IMIDAZOLIUM MAGNETIC IONIC LIQUID SOLUBILITIES IN WATER

by
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ABSTRACT

Magnetic ionic liquids (MILs) are room temperature ionic liquids that exhibit paramagnetic behavior. These liquids have tunable physiochemical properties with proposed applications in separations and drug delivery. It is, therefore, useful to know the solubility and micellar behavior of MILs in aqueous environments. Our group synthesized MILs with a FeCl₄⁻ anion and 1-alkyl-3-methylimidazolium cations and investigated aqueous solubility vs alkyl size (C2 through C10). We measured water solubility (MIL content in water saturated with the MIL) using UV-Vis spectroscopy, total organic carbon (TOC) analysis, and Total Nitrogen (TN) analysis. After observing micellar behavior for C(n)mim[FeCl₄], where n > 6, we investigated the critical micelle concentration (CMC) of these MILs. Finally, we used Linear Free Energy Relationship (LFER) semi-empirical models to correlate the MIL water solubility to the MIL’s molecular volume. In the future, this LFER can predict the solubility of a MIL in water before the MIL is synthesized.
# TABLE OF CONTENTS

- LIST OF FIGURES ................................................................. vi
- LIST OF TABLES ................................................................. vii
- LIST OF ABBREVIATIONS .................................................... viii
- INTRODUCTION ................................................................. 1
- THEORY ................................................................. 4
- EXPERIMENTAL ................................................................. 9
- RESULTS ................................................................. 12
- CONCLUSIONS ................................................................. 16
- BIBLIOGRAPHY ................................................................. 17
LIST OF FIGURES

Figure 1. Response of bmim[FeCl₄] to an external magnet

Figure 2. Structure of Rmim cation

Figure 3. Representation of the various energies involved in dissolution

Figure 4. Reaction Scheme for Synthesis of Rmim[FeCl₄]

Figure 5. Graph of log($C_{iw}^{sat}$) vs molar volume (in mL/mol)

Figure 6. Rmim[FeCl₄] micelle formation

Figure 7. Surface Tension vs Concentration for C(8)mim[FeCl₄]
LIST OF TABLES

Table 1. MILs Used in This Study and Their Abbreviations

Table 2. McGowan Atomic Characteristic Volumes

Table 3. Group Contribution Molar Volumes of MILs

Table 4. Rmim[FeCl₄] solubility in water
LIST OF ABBREVIATIONS

IL: Ionic Liquid
MIL: Magnetic Ionic Liquid
TOC: Total Organic Carbon
TN: Total Nitrogen
CMC: Critical Micelle Concentration
LFER: Linear Free Energy Relationship
Rmim: alkyl-methylimidazolium
Emim: 1-ethyl-3-methylimidazolium
Bmim: 1-butyl-3-methylimidazolium
C(6)mim: 1-hexyl-3-methylimidazolium
C(8)mim: 1-octyl-3-methylimidazolium
C(10)mim: 1-decyl-3-methylimidazolium
ΔG: Change in Free Energy
ΔS: Change in Entropy
ΔH: Change in Enthalpy
\( x_{iw}^{sat} \): aqueous mole fraction of organic compound \( i \) in water
\( y_{iw}^{sat} \): aqueous activity of organic compound \( i \) in water
\( V_{ix} \): molar volume of component \( i \)
DI: De-ionized
INTRODUCTION

Ionic Liquids

Ionic liquids (ILs) are commonly defined as a collection of ions that are liquid at temperatures below 100 °C. Sometimes called molten salts, they are usually composed of bulky organic cations and organic or inorganic cations [1]. ILs have been studied since 1914, when Paul Walden synthesized ethylammonium nitrate, the first reported IL [2]. They commonly exhibit favorable chemical properties such as negligible vapor pressures [3] and wide liquid temperature ranges (from 0°C to 200°C) [4]. Because their physiochemical properties are tunable by selection of a specific cation or anion [5], ILs have applications in drug delivery [6], separations [7], pharmaceutics [8], and as reaction solvents [9].

Magnetic Ionic Liquids

Magnetic ionic liquids (MILs) are a class of the above ILs that possess magnetic properties due to the addition of a ferromagnetic metal to their structure. Unlike nanoparticle ferrofluids, whose magnetism stems from suspended nanoparticles, a MIL’s magnetic properties come from within the cationic or anionic structure [10]. While ILs have been studied since 1914, MILs were not reported until 2004 by Hayashi et al. [11]. Most MILs make use of transition metals with unpaired d orbital electrons, like iron, cobalt, or manganese. These metals give MILs paramagnetic properties, allowing the liquids to respond to an external magnetic field. Figure 1 shows the response of the first
reported MIL, bmim[FeCl₄], to a neodymium magnet, seen below as the fluid is attracted to the magnet and deforms.

![Figure 1. Response of bmim[FeCl₄] to an external magnet][11]

While MILs are only 14 years old, they have already been used or proposed for application in separations [12], [13], [14] membrane science [1], catalysis [15], and drug delivery [6]. Many of the proposed applications in separations or drug delivery consist of MILs contacting an aqueous environment. Data on the behavior of MILs in a liquid-liquid system with water is necessary for the use of MILs in many of the above applications and is also important for evaluating their environmental impact [16]. Keyes and Scovazzo [17], Freire et al. [18], and Kurbia et al. [16] investigated the mutual solubilities of water and ILs, but there exists little data on the water solubility of MILs. Our group, therefore, decided to investigate the water solubility of imidazolium magnetic ionic liquids to provide quantitative data for this class’ behavior in an aqueous environment.

We selected alkyl-methylimidazolium (Rmim) as the cation in our MILs, whose structure is in Figure 2. The reason for the selection of this cation was twofold. We believed that Rmim would be less water soluble than other common organic cations like ammonium, which would be favorable in further research into liquid/liquid extraction from water using MILs. We also hoped that Rmim’s aromatic ring structure
would make it a better aromatic extraction agent than an ammonium cation-MIL. We selected tetrachloroferrate(III) (FeCl₄⁻) anion for this study since it was known to be a paramagnetic anion [11], and its precursor (iron chloride hexahydrate) is easily obtained. Table 1 shows each MIL that we synthesized and measured, as well as their molecular weight and abbreviation used in this paper.

**Table 1. MILs Used in This Study and Their Abbreviations**

<table>
<thead>
<tr>
<th>MIL abbreviation</th>
<th>MIL chemical name</th>
<th>MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emim[FeCl₄]</td>
<td>1-ethyl-3-methylimidazolium tetrachloroferrate(III)</td>
<td>308.82</td>
</tr>
<tr>
<td>Bmim[FeCl₄]</td>
<td>1-butyl-3-methylimidazolium tetrachloroferrate(III)</td>
<td>336.87</td>
</tr>
<tr>
<td>C(6)mim[FeCl₄]</td>
<td>1-hexyl-3-methylimidazolium tetrachloroferrate(III)</td>
<td>364.92</td>
</tr>
<tr>
<td>C(8)mim[FeCl₄]</td>
<td>1-octyl-3-methylimidazolium tetrachloroferrate(III)</td>
<td>392.98</td>
</tr>
<tr>
<td>C(10)mim[FeCl₄]</td>
<td>1-decyl-3-methylimidazolium tetrachloroferrate(III)</td>
<td>421.03</td>
</tr>
</tbody>
</table>

Literature contains several methods for measuring the water solubility of ILs. UV-Vis spectroscopy is a proven technique that is known to be successful in quantifying the concentration of imidazolium compounds in water solutions [19]. The visible method adds pure water to an IL until the IL visibly disappears, but is not often used due to its
tedious nature [20]. Karl Fischer titrations determine the water content of a mixture, which can then be subtracted from the total mixture to give the IL content. However, these can often give significant errors [21]. Total Organic Carbon (TOC), and similarly Total Nitrogen (TN), analysis accurately measures the carbon or nitrogen in a sample and is accurate for determining IL content in water [17]. We used several of the above methods the measure the water solubility of our samples: UV-Vis spectroscopy, TOC analysis, and TN analysis. The results from each of these instruments were in reasonable agreement and will be discussed in full later in this paper.

THEORY

Water Solubility Basics

Consider a pure water phase that is brought into contact with a pure, water-immiscible organic liquid at a certain temperature and pressure. Even though these two phases do not form a continuous mixture, some organic molecules will leave the organic phase and dissolve in the water phase, and some water molecules will do the same in the organic phase [22]. When the net movement of particles from one phase to another reaches a constant, the two phases are in equilibrium. At this point, the number of organic molecules in the water phase has reached a maximum. This maximum concentration of organic molecules in the water phase is the water solubility of the organic compound [22]. The water solubility of an organic compound, and specifically a MIL, is a thermodynamic consideration that is guided by the molecule’s size and polarity [17]. In order for an organic molecule to dissolve in water, the interactions (bonds) between water
molecules and the pure organic liquid must first be broken, and a cavity formed in the water solution. The organic molecule is then inserted into this solute cavity and surrounded by water molecules [22]. The size of an organic molecule affects its ability to be inserted into the cavity, while the polarity of the molecule affects the bonding interactions between the polar water molecules and the largely non-polar organic molecule. A visual representation of this process is given in Figure 3, from Schwarzenbach’s Environmental Organic Chemistry [22].

Figure 3. Representation of the various energies involved in dissolution [22]
The total energy required to perform this process is described by the free energy of dissolution, or $\Delta G$, given in equation 1:

$$\Delta G = \Delta H - T \Delta S$$  \hspace{1cm} (1)$$

where $\Delta G$ is the free energy of solution, $\Delta H$ is the enthalpy of solution, $T$ is temperature, and $\Delta S$ is the entropy of solution. As seen in Figure 3 and equation 1, the free energy of dissolution is dependent on the enthalpy ($\Delta H$) associated with the breaking and reforming of bonds, and the entropy ($\Delta S$) associated with inserting an organic molecule into the water cavity. The $\Delta G$ of dissolution can also be described by the following relationship:

$$\Delta G^{sat} = RT \ln[x_{iw}^{sat} \gamma_{iw}^{sat}]$$  \hspace{1cm} (2)$$

where $R$ is the ideal gas constant, $T$ is temperature, $x_{iw}^{sat}$ is the aqueous mole fraction solubility of an organic liquid, and $\gamma_{iw}^{sat}$ is the aqueous activity coefficient of the organic compound in water. For a pure liquid compound, $\gamma_{iw}^{sat}$ is a function of the size and polarity of the compound. When the two-component mixture of organic compound and water reaches equilibrium, $\Delta G = 0$. This allows Equation 2 to be simplified and written as follows:

$$RT \ln x_{iw}^{sat} = -RT \ln \gamma_{iw}^{sat}$$  \hspace{1cm} (3)$$

If Equation 3 is applied to a single “class” or type of compounds, and water solubility ($C_{iw}^{sat}$) is substituted for mole fraction, then the above equation can be simplified into a relationship between the water solubility and size of an organic compound, as seen below:

$$\log[C_{iw}^{sat}] = -c \times (size) + d$$  \hspace{1cm} (4)$$
where \( c_{iw}^{sat}(L) \) is the aqueous solubility of organic liquid, \( c \) is the slope parameter for linear model, size is the molecular size of the organic liquid, usually given in units of molar volume \( V_{ix} \), and \( d \) is intercept parameter for linear model.

This linear correlation between molecular size and the logarithmic water solubility is an example of a Linear Free Energy Relationship (LFER) semi-empirical model. The above LFER is taken from Chapter 5 of *Environmental Organic Chemistry* [22], which describes the above process in detail and gives examples of other LFERs. The given LFER shows how the water solubility of an organic changes with variable molecular size but can only be used when the “class” of molecule is kept constant, and the only variance is the subtraction or addition of an alkyl group. It is vital that the type of molecule be constant, since variations in the polarity or type of molecule will affect intermolecular interactions between water and organic liquid. The LFER in this study also assumes a liquid solution with no solid phase MILs or micellar behavior.

*Application to Our MILs*

We used the given LFER to correlate the water solubility of Rmim[FeCl₄] compounds with the molar volume, \( V_{ix} \), of each compound, in the hope that this LFER could be used to predict the water solubility of future MILs before synthesis. As we measured the water solubility of each MIL, we plotted the \( \log(c_{iw}^{sat}) \) vs the molar volume of the compound and developed a linear model.

The solute molar volume can be either the intrinsic molar volume (the molecular weight divided by the experimentally determined density), or the group contribution molar volume, calculated from experimentally determined molar volume constants [17]. Our
The group decided to use the group contribution method, since the intrinsic molar volume depends on an experimental density that we would have to determine for each MIL. We calculated the group contribution molar volume using the McGowan characteristic volumes found in literature [23], and the method found in Chapter 5 of Environmental Organic Chemistry [22]. The McGowan atomic volumes for each element in the synthesized MILs are in Table 2.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Vix (mL/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>16.35</td>
</tr>
<tr>
<td>H</td>
<td>8.71</td>
</tr>
<tr>
<td>N</td>
<td>14.39</td>
</tr>
<tr>
<td>Cl</td>
<td>20.95</td>
</tr>
<tr>
<td>Fe</td>
<td>40.65</td>
</tr>
<tr>
<td>bond</td>
<td>-6.56</td>
</tr>
</tbody>
</table>

In this method, all bonds are considered equal and given a contribution volume of (-6.56) mL/mol. The molecular volume is determined by multiplying each element and bond in the molecular structure of a compound by its characteristic volume and combining these values for a final volume. An example calculation using Emim[FeCl$_4$] appears below in Equation 4:

Formula: C$_6$H$_{11}$N$_2$[FeCl$_4$]

bonds: 23
Carbon = 6
Hydrogen = 11
Nitrogen = 2
Iron = 1
Chlorine = 4
\[ V_{ix} = 23(-6.56) + 6(16.35) + 11(8.71) + 2(14.39) + 40.65 + 4(20.95) = 196.26 \text{ mL/mol} \] (5)

The molecular volumes for each MIL used in this study, calculated by this method, are in Table 3.

**Table 3. Group Contribution Molar Volumes of MILs**

<table>
<thead>
<tr>
<th>MIL</th>
<th>Formula</th>
<th>bonds</th>
<th>Vix (mL/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emim[FeCl(_4)]</td>
<td>C(<em>6)H(</em>{11})N(_2)[FeCl(_4)]</td>
<td>23</td>
<td>196.26</td>
</tr>
<tr>
<td>Bmim[FeCl(_4)]</td>
<td>C(<em>8)H(</em>{15})N(_2)[FeCl(_4)]</td>
<td>29</td>
<td>224.44</td>
</tr>
<tr>
<td>C(6)mim[FeCl(_4)]</td>
<td>C(<em>{10})H(</em>{19})N(_2)[FeCl(_4)]</td>
<td>35</td>
<td>252.62</td>
</tr>
<tr>
<td>C(8)mim[FeCl(_4)]</td>
<td>C(<em>{12})H(</em>{23})N(_2)[FeCl(_4)]</td>
<td>41</td>
<td>280.8</td>
</tr>
<tr>
<td>C(10)mim[FeCl(_4)]</td>
<td>C(<em>{14})H(</em>{27})N(_2)[FeCl(_4)]</td>
<td>47</td>
<td>308.98</td>
</tr>
</tbody>
</table>

**EXPERIMENTAL**

**Instruments and Materials**

De-ionized (DI) water with a resistivity of 18.3 MΩ-cm was used throughout the process. The water solubility of MILs was measured using a Shimadzu TOC-L/TNM-L total organic carbon/total nitrogen analyzer and a ThermoFisher Scientific Evolution 201 UV-Vis Spectrophotometer. The cuvettes used in the spectrophotometer were VWR quartz spectrophotometer cells. A ThermoFisher Scientific MaxQ 2000 orbital shaker was used in the solubility measurement procedure. A Heildolph Hei-VAP Rotary Evaporator was used in MIL purification. An Atteness Sigma 701 Force Tensiometer with Titronic 300 solvent dispensers and a platinum Du Nouy ring was used for CMC measurements.
Table 1 lists the MILs synthesized in this study with their abbreviations and molecular weights. These MILs were synthesized using the following materials: 1-ethyl-3-methylimidazolium chloride (CAS 65039-09-0, Sigma Aldrich, >95%), 1-butyl-3-methylimidazolium chloride (CAS 79917-90-1, Sigma Aldrich, >95%), 1-hexyl-3-methylimidazolium chloride (CAS 171058-17-6, Sigma Aldrich, >97%), 1-methyl-3-n-octylimidazolium chloride (CAS 64697-40-1, Alfa Aesar, 97%) 1-decyl-3-methylimidazolium chloride (CAS 171058-18-7, Sigma Aldrich, >96%), iron(III) chloride hexahydrate (CAS 10025-77-1, Sigma Aldrich, >97%).

The standard solutions for the TOC/TN analyzer were made from the following materials: sodium bicarbonate (CAS 144-55-8, Sigma Aldrich, 99.5%), sodium carbonate (CAS 497-19-8, Sigma Aldrich, 99%), potassium nitrate (CAS 7757-79-1, Sigma Aldrich, 99%), and potassium hydrogen phthalate (CAS 877-24-7, Sigma Aldrich, 99.95%).

**Procedures**

**Synthesis of Rmim[FeCl₄]**: The following synthesis method is an adaptation of the procedure for MIL preparation found in literature [24, 25]. Equimolar amounts of Rmim[Cl] and iron(III) chloride hexahydrate (both solids) were added to a flask and stirred under slight heat (30 °C) until the mixture was entirely liquid. The reaction scheme for the synthesis is in Figure 4.
A two-phase mixture developed between the MIL and water after stirring ceased. The organic phase was isolated using a separatory funnel and placed on a rotary evaporator at 10 Torr and 40°C. The recovered MIL was purified by washing the MIL with DI water, allowing a two-phase mixture to develop, and placing the separated organic phase on the rotary evaporator under the same conditions given above. A total of three rinses with water were performed, each consisting of vigorous hand shaking for >3 min.

**Measurement of MIL Water Solubility:** The following is a Shake Flask procedure used to measure the solubility of MILs in water. This procedure is based upon the measurement procedure of Atanassova et al. [26]. Equivolume amounts of MIL and DI water were added to a glass vial and shaken by hand for <3 min, then allowed to separate into a two-phase mixture. The two phases were then equilibrated by placing on a ThermoFisher Scientific MaxQ 2000 orbital shaker and shaking for 24 hours at 100 rpm. The orbital shaker established a gentle circular motion that accelerated the achievement of equilibrium while minimizing the formation of suspended liquid phases [17]. The mixture was then centrifuged for 2 min at 5000 rpm to induce phase separation. An aliquot was then removed from the water phase for testing in TOC/TN and UV-Vis. The above procedure was performed in triplicate to analyze the standard error of the procedure.
**Total Organic Carbon and Total Nitrogen Testing:** The following procedure for TOC/TN testing was adapted from Keyes and Scovazzo [17]. A calibration curve for TOC analysis was developed using stock solutions of potassium hydrogen phthalate, while potassium nitrate was used to develop the curve for TN analysis. Acid water (1 drop of phosphoric acid per 100 mL water) was used to ensure a clean line between samples. The TOC analyzer measured the total organic carbon in a sample, in mg/L. The fraction of carbon in the MIL was found using the number of carbons in the compound and the molecular weight of Carbon and the MIL, seen in Equation 5.

\[ f_c = \frac{MW_C \times C_n}{MW_{MIL}} \]  

(6)

Where \( f_c \) is the fraction of carbon in the MIL, \( MW_C \) is the molecular weight of carbon, \( MW_{MIL} \) is the molecular weight of the MIL, and \( C_n \) is the number of carbons in the MIL. The total organic carbon, in mg/L, was then divided by \( f_c \) to yield the concentration of MIL in the water sample, in mg/L. This value, Equation 6, is the water solubility of an MIL.

\[ C_{iw}^{sat} = \frac{TOC}{f_c} \]  

(7)

where \( C_{iw}^{sat} \) is the water solubility of the MIL in mg/L, TOC is the total organic carbon, in mg/L, and \( f_c \) is the fraction of carbon in the MIL.

The TN analyzer used the same procedure and equations given above but substituted TN for TOC and fraction of nitrogen \( (f_n) \) for fraction of carbon.
**UV-Vis Spectrophotometer Testing:** The following procedure is a method for measuring the solubility of MILs in water using a UV-Vis Spectrophotometer. A UV-Vis calibration curve for each MIL was developed using a serial dilution of a stock solution of the MIL. DI water was the solvent used in the dilution of stock solutions and measured samples. The concentration of MIL in water was then measured by correlating these known concentrations of MIL with the unknown concentration of the MIL aliquot taken from the water solution, described above in *Measurement of MIL Water Solubility*.

**CMC Measurements:** The following procedure is a method for the measurement of the CMC of MILs using a Du Nouy ring on a force tensiometer. The tensiometer vessel was cleansed using ethanol and DI water prior to use. The platinum ring was also cleansed with DI water and ethanol and heated over a Bunsen burner flame until red hot. DI water was used as the solvent in preparation of the MIL and for tensiometer dilution. A concentrated solution (800 mM) of MIL was prepared and added to the tensiometer vessel. The surface tension of the solution was measured, then the solution was diluted with a set amount of water and again measured for surface tension. This dilution and measurement was repeated until the surface tension of the solution reached 99% of the value of pure water. This is the reverse of the standard Du Nouy ring procedure and resulted from working with a limited amount of water immiscible MIL. The CMC of the MIL is found by analyzing the plot of surface tension vs solution concentration. This plot has two distinct sections: first, the reduction of surface tension with increasing MIL concentration, followed by a plateau of constant surface tension with increasing MIL concentration. The CMC is obtained by drawing a linear regression line in each of the two sections, and finding the CMC at the intersection of the two lines.
RESULTS

Water Solubility

Table 4 lists the water solubility of the tested MILs using TOC analysis, TN analysis, and UV-Vis spectroscopy.

<table>
<thead>
<tr>
<th>MIL</th>
<th>TOC</th>
<th>TN</th>
<th>UV-Vis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emim[FeCl₄]</td>
<td>1.52 ± 0.02</td>
<td>1.65 ± 0.04</td>
<td>1.40 ± 0.01</td>
</tr>
<tr>
<td>Bmim[FeCl₄]</td>
<td>1.08 ± 0.04</td>
<td>1.19 ± 0.03</td>
<td>1.10 ± 0.03</td>
</tr>
<tr>
<td>C(6)mim[FeCl₄]</td>
<td>0.89 ± 0.03</td>
<td>0.93 ± 0.04</td>
<td>0.91 ± 0.04</td>
</tr>
<tr>
<td>C(8)mim[FeCl₄]</td>
<td>0.92 ± 0.02</td>
<td>0.96 ± 0.05</td>
<td>0.90 ± 0.03</td>
</tr>
<tr>
<td>C(10)mim[FeCl₄]</td>
<td>0.98 ± 0.02</td>
<td>1.02 ± 0.04</td>
<td>0.92 ± 0.07</td>
</tr>
</tbody>
</table>

As seen in Table 4, the values for the $C_{iw}^{sat}$ of Rmim[FeCl₄] range from 1.65 M to 0.89 M. These values are up to 3000 times more water soluble than imidazolium ILs with Tf₂N instead of FeCl₄ as the counter-ion, such as C(10)mim[Tf₂N] [17]. This high water solubility makes Rmim[FeCl₄] an unlikely agent for liquid-liquid extraction (LLE) of compounds from water, since a large amount of the MIL would dissolve in the water. The above data also shows the importance of this study; instead of adopting a trial-by-error method for finding the best extraction agent in an LLE, groups can use water solubility data as a design constraint in LLE’s.

LFER Analysis

As described in the Theory section, our group used a LFER to correlate the water solubility of the measured MILs with their group contribution molar volume. Holding the class of MIL constant, the water solubility of the MILs in this study should decrease
linearly with increasing molar volume. This is because their relative “size” and nonpolar character is increasing, making it more difficult to insert into the solute cavity. Figure 5 shows a graph of the log($C_{iw}^{sat}$) vs the molar volume (in mL/mol) for each MIL.

![Graph of log($C_{iw}^{sat}$) vs molar volume (in mL/mol)](image)

**Figure 5. Graph of log($C_{iw}^{sat}$) vs molar volume (in mL/mol)**

Figure 5 shows that the log($C_{iw}^{sat}$) of Rmim[FeCl$_4$] initially decreases linearly with increasing molar volume. The first three MILs in the above graph (Emim[FeCl$_4$], Bmim[FeCl$_4$], and C(6)mim[FeCl$_4$]) decrease linearly by the following equation:

$$ y = -0.0072 \cdot x + 0.7379 $$

(8)

where $y$ is log($C_{iw}^{sat}$) and $x$ is molar volume in mL/mol. The $R^2$ for this linear fit is 0.9899. This $R^2$ verifies that the LFER is valid for the three MILs and could be used to predict the water solubility of C(n)mim[FeCl$_4$], where $0 < n \leq 6$. This LFER could be
used to correlate other MILs in the future, and with sufficient data could predict the water solubility of MILs before they are synthesized.

**Micellar Behavior**

While these first three MILs follow a linear relationship, the next two compounds (C(8)mim[FeCl₄], C(10)mim[FeCl₄]) show a positive deviation from the linear trend, as seen in the last two groupings of Figure 5. Our group theorizes that this diversion is the result of micelle formation. As the alkyl chain in Rmim[FeCl₄] increases in length, the nonpolar character and size of the molecule is large enough for the MIL to behave like a surfactant, and to form a micelle like that of Figure 6.

![Figure 6. Rmim[FeCl₄] micelle formation](image)

Brown et al. [27] found a critical micelle concentration (CMC) of 40.6 mM for C(10)mim[FeCl$_4$], well below the compound’s solubility concentration of 0.97 M as given in Table 4. While this data verifies that C(10)mim[FeCl$_4$] forms micelles, there exists no data on the CMC of C(8)mim[FeCl$_4$]. Our group therefore decided to investigate the CMC of this MIL using a surface tensiometer and the procedure given in the Procedures section in this paper. The results of the surface tension measurements can be seen in Figure 7.

![Figure 7. Surface Tension vs Concentration for C(8)mim[FeCl$_4$]](image)

The above graph of the surface tension of C(8)mim[FeCl$_4$] has the two distinct sections indicative of a surfactant. At low concentrations, the surface tension of the solution is close to that of pure water (72.8 mN/m) and decreases with increasing MIL concentration. Surface tension continues to follow this trend until the concentration reaches approximately 0.1 M. After this point the surface tension fluctuates up to 40
mN/m at 0.5 M and down to 37 mN/m at 0.7 M. This fluctuation is consistent with graphs of impure surfactants [28]. Impurities can cause a “dip” in the graph and shift the CMC of the surfactant, as seen in Figure 7, and make the CMC difficult the quantitatively determine. The dip seen in the graph prevented us from determining the exact CMC of pure C(8)mim[FeCl₄], but this graph qualitatively shows that this MIL exhibits micellar behavior. These results, along with those found by the Brown group for C(10)mim[FeCl₄], prove that the plateau seen in Figure 5 is the result of micelles forming. The LFER in this paper assumes that equilibrium is occurring between two liquid phases: MIL and water. The micelles that form in these MIL’s introduce an additional phase into the equilibrium, causing a positive diversion from the linear LFER [17], as seen in Figure 5. This diversion is a reminder that proper understanding of LFERs is necessary for application.

CONCLUSIONS

The MILs in this study are of the Rmim[FeCl₄] class, and were found to have water solubilities of up to 1.65 M. Their high solubility makes this class of MILs unsuitable for an aqueous extraction and shows the importance of establishing a known water solubility for extraction agents before the design of an experiment or process. A LFER was used to correlate the water solubility with molecular volume, and was successful with alkyl chains up to C(6)mim[FeCl₄]. As the size of the alkyl chain increased, the water solubility decreased to a minimum value of 0.89 M for C(6)mim[FeCl₄], until micellar behavior caused a plateau at ~0.9 M.
The similarity between the values for each instrument used in the measurement of water solubility and the strong LFER correlation (R^2 = 0.9899) are proof that the TOC Analysis, TN Analysis, and UV-Vis spectroscopy methods given here are valid for the measurement of MIL water solubility.

Further research on this subject would consist of evaluation of other elements like Manganese (Mn) or Dysprosium (Dy) as the metal in the structure of an MIL, to see if they would be more suitable as an aqueous extraction agent. While the data found in this study and elsewhere [17] prove that LFERs can successfully correlate water solubility and molecular size, further research into other classes of MILs would be useful in establishing known LFER parameters for the prediction of water solubility before synthesis of an MIL.
BIBLIOGRAPHY


