tf$_2$N]: These samples were obtained from Covalent Associates, Inc. and were all electrochemical grade (>99% purity). These samples were used as received. The [C$_2$mim][Tf$_2$N] and [C$_2$mmim][Tf$_2$N] contained approximately 50 ppm chloride. The [C$_3$mmim][Tf$_2$N] contained approximately 38 ppm chloride.

[C$_4$mim][Tf$_2$N]: These samples were either obtained from Covalent Associates, Inc. or synthesized in our laboratory by Sudhir N.V.K. Aki. The sample
from Covalent Associates was electrochemical grade (>99% purity) and was used as received. The bromide content of this sample was less than 10 ppm.

Other ionic liquids were synthesized in our laboratory, as well.

\([C_4mim][Cl]\): This sample was synthesized by Jacob Crosthwaite.

\([C_6mim][Tf_2N]\): This sample was synthesized by Jacob Crosthwaite and contained less than 20 ppm bromide.

\([C_8mim][Tf_2N]\): This sample was synthesized by Berlyn Mellein and contained less than 18 ppm bromide.

\([C_8mim][Tf_2N]\): This sample was synthesized by Jacob Crosthwaite. The bromide content was less than 14 ppm.

All synthesized ionic liquids were analyzed by proton NMR spectroscopy to ascertain the lack of any major impurities. Halide (Cl\(^-\) and Br\(^-\)) and ammonium ion content were measured using an Oakton Ion 510 Series pH/mV/Ion/°C meter with Cole-Parmer Ion Specific Probes (27502-13 for Cl\(^-\), 27502-05 for Br\(^-\), and 27502-03 for NH\(_4^+\)). The water contents of all these ILs were not necessary since they were all mixed with water during the experiment and their concentration was determined by UV-Vis spectroscopy (Cary 3, Varian).
5.1 Accuracy of ThermoCahn Microbalance

Prior to measuring diffusion coefficients of ILs, the diffusion coefficient of carbon dioxide in poly(vinyl acetate) (PVAc) was compared with the literature result to qualitatively check that the microbalance measured diffusion coefficients accurately. PVAc was selected for several reasons. The diffusion coefficient of CO\textsubscript{2} in PVAc could be determined gravimetrically in a simple manner, because it is a solid at room temperature and did not lose mass due to evaporation, unlike an organic liquid. Also, even a liquid with low volatility could have contaminated the balance components with the organic vapor. The small, approximately 100 mg sample of PVAc absorbed measurable amounts of CO\textsubscript{2}, unlike many other solids. The diffusion coefficient of CO\textsubscript{2} in PVAc was measured gravimetrically previously, so the method and results were easily duplicated by the ThermoCahn microbalance. Also, the PVAc was cheaply available.

The diffusion coefficient of CO\textsubscript{2} into PVAc was measured prior to the availability of temperature control, so measurements were taken at room temperature, about 24 degrees Celsius. The measured diffusion coefficient was compared with diffusion coefficients measured by Sato et. al.\textsuperscript{80} using a Rubotherm microbalance at various pressures greater than 1.9 bar and various temperatures. The PVAc used in
this study had the same product description (PVAc, $T_g = 303$ K, $Mn = 1.67 \times 10^5$) and was purchased from the same source, Aldrich, as the PVAc used by Sato et al. Figure 5.1 shows the diffusion coefficient of CO$_2$ in PVAc at 40º C and various pressures. Although the diffusion coefficient at atmospheric pressure, 0.1 MPa, and 24 degrees Celsius was not measured previously, it is expected by following the trend in Figure 5.1 that the diffusion coefficient would be less than $2 \times 10^{-8}$ cm$^2$/s.

![Figure 5.1 Diffusion coefficient of CO$_2$ in PVAc at 40º C](image)

The PVAc sample was prepared by placing fragments of the polymer into a sample bucket, heating the sample until it became rubbery, then molding the pieces together in the bucket. The diffusion coefficient of CO$_2$ into PVAc at 24º C measured using the ThermoCahn microbalance was accurate within an order of magnitude, equal to approximately $1.67 \times 10^{-8}$ cm$^2$/s. This diffusion coefficient was likely higher than actual due to void spaces where the polymer fragments were joined together.
Section 7.2 of this thesis contains recommendations for achieving a greater level of accuracy in the PVAc diffusion coefficient than was performed here. The diffusion coefficient calculation for CO₂ into PVAC is shown in Appendix B.

The saturation concentration of CO₂ was measured in at least two out of the three samples of each IL during the same experiment that the diffusion coefficient was measured to ensure that the mass of CO₂ absorbed to the IL was being measured accurately. At 25°C, the mass of CO₂ absorbed at saturation measured by the ThermoCahn microbalance was within four percent of the value calculated using the Henry’s constant for each IL, except [C₄mim][PF₆]. Although the [C₄mim][PF₆] was washed with water to remove any degradation products immediately prior to conducting diffusion experiments, degradation products may have formed during the four day drying period. At 50°C, the saturation concentration measured by the ThermoCahn microbalance was less than the value measured by the IGA. At 10°C, the saturation concentration measured by the ThermoCahn microbalance was greater than the value measured by the IGA. Convective currents disturbing the ThermoCahn’s balance beam may have caused less precise solubility measurements at temperatures not equal to room temperature. No solubility data was available for CO₂ in [C₄mim][Tf₂N] at 70°C or [C₆mmim][Tf₂N]. Table 5.1 compares the CO₂ solubilities measured by the ThermoCahn microbalance and solubilities calculated from Henry’s constants measured by the IGA.
### TABLE 5.1

COMPARISON OF CO₂ SOLUBILITIES MEASURED BY THE THERMOCAHN AND IGA MICROBALANCES

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<th>Temperature (°C)</th>
<th>Sample Start Date</th>
<th>CO₂ Solubility (mg/mL)</th>
<th>Percent Difference (%)</th>
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</table>
5.2 Diffusion Coefficient Results

The average, upper limit and lower limit of the diffusion coefficients are shown in Table 5.2. The calculations for each diffusion coefficient are shown in Appendix C.

### TABLE 5.2
DIFFUSION COEFFICIENTS

<table>
<thead>
<tr>
<th>IL</th>
<th>Temperature (ºC)</th>
<th>Average Diffusion Coefficient $D \times 10^6$ (cm$^2$/s)</th>
<th>Upper Limit of the Diffusion Coefficient $D \times 10^6$ (cm$^2$/s)</th>
<th>Lower Limit of the Diffusion Coefficient $D \times 10^6$ (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C$_6$mim][Tf$_2$N]</td>
<td>25</td>
<td>5.2</td>
<td>5.6</td>
<td>4.8</td>
</tr>
<tr>
<td>[C$_4$mmim][Tf$_2$N]</td>
<td>10</td>
<td>3.1</td>
<td>3.6</td>
<td>2.8</td>
</tr>
<tr>
<td>[C$_4$mim][Tf$_2$N]</td>
<td>25</td>
<td>4.1</td>
<td>4.9</td>
<td>3.8</td>
</tr>
<tr>
<td>[C$_4$mim][Tf$_2$N]</td>
<td>50</td>
<td>7.9</td>
<td>9.2</td>
<td>6.6</td>
</tr>
<tr>
<td>[C$_6$mim][Tf$_2$N]</td>
<td>70</td>
<td>12</td>
<td>13</td>
<td>9.7</td>
</tr>
<tr>
<td>[C$_4$mim][Tf$_2$N]</td>
<td>25</td>
<td>4.4</td>
<td>5.2</td>
<td>3.7</td>
</tr>
<tr>
<td>[C$_4$mim][Tf$_2$N]</td>
<td>25</td>
<td>3.3</td>
<td>3.8</td>
<td>2.8</td>
</tr>
<tr>
<td>[C$_4$mim][P(CF$_3$)$_3$]</td>
<td>25</td>
<td>4.0</td>
<td>4.3</td>
<td>3.8</td>
</tr>
<tr>
<td>[C$_6$F$_9$H$_4$mim][Tf$_2$N]</td>
<td>25</td>
<td>2.0</td>
<td>2.3</td>
<td>1.8</td>
</tr>
<tr>
<td>[C$_6$mim][PF$_6$]</td>
<td>25</td>
<td>2.0</td>
<td>2.2</td>
<td>1.9</td>
</tr>
<tr>
<td>[C$_6$mim][P(CF$_3$)$_3$F$_3$]</td>
<td>25</td>
<td>4.0</td>
<td>4.6</td>
<td>3.4</td>
</tr>
</tbody>
</table>

5.3 Comparison of Results with Stokes-Einstein and Eyring’s Equation

The Stokes-Einstein (S-E) equation (2.2-10) and Eyring equation (2.2-37) predict that diffusion coefficients are proportional to temperature divided by viscosity. This statement was found to be approximately true for the ILs’ diffusion coefficients. The diffusion coefficient reported by Buzzeo et. al. $^{28}$ for CO$_2$ diffusing into [N$_{6222}$][Tf$_2$N] was consistent with the trend seen for diffusion coefficients versus temperature divided by viscosity reported in this thesis.
Comparison of diffusion coefficients reported in this thesis with diffusion coefficients predicted by S-E and Eyring’s equations show that these equations predict lower diffusion coefficients. Table 5.3 and Figure 5.2 compare experimental diffusion coefficients with diffusion coefficients predicted by S-E and Eyring’s equations. The uncertainty in the temperature divided by viscosity, $\delta(T/\eta)$, shown in Figure 5.2 was approximated by setting the fractional uncertainty in the viscosity equal to the fractional uncertainty in the temperature divided by viscosity term so that:

$$\frac{\delta(T/\eta)}{T/\eta} = \frac{\delta\eta}{\eta}$$

(5.3-1)

Similarly to other gases diffusing into liquids, the experimental % deviation from S-E was between 92% and 100%. The % deviation from Eyring’s equation was between 65% and 96%. % deviation is defined by:

$$\text{% deviation} = \frac{\text{experimental value} - \text{calculated value}}{\text{experimental value}} \times 100$$

(5.3-2)

The S-E equation was described in Section 2.2 and is:

$$D = \frac{k_B T}{6\pi \eta a}$$

(2.2-10)

It can be seen from this equation that a graph of a liquid’s diffusion coefficient following the Stokes-Einstein equation versus the temperature divided by the viscosity would have an intercept equal to zero. The intercept was greater than zero for the measured diffusion coefficients. This finding is typical for a small solute diffusing into a viscous liquid as explained in Section 2.3. Table 5.4 shows the %
deviation from S-E for several gases dissolving in liquids. Eyring’s equation was described in Section 2.2.2 and is:

\[
D_e = \frac{kT}{\lambda \eta}
\]  

(2.2-37)

\[
\lambda = x_1 \left( \frac{V_1}{A_n} \right)^{1/3} + x_2 \left( \frac{V_2}{A_n} \right)^{1/3}
\]  

(2.2-39)

As expected, Eyring’s equation predicts higher diffusion coefficients than S-E, closer to experimental values because Eyring’s model takes solute and solvent size into consideration. Eyring’s equation likely deviates from experimental data because its model of the liquefied state is oversimplified.

TABLE 5.3

COMPARISON OF EXPERIMENTAL \(D\) WITH S-E (2.2-10) AND EYRING’S (2.2-37) \(D\)

<table>
<thead>
<tr>
<th>IL</th>
<th>Temperature (ºK)</th>
<th>Experimental (D) (cm(^2)/s)</th>
<th>Stokes-Einstein (D) (cm(^2)/s)</th>
<th>% Deviation from S-E</th>
<th>Eyring’s (D) (cm(^2)/s)</th>
<th>% Deviation from Eyring’s</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C(_2)mim][Tf(_2)N]</td>
<td>298.15</td>
<td>5.2E-06</td>
<td>4.0E-07</td>
<td>92%</td>
<td>1.8E-06</td>
<td>66%</td>
</tr>
<tr>
<td>[C(_2)mim][Tf(_2)N]</td>
<td>283.15</td>
<td>3.1E-06</td>
<td>1.3E-07</td>
<td>96%</td>
<td>5.7E-07</td>
<td>82%</td>
</tr>
<tr>
<td>[C(_2)mim][Tf(_2)N]</td>
<td>298.15</td>
<td>4.1E-06</td>
<td>2.3E-07</td>
<td>94%</td>
<td>1.1E-06</td>
<td>74%</td>
</tr>
<tr>
<td>[C(_2)mim][Tf(_2)N]</td>
<td>323.15</td>
<td>7.9E-06</td>
<td>5.5E-07</td>
<td>94%</td>
<td>2.5E-06</td>
<td>68%</td>
</tr>
<tr>
<td>[C(_4)mim][Tf(_2)N]</td>
<td>343.15</td>
<td>1.2E-05</td>
<td>9.1E-07</td>
<td>92%</td>
<td>4.2E-06</td>
<td>64%</td>
</tr>
<tr>
<td>[C(_6)mim][Tf(_2)N]</td>
<td>298.15</td>
<td>4.4E-06</td>
<td>1.7E-07</td>
<td>96%</td>
<td>7.2E-07</td>
<td>84%</td>
</tr>
<tr>
<td>[C(_6)mim][Tf(_2)N]</td>
<td>298.15</td>
<td>3.3E-06</td>
<td>8.5E-08</td>
<td>98%</td>
<td>3.5E-07</td>
<td>89%</td>
</tr>
<tr>
<td>[C(_6)mPy][Tf(_2)N]</td>
<td>298.15</td>
<td>4.0E-06</td>
<td>1.6E-07</td>
<td>96%</td>
<td>6.4E-07</td>
<td>84%</td>
</tr>
<tr>
<td>[C(_6)H(_4)mim][Tf(_2)N]</td>
<td>298.15</td>
<td>2.0E-06</td>
<td>1.8E-08</td>
<td>99%</td>
<td>7.4E-08</td>
<td>96%</td>
</tr>
<tr>
<td>[C(_6)mim][PF(_6)]</td>
<td>298.15</td>
<td>2.0E-06</td>
<td>4.7E-08</td>
<td>98%</td>
<td>2.3E-07</td>
<td>89%</td>
</tr>
<tr>
<td>[C(_6)mim][P(C(_2)F(_5))(_3)]</td>
<td>298.15</td>
<td>4.0E-06</td>
<td>1.3E-07</td>
<td>97%</td>
<td>4.9E-07</td>
<td>88%</td>
</tr>
<tr>
<td>[N(_{6222})][Tf(_2)N]*</td>
<td>293.15</td>
<td>2.3E-06</td>
<td>5.0E-08</td>
<td>98%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Measured by Buzzeo et. al. \(^{28}\)
**Figure 5.2** Comparison of experimental data with S-E and Eyring’s Equation

**TABLE 5.4**

DEVIATION FROM S-E FOR SEVERAL GASES DISSOLVED IN LIQUIDS AT 25° C

<table>
<thead>
<tr>
<th>Gas</th>
<th>Liquid</th>
<th>Experimental Diffusion Coefficient x 10^6 (cm^2/s)</th>
<th>% Deviation from Stokes-Einstein</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>Water</td>
<td>19.5</td>
<td>47%</td>
</tr>
<tr>
<td>CO₂</td>
<td>Ethanol</td>
<td>34.2</td>
<td>75%</td>
</tr>
<tr>
<td>CO₂</td>
<td>n-Heptane</td>
<td>60.3</td>
<td>63%</td>
</tr>
<tr>
<td>CO₂</td>
<td>i-Butyl alcohol</td>
<td>22.0</td>
<td>87%</td>
</tr>
<tr>
<td>CH₄</td>
<td>Glycerol</td>
<td>9.5</td>
<td>99%</td>
</tr>
<tr>
<td>H₂</td>
<td>Ethylene Glycol</td>
<td>7.5</td>
<td>90%</td>
</tr>
</tbody>
</table>
5.4 Comparison of Results with Empirical Correlations

The experimental diffusion coefficients versus viscosities were plotted to find the coefficients in Hayduk and Cheng’s equation\textsuperscript{51}.

\[ D = A \eta^B \quad (2.3-1) \]

Similar to Hayduk and Cheng’s observation that the coefficients $A$ and $B$ were equal to $3.5 \times 10^{-5}$ cm\textsuperscript{2}/s and $-0.44$, respectively, for CO\textsubscript{2} diffusing into various solvents, the coefficients $A$ and $B$ for CO\textsubscript{2} diffusing into ILs were equal to $2.9 \times 10^{-5}$ cm\textsuperscript{2}/s and $-0.46$ respectively. The graph of the ILs’ average diffusion coefficients versus viscosity is shown in Figure 5.3.
The Wilke-Chang equation was fitted to the average diffusion coefficients and the association factor was determined. The Wilke-Chang equation is:

\[ D = 2.92 \times 10^{-5} \eta^{-0.461} \]

\[ R^2 = 0.884 \]

Figure 5.3  Analysis of Hayduk-Cheng Coefficients

The association factor was calculated by plotting the average experimental diffusion coefficients versus \( 7.4 \times 10^{-8} \frac{M^{0.2} T}{\eta V^{0.6}} \) as shown in Figure 5.4. For reasons previously explained in the S-E discussion, the intercept of the graph was greater than zero, equal to \( 1.95 \times 10^{-6} \text{ cm}^2/\text{s} \). The square root of the slope, equal to the average association factor of the ILs was approximately 1.47, approximately the same as the
association factor of ethanol, which is 1.5. An association factor equal to one indicates that the solvent does not associate. The association factor of water is 2.6.

Figure 5.4 Determination of the association factor in Wilke-Chang correlation
6.1 Extinction Coefficient Results

Extinction coefficients, $\varepsilon$, of the ILs in octanol and water were necessary for determining the concentrations of IL in each phase, and the resulting $K_{OW}$ values. Thus, extinction coefficients for each of the ILs were measured, and are shown in Table 6.1. The extinction coefficient for $[C_4\text{mim}][\text{Cl}]$ used to determine the $K_{OW}$ was measured by Belveze$^{20}$. Also shown in Table 6.1 is the extinction coefficient of benzaldehyde, which is a compound that was chosen to verify the experimental technique for measuring $K_{OW}$ values. The reported extinction coefficients are the average values obtained using at least three “stock” solutions containing IL/octanol, IL/octanol saturated with water, or IL/water. Since the solubility of octanol in water was below the detection limit of the apparatus, the ILs’ extinction coefficients in pure water were used to determine IL concentrations in the water phase. For the octanol-rich phase, the calibration was made with either pure octanol, or octanol saturated with water. The latter was necessary when the extinction coefficient in pure octanol and pure water were very different, so that the presence of the water dissolved in the octanol-rich phase significantly changed the value of $\varepsilon$. This was the case for $[C_6\text{mmim}][\text{Tf}_2\text{N}]$ and $[C_8\text{mim}][\text{Tf}_2\text{N}]$. The reported uncertainties in the extinction coefficients are the standard deviations for all of the “stock” solutions (at least three)
used for a particular IL/solvent system. All of the extinction coefficients were measured at the wavelength of maximum absorption ($\lambda_{\text{max}}$). The extinction coefficient calculations are shown in Appendix D.
### TABLE 6.1

**EXTINCTION COEFFICIENTS OF BENZALDEHYDE AND IMIDAZOLIUM BASED IONIC LIQUIDS IN WATER AND OCTANOL**

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ(_{\text{max}}) in water (nm)</th>
<th>ε in water (L mol(^{-1}) cm(^{-1}))</th>
<th>λ(_{\text{max}}) in octanol (nm)</th>
<th>ε in octanol (L mol(^{-1}) cm(^{-1}))</th>
<th>λ(_{\text{max}}) in octanol saturated with water (nm)</th>
<th>ε in octanol saturated with water (L mol(^{-1}) cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzaldehyde</td>
<td>250</td>
<td>13710 ± 510</td>
<td>245</td>
<td>12980 ± 280</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[C(_4)mim][Cl] (^{20})</td>
<td>211</td>
<td>4880 ± 210</td>
<td>213</td>
<td>4510 ± 220</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[C(_2)mim][Tf(_2)N]</td>
<td>211</td>
<td>4380 ± 28</td>
<td>213</td>
<td>4354 ± 83</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[C(_2)mmim][Tf(_2)N]</td>
<td>211</td>
<td>5788 ± 63</td>
<td>213</td>
<td>5941 ± 156</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[C(_3)mmim][Tf(_2)N]</td>
<td>211</td>
<td>5780 ± 177</td>
<td>213</td>
<td>5768 ± 152</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[C(_4)mim][Tf(_2)N]</td>
<td>211</td>
<td>4407 ± 20</td>
<td>212</td>
<td>4582 ± 114</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[C(_6)mim][Tf(_2)N]</td>
<td>211</td>
<td>4434 ± 102</td>
<td>213</td>
<td>4509 ± 96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[C(_6)mmim][Tf(_2)N]</td>
<td>211</td>
<td>5480 ± 109</td>
<td>213</td>
<td>5683 ± 20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[C(_8)mim][Tf(_2)N]</td>
<td>211</td>
<td>4279 ± 79</td>
<td>212</td>
<td>4575 ± 104</td>
<td>212</td>
<td>4373 ± 23</td>
</tr>
</tbody>
</table>
6.2 $K_{OW}$ Values

The values of the $K_{OWs}$ studied by Belveze$^{20}$ and the author of this thesis are shown in Table 6.2. As indicated in section 4.2, concentrations were measured in the two phases until the $K_{OW}$ values no longer changed with time. The uncertainties reported are either standard deviations of multiple vials prepared from the same stock solution or multiple vials prepared from different stock solutions, as detailed in section 4.2. These uncertainties are greater than the uncertainty determined by propagation of error in the various measurements including what we would expect from the variation in room temperature over the course of the experiments. The $K_{OW}$ values for the [Tf$_2$N] ILs are given as ranges since even in the dilute region, the $K_{OW}$ values for these compounds varied with concentration.
### TABLE 6.2

**OCTANOL/WATER PARTITION COEFFICIENTS ($K_{OW}$S) STUDIED**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$K_{OW}$</th>
<th>Concentration range in water phase (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzaldehyde – literature value</td>
<td>30.2</td>
<td></td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>29.6</td>
<td></td>
</tr>
<tr>
<td>[C$_4$mim][BF$_4$]*</td>
<td>0.0030 ± 0.0002</td>
<td></td>
</tr>
<tr>
<td>[C$_4$mim][NO$_3$]*</td>
<td>0.0038 ± 0.0001</td>
<td></td>
</tr>
<tr>
<td>[C$_4$mim][PF$_6$]*</td>
<td>0.0220 ± 0.0008</td>
<td></td>
</tr>
<tr>
<td>[C$_4$mim][Br]*</td>
<td>0.0033 ± 0.0005</td>
<td></td>
</tr>
<tr>
<td>[C$_4$mim][Cl]</td>
<td>0.0040 ± 0.0003</td>
<td></td>
</tr>
<tr>
<td>[C$_2$mim][Tf$_2$N]</td>
<td>0.09 – 0.11</td>
<td>$2.8 \times 10^{-4} – 2.8 \times 10^{-3}$</td>
</tr>
<tr>
<td>[C$_4$mim][Tf$_2$N]</td>
<td>0.12 – 0.24</td>
<td>$1.4 \times 10^{-3} – 2.8 \times 10^{-3}$</td>
</tr>
<tr>
<td>[C$_6$mim][Tf$_2$N]</td>
<td>0.11 – 0.62</td>
<td>$1.5 \times 10^{-4} – 2.2 \times 10^{-3}$</td>
</tr>
<tr>
<td>[C$_8$mim][Tf$_2$N]</td>
<td>1.42 – 1.66</td>
<td>$3.2 \times 10^{-4} – 3.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>[C$_6$mim][Tf$_2$N]</td>
<td>1.35 – 1.79</td>
<td>$3.6 \times 10^{-4} – 4.9 \times 10^{-4}$</td>
</tr>
<tr>
<td>[C$_8$mim][Tf$_2$N]</td>
<td>6.3 - 11.1</td>
<td>$9.9 \times 10^{-5} – 2.1 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

*Measured by Belveze$^{20}$

As shown in Table 6.2, the literature value of benzaldehyde was reproduced satisfactorily. Thus, the apparatus and experimental technique was adequate for $K_{OW}$ measurements. Measurements of [Tf$_2$N] ILs with varying alkyl chain lengths on the cation (compare [C$_2$mim][Tf$_2$N], [C$_4$mim][Tf$_2$N], [C$_6$mim][Tf$_2$N] and [C$_8$mim][Tf$_2$N]) show that $K_{OW}$ increases as alkyl chain length on the cation increases, as shown in Figure 6.1. Increasing affinity for more hydrophobic compounds with increasing cation alkyl chain length is consistent with previous
studies\textsuperscript{38,100} discussed in Section 1.3.4, where it was found that the solubility of imidazolium based ionic liquids in alcohols increased as alkyl chain length on the cation increased. Thus, the $K_{OW}$ increases with increasing number of carbons on the cation alkyl chain, as one would expect.

<table>
<thead>
<tr>
<th>Number of carbons in alkyl chain</th>
<th>$K_{OW}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.00</td>
</tr>
<tr>
<td>2</td>
<td>3.00</td>
</tr>
<tr>
<td>3</td>
<td>5.00</td>
</tr>
<tr>
<td>4</td>
<td>7.00</td>
</tr>
<tr>
<td>5</td>
<td>9.00</td>
</tr>
<tr>
<td>6</td>
<td>11.00</td>
</tr>
<tr>
<td>7</td>
<td>13.00</td>
</tr>
<tr>
<td>8</td>
<td>15.00</td>
</tr>
<tr>
<td>9</td>
<td>17.00</td>
</tr>
</tbody>
</table>

Figure 6.1: Relationship between the $K_{OW}$ and the number of carbons in the alkyl chain on the cation of [C\textsubscript{n}mim][Tf\textsubscript{2}N]

In addition, replacing the hydrogen atom attached to the carbon between the nitrogens in the imidazolium ring with a methyl group had very little effect on the $K_{OW}$. This can be seen by comparing the measured $K_{OW}$ of [C\textsubscript{2}mim][Tf\textsubscript{2}N] with [C\textsubscript{2}mmim][Tf\textsubscript{2}N] or by comparing [C\textsubscript{6}mim][Tf\textsubscript{2}N] with [C\textsubscript{6}mmim][Tf\textsubscript{2}N]. As shown by Crosthwaite \textit{et al.}\textsuperscript{38} and discussed in Sections 1.3.4 and 1.3.5, adding a methyl
group to the imidazolium ring eliminates a hydrogen bonding site, thus reducing water solubility and alcohol solubility. Since the $K_{OW}$ is the ratio of the concentration dissolved in the water-rich phase and the octanol-rich phase, the additional methyl group did not affect the $K_{OW}$ value.

By examining the $K_{OW}$ values of all the salts with the [C$_4$mim] cation, one can determine the effect of the anion. [C$_4$mim][Br], [C$_4$mim][BF$_4$], [C$_4$mim][NO$_3$] and [C$_4$mim][Cl] are all completely miscible with water at room temperature. Conversely, [C$_4$mim][PF$_6$] and [C$_4$mim][Tf$_2$N] are only partially miscible with water at room temperature, with [C$_4$mim][Tf$_2$N] showing the lowest mutual solubilities.$^{30}$ The $K_{OW}$ values follow this trend of anion hydrophilicity. The $K_{OW}$ of [C$_4$mim][Tf$_2$N] is more than an order of magnitude higher than that of [C$_4$mim][PF$_6$], which is itself almost five times greater than the $K_{OW}$ values of [C$_4$mim][Br], [C$_4$mim][Cl], [C$_4$mim][BF$_4$] and [C$_4$mim][NO$_3$].

The $K_{OWs}$ of the [Tf$_2$N] ILs were dependent upon concentration, even in the relatively dilute region investigated here. This is shown clearly in Figure 6.2, where the $K_{OW}$ values obtained for [C$_4$mim][Tf$_2$N] are plotted at various concentrations in the water-rich phase. At higher concentrations, the apparent $K_{OW}$ increases, essentially in a linear fashion. Plotted on this graph are values obtained with both the sample from Covalent Associates and the sample made in our laboratory. Initially there was concern that an impurity (our laboratory observed the formation of some solids in the Covalent [C$_4$mim][Tf$_2$N] sample in some unrelated experiments) in the Covalent sample was causing anomalous results and, thus, synthesized our own sample. However, careful investigation showed that the results from the two samples
were entirely consistent, as shown in Figure 6.2. The main problem is that infinite dilution is not achieved even at the dilute concentrations (10^{-4} – 10^{-3} M in the water-rich phase) of these experiments. Ability to perform the experiments is limited at even lower concentrations by the detection limits of the UV-vis spectrometer. Thus, all the $K_{OW}$ values for ILs with the [Tf$_2$N] anion are reported as rough ranges, with the knowledge that the actual, infinite dilution, $K_{OW}$ values are probably somewhat smaller than those reported here. If data is available over a wide enough range of composition (i.e. like [C$_4$mim][Tf$_2$N]), one could extrapolate the $K_{OW}$ values as a function of concentration to infinite dilution to get infinite dilution $K_{OW}$ values. Since this is not the case for most of the compounds studied here, this avenue was not pursued. No concentration dependences were observed in the $K_{OW}$ values of the ILs with any of the other anions.

Figure 6.2: Variation of [C$_4$mim][Tf$_2$N] $K_{OW}$ with concentration
6.3 Comparison of Results with Published data

$K_{OW}$ values measured by our laboratory differ significantly from results presented by Chou et al. \cite{34} and Domanska et al. \cite{42}. Chou et al. reported $K_{OW}$ values for [C$_4$mim][PF$_6$] and [C$_2$mim][PF$_6$] of 0.005 and 0.012, respectively, at their lowest concentrations. Their value for [C$_4$mim][PF$_6$] is significantly lower than our laboratory’s value measured by Belveze\cite{20} of 0.022. Although Chou et al. used somewhat higher concentrations than used in this study (3 x 10$^{-2}$ mol/L, compared with Belveze’s maximum aqueous concentration of 7.7 x 10$^{-3}$ mol/L), this probably does not explain the discrepancy since Belveze’s $K_{OW}$ values of [C$_4$mim][PF$_6$] were essentially independent of concentration in the range investigated. There are several other possible reasons for the discrepancy. First, Chou et al. used the shake-flask method without centrifugation. Since octanol and water form an emulsion, it is entirely possible that their phases were not properly separated. The fact that they report a larger $K_{OW}$ value at their lowest concentrations for a more hydrophilic compound ([C$_2$mim][PF$_6$]), which is entirely unexpected, gives further support to the possibility of experimental difficulties with their technique. A second possibility is that the differences are due to different rates of [C$_4$mim][PF$_6$] degradation in water. Hardacre and coworkers\cite{90} have shown that PF$_6$ and BF$_4$ anions can hydrolyze at rates that are significant even at room temperature. Thus, the results for [C$_4$mim][PF$_6$] and [C$_4$mim][BF$_4$] may have additional uncertainty due to the influence of hydrolysis products. Domanska et al. estimated $K_{OW}$ values for [C$_n$mim][Cl] ILs at 298.15 K by dividing the solubility of the IL in octanol by the solubility of the IL in water. Domanska et al. concluded that $K_{OWs}$ generally increase as the alkyl chain length on
the imidazolium cation increases, which is consistent with our findings. Similar to our observations, Domanska et al. found that [C₄mim][Cl] is more soluble in water than octanol, but their $K_{OW}$ value (0.48) is several orders of magnitude higher than the one reported here (0.004). The difference is likely due to the fact that Domanska et al. were simply reporting the ratio of solubility of the IL in pure octanol and pure water, rather than an actual infinite dilution partitioning of the IL between the aqueous phase and the octanol-rich phase. The slow stirring method followed to actually measure the $K_{OW}$ is generally considered a better representation of ecological conditions, where the oil and the water are equilibrated with each other and the IL is present in very dilute amounts.

6.4 Comparison of IL $K_{OW}$ Values with Common Organic Liquids

The results indicate that the imidazolium based ILs measured here are extremely hydrophilic. In particular, the $K_{OWs}$ of all of the imidazolium based ILs with any anion other than the Tf₂N anion are much lower than many commonly used industrial solvents, as seen in the comparisons shown in Table 6.3, where one of the most hydrophilic and one of the most hydrophobic ionic liquids is included. ILs containing [Tf₂N] have slightly larger $K_{OW}$ values, similar to polar solvents such as methanol and acetone, but they are still much lower than nonpolar solvents, such as benzene or hexane.
TABLE 6.3

COMPARISON OF IL’S $K_{OW}$ VALUES WITH
$K_{OW}$ VALUES OF COMMON ORGANIC COMPOUNDS

<table>
<thead>
<tr>
<th>Compound</th>
<th>$K_{OW}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[C_4\text{mim}][\text{Cl}]$</td>
<td>0.004</td>
</tr>
<tr>
<td>Methanol $^61$</td>
<td>0.17</td>
</tr>
<tr>
<td>Acetone $^61$</td>
<td>0.575</td>
</tr>
<tr>
<td>Caffeine $^66$</td>
<td>0.85</td>
</tr>
<tr>
<td>$[C_8\text{mim}][\text{Tf}_2\text{N}]$</td>
<td>6.3 - 11.1</td>
</tr>
<tr>
<td>Benzene $^61$</td>
<td>135</td>
</tr>
<tr>
<td>Cyclohexane $^78$</td>
<td>2,754</td>
</tr>
<tr>
<td>N-hexane $^78$</td>
<td>10,000</td>
</tr>
</tbody>
</table>

6.6 Estimation of Ecosystem Risk Parameters

As explained in Section 1.6.3, ecosystem risk parameters can be estimated using the $K_{OW}$ values. Estimates of bioconcentration factors (BCF), soil sorption coefficients ($K_{OC}$), and toxicity in guppies ($LC_{50}$) can be calculated using the equations in Table 1.10. The ecosystem risk parameters for $[C_8\text{mim}][\text{Tf}_2\text{N}]$, the IL with the highest measured $K_{OW}$ of approximately 8.7, indicate that imidazolium-based ILs are not likely to accumulate in organisms, adhere to soil, or be toxic to guppies. Calculated values of the BCF, $K_{OC}$, and $LC_{50}$ for guppies are 2.2, 77.3 and 11264 µmol/L, respectively. Compounds with BCF values less than 250 are considered to have low bioaccumulation potential. Compounds with $K_{OC}$ less than 316 are considered to have low soil sorption potential $^{10}$. Comparison of the ILs’ $K_{OW}$ values
with compounds in Table 6.3 indicates that ILs have relatively low toxicity to guppies.
CHAPTER 7
CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

This study investigated whether ILs’ cation, anion, alkyl chain length on an imidazolium cation, or the methyl group at the C2 position on the imidazolium cation affected the diffusion coefficient of CO$_2$ into the IL. The diffusion coefficients measured at temperatures between 10 and 70 ºC ranged between $1.8 \times 10^{-6}$ and $1.3 \times 10^{-5}$ cm$^2$/s. A plot of the diffusion coefficients versus temperature divided by viscosity shown in Figure 5.2 indicates that the IL’s viscosity impacts the diffusion coefficient more than changes to the IL’s structure. The diffusion coefficients increase in a linear fashion with a corresponding decrease in the temperature divided by viscosity. The Stokes-Einstein and Eyring’s equations predicted diffusion coefficients lower than measured values at percent deviations similar to gases diffusing into other solvents. The empirical Hayduk-Cheng coefficients calculated by fitting diffusion coefficients reported in this thesis and viscosities to the Hayduk-Cheng equation were similar to coefficients reported by Hayduk-Cheng for CO$_2$ diffusing into various solvents. An average association factor for all the ILs used in the empirical Wilke-Chang correlation was equal to the approximately same association factor as ethanol.
The $K_{OW}$ values of dialkylimidazolium ILs range between 0.003 and 11.1 at room temperature. The $K_{OW}$ values increase with the hydrophobicity of the anion, with the Tf$_2$N anion causing a higher $K_{OW}$ value than the PF$_6$ anion and the water miscible anions. The $K_{OW}$ also increases with increasing alkyl chain length on the imidazolium cation. Replacing the acidic hydrogen on the C2 carbon in the imidazolium ring with a methyl group has essentially no effect on the $K_{OW}$. All of the $K_{OW}$ values are relatively small, thus it is unlikely that these ILs will accumulate or concentrate in the environment.

7.2 Recommendations

In future experiments, several improvements could be made to the techniques employed for measuring diffusion coefficients of gases into ILs and octanol-water partition coefficients of ILs. Maintaining the balance and the sample at the same temperature using an air bath may reduce gaseous convection throughout the balance chamber and consequently reduce noise in the diffusion coefficient measurements. Replacement of the oil-filled vacuum pump with a dry vacuum pump would eliminate the possibility of oil-contamination inside the balance chamber. The octanol-water partition coefficients of hydrophobic ILs could be linearly extrapolated to infinite dilution when measured at various low concentrations.

Diffusion coefficient accuracy was supported in several ways. Accuracy of the mass of CO$_2$ absorbed to the IL sample was confirmed by comparing the mass absorbed at saturation with measurements made on the IGA. The diffusion coefficient measurements were performed using a well-established method with simple calculations. The diffusion coefficient values and trends reported are
reasonable based on comparisons with other systems of gases diffusing into organic liquids. The values are also consistent with a diffusion coefficient for CO₂ diffusing into [N₆₂₂][Tf₂N] measured by Buzzeo et. al[Buzzeo, 2004 #71]. However, additional confirmation of the technique’s accuracy should be made by performing additional experiments.

The diffusion coefficient of CO₂ into a solid PVAc sample should be measured at 40 degrees Celsius, the same temperature that has been previously published[Sato, 2001 #94]. The diffusion coefficient of CO₂ into a solid PVAc sample may be measured more accurately than into a PVAc sample where fragments were molded together. The PVAc pellets purchased are roughly disk-shaped having diameters of about 7 mm and thickness of about 1.5 mm. A single pellet could be melt molded into a glass basket with 8 mm inside diameter and 3 mm inside depth. The polymer surface should be as flat and smooth in the basket as possible. For a minimum depth of 1 mm and maximum diffusion coefficient of 2 x 10⁻⁸ cm²/s and from (3.6-32), the diffusion coefficient could be calculated using the equation for diffusion into a semi-infinite medium (3.6-31) for times less than 520 minutes. The diffusion coefficient can be verified over long times using the equation for diffusion into a flat plate (3.6-48). The actual depth of the sample should be calculated based on the measured sample volume, where the measured volume is simply the measured sample mass divided by the density of PVAc at 40 degrees Celsius. The density of PVAc at 40 degrees Celsius can be calculated from the empirical Tait equation [Rodgers, 1993 #114]:

\[ V(P, T) = V(0, T) \left\{1 - C \ln[1 + P / B(T)]\right\} \]  

(7.2-1)
\[ V(0,T) = 0.82496 + 5.820 \times 10^{-4} T + 2.940 \times 10^{-7} T^2 \]  \hspace{1cm} (7.2-2)

\[ B(T) = 2049 \exp(-4.346 \times 10^{-3} T) \]  \hspace{1cm} (7.2-3)

where \( V \) is the specific volume in \( \text{cm}^3/\text{g} \), \( T \) is temperature in Celsius, \( P \) is pressure in bar, and \( C \) is a constant equal to 0.0894. From equations (7.2-1) through (7.2-3), at 40 degrees Celsius and 0.995 bar, the density of PVAc is approximately 1.178 g/cm\(^3\). The saturation concentration should be calculated similarly to the sample at 24 degrees Celsius as shown in Appendix B.
APPENDIX A

DERIVATION OF STOKES’ LAW

Stokes’ Law is derived from the creeping flow equations. The continuity equation written in spherical coordinates is:

\[
\frac{1}{r^2} \frac{d}{dr} \left( r^2 u_r \right) + \frac{1}{r \sin \theta} \left( \frac{d}{d \theta} \left( \sin \theta u_\theta \right) \right) = 0
\]

A.1

Directions \( \theta \) and \( r \) (radial) are shown in Figure 2.2. \( u \) represents the dimensionless velocity and \( r \) represents the dimensionless radius. The radial Navier-Stokes equation is:

\[
\frac{1}{r^2} \frac{d}{dr} \left[ r^2 \left( \frac{d}{dr} u_r \right) \right] + \frac{1}{r \sin \theta} \left[ \frac{d}{d \theta} \left( \sin \theta \left( \frac{d}{d \theta} u_r \right) \right) \right] - 2u_r + \ldots - \frac{d}{dr} p = 0
\]

A.2

\( p \) is the dynamic pressure of the fluid on the sphere. The angular Navier-Stokes equation is:

\[
\frac{1}{r^2} \frac{d}{dr} \left[ r^2 \left( \frac{d}{dr} u_\theta \right) \right] + \frac{1}{r \sin \theta} \left[ \frac{d}{d \theta} \left( \sin \theta \left( \frac{d}{d \theta} u_\theta \right) \right) \right] + \ldots - \frac{1}{r} \frac{d}{d \theta} p = 0
\]

A.3

The boundary conditions are:

\( u_r = u_\theta = 0 \) at \( r = 1 \) Note: assumes no slip at sphere's surface A.4

\( u_r = \cos \Theta \) as \( r \) goes to infinity A.5
\( u_\Theta = -\sin \Theta \) as \( r \) goes to infinity \( \text{A.6} \)

Based on the linearity of the velocity far from the sphere, the velocity field can be approximated as:

\[ u_r = \cos \theta \cdot f(r) \quad \text{A.7} \]

\[ u_\theta = \sin \theta \cdot g(r) \quad \text{A.8} \]

where \( f \) and \( g \) are arbitrary functions to be solved. Substituting equations A.7 and A.8 into the continuity equation A.1 yields after simplification:

\[ g = -f - \frac{r}{2} \left( \frac{d}{dr} f \right) \quad \text{A.9} \]

Substituting A.7 and A.8 into A.2 yields after simplification:

\[
\frac{\cos \theta}{r^2} \left[ \frac{d}{dr} \left( \frac{2r \left( \frac{d}{dr} f \right)}{r^2} \right) \right] - \frac{4f - 4g}{r^2} = \frac{d}{dr} p
\]

\[ \text{A.10} \]

From this expression we know \( dp/dr = H(r) \cos \theta \), where \( H(r) \) is a function of \( r \) that involves \( f(r) \) and \( g(r) \). Therefore, the pressure should take the form:

\[ p = 1 + P(r) \cos \theta \quad \text{A.11} \]

where \( P(r) \) is the integral of \( H(r) \) and equals zero as \( r \) goes to infinity. Taking the derivative of A.11 with respect to \( \theta \) yields:

\[
\frac{1}{r} \left[ \frac{d}{dr} \left( \frac{2r \left( \frac{d}{dr} f \right)}{r^2} \right) \right] - \frac{4f}{r^2} - \frac{4g}{r^2} = \frac{d}{dr} p
\]

\[ \text{A.12} \]

Substituting A.7 and A.8 into A.3 yields after simplification:

\[
\frac{d}{d\Theta} p = \left[ \frac{1}{r} \left( \frac{d}{dr} \left( \frac{2r \left( \frac{d}{dr} g \right)}{r^2} \right) \right) \right] - \frac{2g}{r} - \frac{2f}{r} \sin \Theta
\]

\[ \text{A.13} \]

Derivating A.11 with respect to \( \theta \) yields:
\[ \frac{d}{d\Theta} p = -p(r) \sin \Theta \quad \text{(A.14)} \]

Substituting A.14 into A.13 yields:

\[ \frac{1}{r} \left[ \frac{d}{dr} \left( \frac{2}{r} \left( \frac{d}{dr} f \right) \right) \right] - \frac{2g}{r} - \frac{2f}{r} + P = 0 \quad \text{(A.15)} \]

Derivating A.15 with respect to r yields:

\[ \frac{d}{dr} \left[ \frac{1}{r} \left[ \frac{d}{dr} \left( \frac{2}{r} \left( \frac{d}{dr} f \right) \right) \right] \right] - \frac{d}{dr} \left( \frac{2g}{r} \right) - \frac{d}{dr} \left( \frac{2f}{r} \right) + \frac{d}{dr} P = 0 \quad \text{(A.16)} \]

To put A.16 in terms of f and r, substitute A.9 into A.16 and simplify to yield:

\[ -\frac{r^2}{2} \frac{d^4 f}{dr^4} - 4r \frac{d^3 f}{dr^3} + 5 \frac{d^2 f}{dr^2} + \frac{d}{dr} P = 0 \quad \text{(A.17)} \]

To put A.12 in terms of f and r, substituting A.9 into A.12 and simplify to yield:

\[ \frac{4}{r} \left( \frac{d}{dr} f \right) + \frac{d^2}{dr^2} f - \frac{d}{dr} P = 0 \quad \text{(A.18)} \]

The sum of A.17 and A.18 is:

\[ \frac{-r^2}{2} \frac{d^4 f}{dr^4} - 4r \frac{d^3 f}{dr^3} + 4 \frac{d^2 f}{dr^2} - \frac{4}{r} \left( \frac{d}{dr} f \right) = 0 \quad \text{(A.19)} \]

Multiplying by \(-r^2/4\) yields:

\[ \frac{r^4}{8} \frac{d^4 f}{dr^4} + r \frac{d^3 f}{dr^3} - 2 \frac{d^2 f}{dr^2} - r \left( \frac{d}{dr} f \right) = 0 \quad \text{(A.20)} \]

This is a fourth order Euler equation with four independent solutions of the form:

\[ f = r^k \quad \text{(A.21)} \]

Substituting the respective derivatives of A.21 into A.20 yields after simplification:

\[ k^4 + 2k^3 - 5k^2 - 6k = 0 \quad \text{(A.22)} \]
The four roots of A.22 are: \( k = 0, -1, -3 \) and 2. Substituting these values into A.21 yields:

\[
 f(r) = c_1 r^0 + c_2 r^{-1} + c_3 r^{-3} + c_4 r^2
\]  

A.23

From the boundary conditions,

\[ u_r = \cos \Theta \]

when \( r \) goes to infinity. From A.7, \( f(r) \) must equal one when \( r \) goes to infinity. From this specification, it can be seen that \( c_4 \) must equal zero and \( c_1 \) must equal one.

Substituting the no slip boundary conditions, A.4, into A.7 and A.8:

\[
 0 = \cos \Theta f(1) \quad \text{A.24}
\]

\[
 0 = \sin \Theta g(1) \quad \text{A.25}
\]

For A.24 and A.25 to be valid, \( f(r) \) and \( g(r) \) must equal zero when \( r = 1 \).

\[
 f(1) = 0 = 1 + c_2 + c_3 \quad \text{A.26}
\]

\[
 g(1) = 0 = -2 - c_2 + c_3 \quad \text{A.27}
\]

The solutions to A.26 and A.27 are \( c_2 = -3/2 \) and \( c_3 = 1/2 \).

Substituting the constants into the functions \( f(r) \) and \( g(r) \):

\[
 f(r) = 1 - \frac{3}{2r} + \frac{1}{2r^3} \quad \text{A.28}
\]

\[
 g(r) = -1 + \frac{3r}{4} + \frac{1}{4r^3} \quad \text{A.29}
\]

Substitute A.29 and A.30 into A.15 to solve for \( P(r) \).

\[
 P(r) = \frac{-3}{2r^2} \quad \text{A.30}
\]
Substituting A.29 through A.30 into A.7, A.8 and A.11 in terms of dimensional variables yields:

\[ u_r = u_{\text{infinity}} \left[ 1 - \frac{3}{4} \left( \frac{a}{r} \right) + \frac{1}{4} \left( \frac{a}{r} \right)^3 \right] \cos \Theta \]  

A.32

\[ u_{\Theta} = -u_{\text{infinity}} \left[ 1 - \frac{3}{4} \left( \frac{a}{r} \right) - \frac{1}{4} \left( \frac{a}{r} \right)^3 \right] \sin \Theta \]  

A.33

\[ p = P_{\text{infinity}} - \frac{3 \cdot \eta \cdot u_{\text{infinity}}}{2a} \left( \frac{a}{r} \right)^2 \cos \Theta \]  

A.34

The drag force on the sphere's surface is:

\[ F_D = \int e_Z (\sigma \cdot e_r) \, dA \]  

A.35

In spherical coordinates, A.35 is written:

\[ F_D(\text{at } r = a) = \int_0^{2\pi} \int_0^{\pi} \left( \cos \Theta \cdot \sigma_{rr} - \sin \Theta \cdot \sigma_{r\Theta} \right) a^2 \sin \theta \, d\theta \, d\phi \]  

A.36

where \( \sigma_{r\Theta} \) is the surface stress force component in the \( \theta \) direction acting on a surface with unit normal in the \( r \) direction. For an incompressible fluid:

\[ \sigma_{rr} = -p + 2 \cdot \eta \left( \frac{d}{dr} u_r \right) \]  

A.37

\[ \sigma_{r\Theta} = \eta \left[ \frac{d}{dr} \left( \frac{d u_r}{d\Theta} \right) + \frac{1}{r} \left( \frac{d}{d\Theta} u_r \right) \right] \]  

A.38

From the boundary conditions at the sphere's surface:

\[ \frac{d}{dr} u_r = \frac{d}{d\Theta} u_r = 0 \]  

at \( r = a \)  

A.39

Substituting A.32 through A.34, and A.39 into A.37 and A.38:
\[ \sigma_{rr} = -P_0 + \frac{3\eta \cdot u_{\infty}}{2a} \cos \Theta \]  
\[ \sigma_{r\Theta} = \frac{-3\eta \cdot u_{\infty}}{2a} \sin \Theta \]

Substituting A.40 and A.41 into A.36:

\[
F_D = \left[ 2\pi \int_{0}^{2\pi} \int_{0}^{\pi} \left( -\cos \Theta P_0 + \cos \Theta \cdot \frac{3\eta \cdot u_{\infty}}{2a} \cdots + \frac{3\sin \cdot \theta \cdot \eta \cdot u_{\infty}}{2a} \right)^2 \sin \Theta \, d\Theta \, d\Phi \right]
\]

The solution is Stokes’ Law:

\[
F_D = \left( \frac{3\eta \cdot u_{\infty}}{2a} + \frac{3\eta \cdot u_{\infty}}{2a} \right) a^2 \cdot 2\pi = 6\pi \cdot \eta \cdot a \cdot u_{\infty}
\]
APPENDIX B

DIFFUSION COEFFICIENT OF CO\(_2\) INTO PVAc CALCULATION

This appendix explains the calculation of the diffusion coefficient of CO\(_2\) into PVAc at 24 degrees Celsius and 1 bar. The diffusion coefficient was calculated using the equation for diffusion into a semi-infinite medium.

\[
D^{1/2} = \left(\frac{\pi}{t}\right)^{1/2} \frac{m_{\text{diff.}}}{2AC^3}
\]  

(3.6-31)

The solubility of CO\(_2\) in PVAc at 24 degrees Celsius was approximated from\(^2\):

\[
\ln \frac{1}{K_p} = 6.914 + 2.924 \left(\frac{T_c}{T}\right)^2
\]

(B-1)

where \(1/K_p\) is the solubility (cm\(^3\) CO\(_2\) (STP)/(kg PVAc*MPa)), \(T_c\) is the critical temperature of carbon dioxide\(^3\) equal to 304.128 K and \(T\) is the absolute temperature equal to 297.15 K. The density of CO\(_2\) was approximated as 0.00178 g/cm\(^3\) at standard temperature and pressure using the Span-Wagner equation of state\(^3\). Using (B-1), the solubility of CO\(_2\) in PVAc at 297.15 degrees Kelvin and 0.1 MPa is approximately:

\[
0.00178 \cdot 0.1 \cdot \exp \left[ 6.914 + 2.924 \left(\frac{304.128}{297.15}\right)^2 \right] = 3.83 \text{ g CO}_2 \text{ kg PVAc}
\]

(B-2)

The effect of polymer swelling on solubility at atmospheric pressure was considered negligible for this qualitative calculation based on Sato et. al.’s data comparing the solubility without swelling at 40 degrees Celsius and 0.199 MPa of 5.49 g CO\(_2\)/kg.
PVAc versus the solubility with swelling of 5.51 g CO$_2$/kg PVAc$^2$. The density of PVAc at 24 degrees Celsius$^1$ is approximately 1.19 g/cm$^3$. Therefore, the saturation concentration was approximately 3.83/1000*1.178 = 4.56 x 10$^{-3}$ g CO$_2$/cm$^3$ PVAc.

The sample mass was measured using the ThermoCahn microbalance as 100.435 mg. Unlike the IL measurements, after drawing a vacuum on the sample and filling the balance chamber to 1 bar pressure with CO$_2$, the initial mass reading was 13 micrograms less than the expected mass reading of about 0 mg calculated using (3.6-4).

\[ M(t = 0) - m_{	ext{sample}} - m_s + \rho_g (V_s) = 100.342 - 0.07125 - 100.435 + 1.790 \times 0.084399 = m_{\text{diff}} = -0.013 \text{ mg} \]  

(3.6-4)

The calculated mass of CO$_2$ absorbed equaled zero after about 18 minutes of absorption. The slightly lower value was likely due to reduced polymer density caused by the fragments swelling. The graph of \( \frac{\pi^{1/2} m_{\text{diff}}}{2AC^2} \) versus \( t^{1/2} \) used to calculate the diffusion coefficient is shown in Figure B-1. The diffusion coefficient was approximately 1.67 x 10$^{-8}$ cm$^2$/s, the squared slope of the graph.
Figure B-1 Diffusion coefficient of CO\textsubscript{2} in PVAc at 24 degrees Celsius and 1 bar

The maximum time that the semi-infinite medium approximation is valid was calculated using (3.6-32).

\[ t < \frac{y^2}{16D} \]  

(3.6-32)

The maximum diffusion coefficient was estimated as 2.15 x 10\textsuperscript{-8} cm\textsuperscript{2}/s, the value measured by Sato et. al. at 40 degrees Celsius and 0.329 MPa. The depth, \( y \), of the sample was approximately 0.43 cm. Therefore, the maximum time that the semi-infinite medium approximation was valid was approximately 8950 minutes for this sample.
APPENDIX C

DIFFUSION COEFFICIENT CALCULATIONS

This appendix describes how each diffusion coefficient was calculated. Table C.1 shows diffusion coefficients measured for each IL sample and the standard deviation. Diffusion coefficients were measured following the procedure described in Sections 3.5 and 3.6. Diffusion coefficients for all ILs, except [C₄mim][Tf₂N] at 50 and 70 degrees Celsius, were calculated using the equation for diffusion into a semi-infinite medium.

\[
D^{1/2} = \left( \frac{\pi}{t} \right)^{1/2} \frac{m_{\text{diff}}}{2AC^5}
\]  

(3.6-31)

The diffusion coefficient was equal to the slope on the graph of \( \frac{\pi^{1/2} m_{\text{diff}}}{2AC^5} \) vs \( t^{1/2} \) during short times less than the maximum time valid for the semi-infinite medium approximation given in Table 3.1. Figures C.1 through C.27 show the graphs for each sample used in calculating the average diffusion coefficient. The diffusion coefficient is also shown for data calculated at times through 100 minutes. This diffusion coefficient was used in calculating the maximum time valid for the semi-infinite medium approximation described in section 3.6.2. Equation (3.6-31) indicates that the value of the y-intercept equals zero. It can be seen from Figures C.1 through C.27 that the measured value at the y-intercept is very close to zero. The nonzero value can be explained by the time (less than two minutes) required to
pressurize the balance chamber. Equation (3.6-31) assumes that the saturation concentration is reached at the sample’s surface immediately. The diffusion coefficients for $[\text{C}_4\text{mim}][\text{TF}_2\text{N}]$ at 50 and 70 ºC were calculated using the equation for diffusion into a plane sheet (3.6-48) solved by SigmaPlot. The graphs of the predicted mass absorbed using equation (3.6-49) and the calculated diffusion coefficient are shown in figures C.28 through C.39.
<table>
<thead>
<tr>
<th>IL</th>
<th>Temperature (Celsius)</th>
<th>Date</th>
<th>Diffusion Coefficient $D$ (cm$^2$/s)</th>
<th>Average $D$ (cm$^2$/s)</th>
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</thead>
<tbody>
<tr>
<td>[C$_2$mim][Tf$_2$N]</td>
<td>25</td>
<td>9/23/04</td>
<td>5.16E-06</td>
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<td>[C$_6$F$_3$H$_4$mim][Tf$_2$N]</td>
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<td>2.0E-06</td>
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<td></td>
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<td>[C$_6$mim][PF$_6$]</td>
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<td>7/17/04</td>
<td>2.02E-06</td>
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<td></td>
<td>7/22/04</td>
<td>2.13E-06</td>
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TABLE C.1 (CONTINUED)

<table>
<thead>
<tr>
<th>IL</th>
<th>Temperature (Celsius)</th>
<th>Date Measured</th>
<th>Diffusion Coefficient $D$ (cm$^2$/s)</th>
<th>Average $D$ (cm$^2$/s)</th>
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</thead>
<tbody>
<tr>
<td>$[\text{C}_6\text{mim}][\text{P(C}_2\text{F}_5)_3\text{F}_3]$</td>
<td>25</td>
<td>9/17/04</td>
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<td>9/21/04</td>
<td>4.37E-06</td>
<td></td>
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</tbody>
</table>

*Diffusion coefficient was calculated using the measured saturation concentration

---

Figure C.1  Diffusion coefficient of $[\text{C}_2\text{mim}][\text{TF}_2\text{N}]$ at 25 °C measured 9/23/04
18 min:  
\[ y = 0.0177x + 0.0060 \]
\[ R^2 = 0.9982 \]

100 min:  
\[ y = 0.0164x + 0.0117 \]
\[ R^2 = 0.9997 \]

18 min:  
\[ 0.0177^2 = 3.13 \times 10^{-4} \text{ cm}^2/\text{min} = 5.22 \times 10^{-6} \text{ cm}^2/\text{s} \]

100 min:  
\[ 0.0164^2 = 2.68 \times 10^{-4} \text{ cm}^2/\text{min} = 4.48 \times 10^{-6} \text{ cm}^2/\text{s} \]

Figure C.2 Diffusion coefficient of [C$_2$ mim][Tf$_2$ N] at 25 ºC measured 9/26/04

23 min:  
\[ y = 0.0177x + 0.001 \]
\[ R^2 = 0.9982 \]

100 min:  
\[ y = 0.0170x + 0.0045 \]
\[ R^2 = 0.9997 \]

23 min:  
\[ 0.0177^2 = 3.13 \times 10^{-4} \text{ cm}^2/\text{min} = 5.22 \times 10^{-6} \text{ cm}^2/\text{s} \]

100 min:  
\[ 0.0170^2 = 2.89 \times 10^{-4} \text{ cm}^2/\text{min} = 4.82 \times 10^{-6} \text{ cm}^2/\text{s} \]

Figure C.3 Diffusion coefficient of [C$_2$ mim][Tf$_2$ N] at 25 ºC measured 9/28/04
Figure C.4 Diffusion coefficient of [C₄mim][Tf₂N] at 10 ºC measured 6/17/04

Figure C.5 Diffusion coefficient of [C₄mim][Tf₂N] at 10 ºC measured 6/21/04
Figure C.6 Diffusion coefficient of [C₄mim][Tf₂N] at 10 ºC measured 6/22/04

Figure C.7 Diffusion coefficient of [C₄mim][Tf₂N] at 25 ºC measured 6/8/04
Figure C.8 Diffusion coefficient of $[\text{C}_4\text{mim}]^+\text{[Tf}_2\text{N}]^-$ at 25 °C measured 6/9/04

Figure C.9 Diffusion coefficient of $[\text{C}_4\text{mim}]^+\text{[Tf}_2\text{N}]^-$ at 25 °C measured 6/11/04
Figure C.10 Diffusion coefficient of [C₆mim][Tf₂N] at 25 ºC measured 8/30/04

Figure C.11 Diffusion coefficient of [C₆mim][Tf₂N] at 25 ºC measured 9/2/04
Figure C.12 Diffusion coefficient of \([C_6\text{mmim}][\text{TF}_2\text{N}]\) at 25 °C measured 9/6/04

Figure C.13 Diffusion coefficient of \([C_6\text{mmim}][\text{TF}_2\text{N}]\) at 25 °C measured 9/8/04
Figure C.14 Diffusion coefficient of [C₆mmim][Tf₂N] at 25 °C measured 9/12/04

Figure C.15 Diffusion coefficient of [C₆mmim][Tf₂N] at 25 °C measured 9/14/04
Figure C.16 Diffusion coefficient of [C$_6$mPy][Tf$_2$N] at 25 °C measured 8/16/04

Figure C.17 Diffusion coefficient of [C$_6$mPy][Tf$_2$N] at 25 °C measured 8/23/04
Figure C.18 Diffusion coefficient of [C₆mPy][Tf₂N] at 25 °C measured 8/26/04

Figure C.19 Diffusion coefficient of [C₆F₉H₄mim][Tf₂N] at 25 °C measured 7/28/04
Figure C.20 Diffusion coefficient of [C₆F₆H₄mim][Tf₂N] at 25 ºC measured 8/4/04

Figure C.21 Diffusion coefficient of [C₆F₆H₄mim][Tf₂N] at 25 ºC measured 10/1/04
Figure C.22 Diffusion coefficient of [C₄mim][PF₆] at 25 °C measured 7/16/04

Figure C.23 Diffusion coefficient of [C₄mim][PF₆] at 25 °C measured 7/18/04
Figure C.24 Diffusion coefficient of \([\text{C}_4\text{mim}][\text{PF}_6]\) at 25 ºC measured 7/22/04

Figure C.25 Diffusion coefficient of \([\text{C}_6\text{mim}][\text{P(C}_2\text{F}_5)_3\text{F}_3]\) at 25 ºC measured 9/17/04
Figure C.26 Diffusion coefficient of [C$_6$mim][P(C$_2$F$_5$)$_3$F$_3$] at 25 °C measured 9/19/04

Figure C.27 Diffusion coefficient of [C$_6$mim][P(C$_2$F$_5$)$_3$F$_3$] at 25 °C measured 9/21/04
Figure C.28 Diffusion coefficient of \([C_4\text{mim}][\text{Tf}_2\text{N}]\) at 50 °C measured 6/23/04 calculated using measured \(M_{sat}\)

\[
R^2 = 0.9985 \\
a = 0.04311 \\
D = 8.5E-6 \text{ cm}^2/\text{s}
\]

Figure C.29 Diffusion coefficient of \([C_4\text{mim}][\text{Tf}_2\text{N}]\) at 50 °C measured 6/27/04 calculated using measured \(M_{sat}\)

\[
R^2 = 0.9917 \\
a = 0.04673 \\
D = 1.0E-5 \text{ cm}^2/\text{s}
\]
Figure C.30 Diffusion coefficient of [C₄mim][Tf₂N] at 50 °C measured 7/1/04 calculated using measured $M_{sat}$

Figure C.31 Diffusion coefficient of [C₄mim][Tf₂N] at 70 °C measured 7/8/04 calculated using measured $M_{sat}$
Figure C.32 Diffusion coefficient of [C4mim][Tf2N] at 70 °C measured 7/12/04 calculated using measured $M_{sat}$

Figure C.33 Diffusion coefficient of [C4mim][Tf2N] at 70 °C measured 7/14/04 calculated using measured $M_{sat}$
Figure C.34 Diffusion coefficient of [C₄mim][Tf₂N] at 50 ºC measured 6/23/04 with $M_{sat}$ calculated from Henry’s constant

$R^2 = 0.9892$
$a = 0.03466$
$D = 6.84E-6$ cm$^2$/s

Figure C.35 Diffusion coefficient of [C₄mim][Tf₂N] at 50 ºC measured 6/27/04 with $M_{sat}$ calculated from Henry’s constant

$R^2 = 0.9544$
$a = 0.03349$
$D = 7.26E-6$ cm$^2$/s
Figure C.36 Diffusion coefficient of [C₄mim][Tf₂N] at 50 ºC measured 7/1/04 with $M_{sat}$ calculated from Henry’s constant

Figure C.37 Diffusion coefficient of [C₄mim][Tf₂N] at 70 ºC measured 7/8/04 with $M_{sat}$ extrapolated from Henry’s constants
Figure C.38 Diffusion coefficient of [C₄mim][Tf₂N] at 70 °C measured 7/12/04 with $M_{sat}$ extrapolated from Henry’s constants

$R^2 = 0.9756$
$a = 0.0471$
$D = 9.71 \times 10^{-6} \text{ cm}^2/\text{s}$

Figure C.39 Diffusion coefficient of [C₄mim][Tf₂N] at 70 °C measured 7/14/04 with $M_{sat}$ extrapolated from Henry’s constants

$R^2 = 0.9887$
$a = 0.06313$
$D = 1.22 \times 10^{-5} \text{ cm}^2/\text{s}$
Extinction coefficients were calculated using the Beer-Lambert law:

\[ A = l C \varepsilon \]  \hspace{1cm} (D.1)

where \( A \) is the absorbance at the maximum wavelength measured on the UV-Visible spectrometer, \( l \) is the distance that light passes through the cuvette equal one centimeter, \( C \) is the molar concentration of IL in water or octanol, and \( \varepsilon \) is the extinction coefficient. Extinction coefficients were calculated graphically by plotting the measured absorbance of at least four concentrations of at least three stock solutions. The extinction coefficient was equal to the average of the slopes on a graph of absorbance versus molar concentration. The following figures show the spectrometric data and calculated extinction coefficients.
Figure D.1  \([\text{C}_2\text{mim}][\text{Tf}_2\text{N}]\) in water extinction coefficient measurement

Figure D.2  \([\text{C}_2\text{mim}][\text{Tf}_2\text{N}]\) in octanol extinction coefficient measurement
Figure D.3 [C$_2$mmim][Tf$_2$N] in water extinction coefficient measurement

Figure D.4 [C$_2$mmim][Tf$_2$N] in octanol extinction coefficient measurement
Figure D.5  $[C_{3}mmim][Tf_{2}N]$ in water extinction coefficient measurement

Figure D.6  $[C_{3}mmim][Tf_{2}N]$ in octanol extinction coefficient measurement
Figure D.7  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ in water extinction coefficient measurement

Figure D.8  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ in octanol extinction coefficient measurement
Figure D.9  

Figure D.10  

165
Stock 1
\[ y = 5595.5x \]
\[ R^2 = 0.9968 \]

Stock 2
\[ y = 5465.2x \]
\[ R^2 = 0.9992 \]

Stock 3
\[ y = 5378.5x \]
\[ R^2 = 0.9963 \]

Figure D.11  \([C_6\text{mmim}][\text{Tf}_2\text{N}]\) in water extinction coefficient measurement

Figure D.12  \([C_6\text{mmim}][\text{Tf}_2\text{N}]\) in octanol saturated with water extinction coefficient measurement
Figure D.13  [C₈mim][Tf₂N] in water extinction coefficient measurement

Figure D.14  [C₈mim][Tf₂N] in octanol extinction coefficient measurement
Figure D.15  [C₈mim][Tf₂N] in octanol saturated with water extinction coefficient measurement
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