Effect of Water on Removal Efficiency of Sulfur-Containing Compounds from Crude Oil Models Using Ionic Liquids

by

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CERTIFICATION OF APPROVAL

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Approved by,

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Project Supervisor

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December 2009

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

NURUL NADIAH BINTI NOOR AZLI

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ABSTRACT

The objective of the project is to determine the effect of water on sulfur-compounds removal efficiency of ionic liquids from crude oil models using ionic liquids.

Six types of Ionic Liquids (ILs) were employed:

- Bmim $OcSO_4$ (1-butyl-3-methylimidazolium octylsulfate)
- Bmim OTf (1-butyl-3-methylimidazolium trifluoromethanesulfonate)
- Hmim NTf_2 (1-hexyl-3-methylimidazolium bis {(trifluoromethyl) sulfonyl} amide)
- Mmim DMP (1-methyl-3-methylimidazolium dimethylphosphate)
- Emim DEP (1-ethyl-3-methylimidazolium diethyl phosphate)
- Bmim DBP (1-butyl-3-methylimidazolium-dibutyl-phosphate)

All ILs were exposed to the surroundings for four hours, and the water content of each IL were monitored as a fraction of time using Karl-Fisher Titration. The sulfur removal efficiency was also determined.

After four hours of exposure, the water content for all the ionic liquids increased by 36.2%, 43.5%, 211.7%, 396.6%, 487.1%, and 1192.9% for Bmim $OcSO_4$, Bmim DBP, Mmim DMP, Emim DEP, Hmim NTf_2 and Bmim OTf.

After four hours of exposure, all ILs showed that the sulfur removal efficiency decreased by 25.5%, 33.4%, 1.6%, 10.9%, 5.4% and 3.2% for Emim DEP, Hmim NTf_2, Bmim OTf, Bmim $OcSO_4$, Bmim DBP and Mmim DMP.

Bmim OTf although has the highest capacity to absorb water, it displayed the lowest sensitivity to the effect of water on sulfur of water on sulfur removal efficiency. Thus, further work can be done to test on the capability of Bmim Otf to remove sulfur with the presence of water.

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INTRODUCTION

1.1 Problem Statement

Hydrodesulfurization, (HDS) is a catalytic chemical process widely used to remove sulfur in the industry. HDS reaction takes place in a reactor at elevated temperatures ranging from 300^0C to 400^0C and elevated pressure ranging from 30 to 130 bar hydrogen pressure. It is typically in the presence of a catalyst of alumina base impregnated with cobalt and molybdenum. This process produces hydrogen sulfide, (H_2S).

The purpose of removing the sulfur compounds is to reduce the sulfur dioxide (SO_2) emissions that result from the exhaust of automotive vehicles, aircraft, railroad locomotives, ships, gas or oil burning power plants, residential and industrial furnaces, and other forms of fuel combustion.

Hydrogenation is a class of chemical reactions in which the net result is the addition of hydrogen (H_2). Hydrogenolysis is a type of hydrogenation and results in the cleavage of the C-X chemical bond, where C is a carbon atom and X is sulfur, nitrogen (N) or oxygen (O) atom. The net result of a hydrogenolysis reaction is the formation of C-H and H-X chemical bonds. Thus, hydrodesulfurization is a hydrogenolysis reaction. Using ethanethiol (C_2H_5SH), a sulfur compound present in some petroleum products, as an example, the hydrodesulfurization reaction can be simply expressed as:

$$\underset{\text{(Ethanethiol)}}{C_2H_5SH} + H_2 \rightarrow \underset{\text{(ethane)}}{C_2H_6} + H_2S$$

Hydrogen sulfide will then being oxidized catalytically with air into elemental sulfur. However, one of the major drawbacks is some S-compounds such as dibenzothiophene, methyl dibenzothiophene, and 4,6-dimethyl dibenzothiophene are less reactive to HDS. Therefore, extraction or reactive extraction of S-compounds from crude oil could be an alternative to HDS. Ionic liquid which being widely used in the industry, due to its unique characteristic both as extractant and catalyst has been chosen to remove the less reactive S-compounds in the crude oil.

1.2 Objective and Scope of Study

The main objective of this research is to determine the effect of water content on sulfur-compounds removal efficiency from crude oil models using ionic liquids. The project deals mainly with desulfurization process using ionic liquids.

The variables that will be considered:

- Different categories of ionic liquids:

Table 1.1: List of Ionic Liquids Used in the Projects

Nomenclature	Ionic Liquid
Bmim $OcSO_4$	1-butyl-3-methylimidazolium octylsulfate
Bmim OTf	1-butyl-3-methylimidazolium trifluoromethanesulfonate
Hmim NTf_2	1-hexyl-3-methylimidazolium bis {(trifluoromethyl) sulfonyl} amide
Mmim DMP	1-methyl-3-methylimidazolium dimethylphosphate
Emim DEP	1-ethyl-3-methylimidazolium diethyl phosphate
Bmim DBP	1-butyl-3-methylimidazolium-dibutyl-phosphate

- Different exposure time of the ionic liquids to the surroundings (0 hour – 4 hour)

Liquid-liquid Extraction (LLE) using ionic liquid will be conducted on the crude oil models and the efficiency of the process will be determined using CHNS analyzer. Other relevant analytical equipments may be proposed for the purpose.

CHAPTER 2

LITERATURE REVIEW

2.1 Definition of Sulfur

Sulfur or sulphur is the chemical element that has the atomic number 16. It is denoted with the symbol **S**. It is an abundant multivalent non-metal. Sulfur, in its native form, is a yellow crystalline solid. In nature, it can be found as the pure element and as sulfide and sulfate minerals. It is an essential element for life and is found in two amino acids; cysteine and methionine. Its commercial uses are primarily in fertilizers, but it is also widely used in black gunpowder, matches, insecticides and fungicides. Elemental sulfur crystals are commonly sought after by mineral collectors for their brightly colored polyhedron shapes.

Figure 2.1: Lemon Yellow Crystal of Sulfur

Common naturally occurring sulfur compounds include the sulfide minerals, such as pyrite (iron sulfide), cinnabar (mercury sulfide), galena (lead sulfide), sphalerite (zinc sulfide) and stibnite (antimony sulfide); and the sulfates, such as gypsum (calcium sulfate), alunite (potassium aluminium sulfate), and barite (barium sulfate). It occurs naturally in volcanic emissions, such as from hydrothermal vents, and from bacterial action on decaying sulfur-containing organic matter.

2.2 Organic Compounds Containing Sulfur

Many of the unpleasant odors of organic matter are based on sulfur-containing compounds such as methyl mercaptan and dimethyl sulfide. Thiols and sulfides are used in the odoration of natural gas, notably, 2-methyl-2-propanethiol (t-butyl mercaptan). The odor of garlic and "skunk stink" are also caused by sulfur-containing organic compounds.

Not all organic sulfur compounds smell unpleasant; for example, grapefruit mercaptan, a sulfur-containing monoterpenoid is responsible for the characteristic scent of grapefruit. It should be noted that this thiol is present in very low concentrations. In larger concentrations, the odor of this compound is that typical of all thiols, unpleasant.

Sulfur-containing organic compounds include the following (where R, R', and R are alkyl groups such as CH_3):

- Thioethers have the form *R*-S-*R′*. These compounds are the sulfur equivalents of ethers.
- Sulfonium ions have the formula RR'S-'R''', where three groups are attached to the cationic sulfur center. Dimethylsulfoniopropionate (DMSP; $(CH_3)_2S^+CH_2CH_2COO^-$) is a sulfonium ion, which is important in the marine organic sulfur cycle.
- Thiols (also known as mercaptans) have the form R-SH. These are the sulfur equivalents of alcohols.
- Thiolates ions have the form $R\text{-}S^-$. Such anions arise upon treatment of thiols with base.
- Sulfoxides have the form *R*-S(=O)-*R′*. The simplest sulfoxide, DMSO, is a common solvent.
- Sulfones have the form $R\text{-}S(=O)_2\text{-}R'$. A common sulfone is sulfolane $C_4H_8SO_2$.

2.2.1 Dibenzothiophene

Dibenzothiophene ($C_{12}H_8S$) is the organic compound consisting of two benzene rings fused to a centralthiophene ring. This tricyclic heterocycle, and especially its alkyl substituted derivatives occur widely in heavier fractions of petroleum. Dibenzothiophene is prepared by the reaction of biphenyl with sulfur dichloride in the presence of aluminium trichloride.

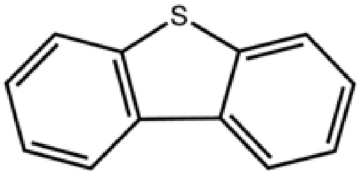


Figure 2.2: Dibenzothiophene Molecular Compound

2.2.2 Benzothiophene

Benzothiophene (C_8H_6S) is an aromatic organic compound and an odor similar to naphthalene (mothballs). It occurs naturally as a constituent of petroleum-related deposits such as lignite tar. Benzothiophene has no household use. It is used primarily in industry and research.

Being a heterocyclic compound, benzothiophene finds use in research as a starting material for the synthesis of larger, usually bioactive structures. It is found within the chemical structures of pharmaceutical drugs such as raloxifene, zileuton, and sertaconazole. It is also used in the manufacturing of dyes such as thioindigo.
Its aromaticity makes it relatively stable, although as a heterocycle, it has reactive sites which allow for functionalization

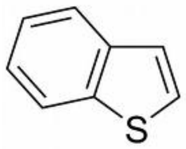


Figure 2.3: Benzothiophene Molecular Compound

2.3 Inorganic Compounds Containing Sulfur

When dissolved in water, hydrogen sulfide is acidic and will react with metals to form a series of metal sulfides. Natural metal sulfides are common, especially those of iron. Iron sulfide is called pyrite. Pyrite can show semiconductor properties. Galena, a naturally occurring lead sulfide, was the first semiconductor discovered and found a use as a signal rectifier in the cat's whiskers of earlycrystal radios.

Polymeric sulfur nitride has metallic properties even though it does not contain any metal atoms. This compound also has unusual electrical and optical properties. This polymer can be made from tetrasulfur tetranitride S_4N_4. Phosphorus sulfides are useful in synthesis. For example, P_4S_{10} and its derivatives Lawesson's reagentand naphthalen-1,8-diyl 1,3,2,4-dithiadiphosphetane 2,4-disulfide are used to replace oxygen from some organic molecules with sulfur. Here are some of the inorganic compounds containing sulfur:

- Thiocyanates contain the SCN^- group. Oxidation of thiocyanoate gives thiocyanogen, $(SCN)_2$ with the connectivity NCS-SCN.
- Sulfides (S^{2-}), a complex family of compounds usually derived from S^{2-}. Cadmium sulfide (CdS) is an example.
- Sulfites (SO_3^{2-}), the salts of sulfurous acid (H_2SO_3) which is generated by dissolving SO_2 in water. Sulfurous acid and the corresponding sulfites are fairly strong reducing agents. Other compounds derived from SO_2 include the pyrosulfite or metabisulfite ion ($S_2O_5^{2-}$).
- Sulfates (SO_4^{2-}), the salts of sulfuric acid. Sulfuric acid also reacts with SO_3 in equimolar ratios to formpyrosulfuric acid ($H_2S_2O_7$).
- Thiosulfates ($S_2O_3^{2-}$). Sometimes referred as thiosulfites or "hyposulfites", Thiosulfates are used in photographic fixing (HYPO) as reducing agents. Ammonium thiosulfate is being investigated as acyanide replacement in leaching gold

2.4 Crude Oil

Crude oil varies greatly in appearance depending on its composition. It is usually black or dark brown (although it may be yellowish or even greenish). In the reservoir it is usually found in association with natural gas, which being lighter forms a gas cap over the petroleum, and saline water which, being heavier than most forms of crude oil, generally sinks beneath it.

Crude oil is a mixture of a very large number of different hydrocarbons; the most commonly found molecules are alkanes (linear or branched), cycloalkanes, aromatic hydrocarbons, or more complicated chemicals like asphaltenes. Each crude oil variety has a unique mix of molecules, which define its physical and chemical properties, like color and viscosity.

The alkanes, also known as paraffins, are saturated hydrocarbons with straight or branched chains which contain only carbon and hydrogen and have the general formula C_nH_{2n+2}. They generally have from 5 to 40 carbon atoms per molecule, although trace amounts of shorter or longer molecules may be present in the mixture.

The cycloalkanes, also known as naphthenes, are saturated hydrocarbons which have one or more carbon rings to which hydrogen atoms are attached according to the formula C_nH_{2n}. Cycloalkanes have similar properties to alkanes but have higher boiling points.

The aromatic hydrocarbons are unsaturated hydrocarbons which have one or more planar six-carbon rings called benzene rings, to which hydrogen atoms are attached with the formula C_nH_n. They tend to burn with a sooty flame, and many have a sweet aroma. Some of the aromatic hydrocarbon are carcinogenic.

Crude oil can be categorized into two, which are, sweet crude oil and sour crude oil.

2.4.1 Sweet Crude Oil

Sweet crude oil is a type of petroleum. Petroleum is considered "sweet" if it contains less than 0.5% sulfur, compared to a higher level of sulfur in sour crude oil, which has more than 0.5% sulfur. Sweet crude oil contains small amounts of hydrogen sulfide and carbon dioxide. High quality, low sulfur crude oil is commonly used for processing into gasoline and is in high demand, particularly in the industrialized nations.

"Light sweet crude oil" is the most sought-after version of crude oil as it contains a proportionally large amount of these fractions that are used to produce gasoline, kerosene, and high-quality diesel. The term "sweet" originated because the low level of sulfur provides the oil with a mildly sweet and pleasant smell.

Some of the producers of sweet crude oil include:

The Appalachian Basin Eastern North America which are Pennsylvania Grade Crude Oil, some Mid-Continent Oil Field United States which are Louisiana Sweet and West Texas Intermediate a.k.a. Texas Sweet Light, The North Sea area of Northern Europe which are Norway and United Kingdom (Brent Crude), North Africa which are Libya and Algeria. Western Africa: Nigeria. Central Africa: Republic of the Congo, Democratic Republic of the Congo and Angola, and The Far East which are China, Indonesia, Malaysia, Brunei, India, Vietnam and Australia.

2.4.2 Sour Crude Oil

It is common to find crude oil containing some impurities such as sulfur. When the total sulfur level in the oil is > 0.5 % the oil is categorized as sour crude.

The impurities need to be removed before this lower quality crude can be refined, thereby increasing the cost of processing. This results in a higher-priced gasoline than that made from sweet crude oil, which has less that 0.5% of sulfur. Thus, sour crude is usually processed into heavy oil such as diesel and fuel oil rather than gasoline to reduce processing cost.

The majority of the sulfur in crude oil occurs bonded to carbon atoms, with a small amount occurring as elemental sulfur in solution and as hydrogen sulfide gas. Sour oil can be toxic and corrosive, especially when the oil contains high levels of hydrogen sulfide. At low concentrations the oil has the smell of rotten eggs, but at high concentrations, the inhalation of hydrogen sulfide could be fatal. At higher concentrations, the hydrogen sulfide can damage the olfactory nerve, rendering the gas effectively odorless and undetectable, while paralyzing the respiratory system.

If exposure is not fatal, its effects on the human body are similar to that of Gulf War Syndrome including chronic fatigue, headaches, dizziness, skin problems, memory problems, birth defects, and a host of breathing problems such as asthma. Such sour crude oil needs to be stabilized by having hydrogen sulfide gas (H_2S) removed from it before being transported by oil tankers for safety reasons.

Major producers of sour crude oil include North America (Alberta, Canada and Mexico), South America (Venezuela and Colombia) and Middle East (Saudi Arabia, Iraq, Kuwait and Iran).

2.5 Ionic Liquids Perspective

For almost a century, the study of molten salts was the near-exclusive domain of electrochemists. However since the early 1990s, there has been growing interest in expanding the sphere of use of certain molten salts – ionic liquids (IL) - to other application as well. It is defined as salts which melt below $100^{o}C$, and which in their molten forms are composed solely of ions, ionic liquids constitute a remarkably promising class of technology useful and fundamentally interesting materials, (Wasserchied et al. , 2003).

ILs have been used as alternatives to classical molecular solvents in a range of fundamentals research and application, including catalysis, synthesis and separations, (Liu et al. , 2005). The extractive desulfurization process using ionic liquids can be a complementary technology for HDS process. Extractive desulfurization is based on the fact those sulfur-containing compounds are more soluble than hydrocarbon in an appropriate solvent, (Alonso et al. , 2008). In this way, remarkable solvation ability and negligible vapor pressure of ILs will make them potential solvents of great interest.

Many ionic liquids are immiscible or only partially miscible with hydrocarbons. So through out this research, this unique characteristics of ionic liquids will provide higher extraction ratios and greater selectivity compared to molecular solvents. The principal focus of these studies are the extraction of refractory sulfur-containing polyaromatics, such as dibenzothiophene and 4,6-dimethyldibenzothiophene from dodecane as a model oil system. The ionic liquids are chosen based on their availability at relatively low cost and environmental impact, (Holbrey et al. , 2008).

The term liquid-liquid extraction (LLE) refers to the distribution of the solute between two immiscible liquid phases in contact with each other. In a solution, the ions interact with solvent molecules. It will provide sufficiently high concentration of the solute with the other solute particles. These interactions play major role in the distribution of a solute between the two liquid layers in liquid-liquid extraction systems, (Rydberg et al. , 2004). Ionic Liquids extraction used this type of LLE to remove sulfur species from the crude oil models.

2.6 Ionic Liquids Features

Ionic liquids are mixture of salts with low melting points (below 100^{o}C). This characteristic has substantial scientific and commercial implications. Similar to table salt, they consist of positively and negatively charged ions, but these anions and cations are larger and more complex. The crystalline structure breaks down easily and the salt becomes liquid, resulting in Ionic Liquids. They have many attractive properties which made them ideal solvents for extraction operations, (Arce et al. , 2007).

ILs has negligible vapor pressure which for this reason, they are called ‘green solvent’, chemical and thermal stability, non-flammability and adjustable miscibility and polarity. They have specific properties that make them indispensable in applications. These properties include, for instance, very good dissolution properties, thermal and electrochemical stability, and reduced risk of fire or explosion due to the barely measurable vapor pressure.

ILs are tuneable, cation and anion can be varied to find the optimum IL for a specific objectives, (Alonso et al. , 2008). Different type of cations and anions, will give different influence to the extracting process. Depending on the ratio of cation/anion IL, it can be Lewis-acidic, neutral or Lewis-basic, (Davis et al. , 2003).

2.7 Influence of Water on the Physical Properties of Ionic Liquids

A group of researchers has conducted a study on the miscibility of IL with water. (Seddon et al. , 2000) The main objective is to determine the effect on their physical properties.

At room temperature, all $[C_n\text{mim}][PF_6]$ and $[C_n\text{mim}][(CF_3SO_2)_2N]$ ionic liquids are insoluble in water, and all halide-, ethanoate-, nitrate-, and trifluoroacetate-based ionic liquids are fully water-soluble. However, ionic liquids based on $[BF_4]^-$ and $[CF_3SO_3]^-$ are positioned somewhere in between. Depending on the alkyl chain length on the cation, they are either fully miscible with water (e.g., $[C_2\text{mim}][BF_4]$ and $[C_4\text{mim}][BF_4]$) or form biphasic systems ($[C_n\text{mim}][BF_4]$, $n > 4$). Thus, the anion has a primary effect on water miscibility and the cation a secondary effect.

1-alkyl-3-methylimidazolium hexafluorophosphate ionic liquids form biphasic systems with water, and are therefore commonly referred to as “hydrophobic” by ionic liquid researchers. This is in fact misleading: Figure 2.4 shows the water-saturation of the so-called hydrophobic ionic liquids $[C_{4\text{–}8}\text{mim}][PF_6]$ and $[C_{6\text{–}10}\text{mim}][BF_4]$, which is a function of the alkyl chain length and the anion. As a rule, the $[PF_6]^-$-based ionic liquids dissolve less water than the $[BF_4]^-$ ionic liquids, and the solubility of water decreases with increasing alkyl chain length. Additionally, the so-called hydrophobic ionic liquids are in fact hygroscopic.

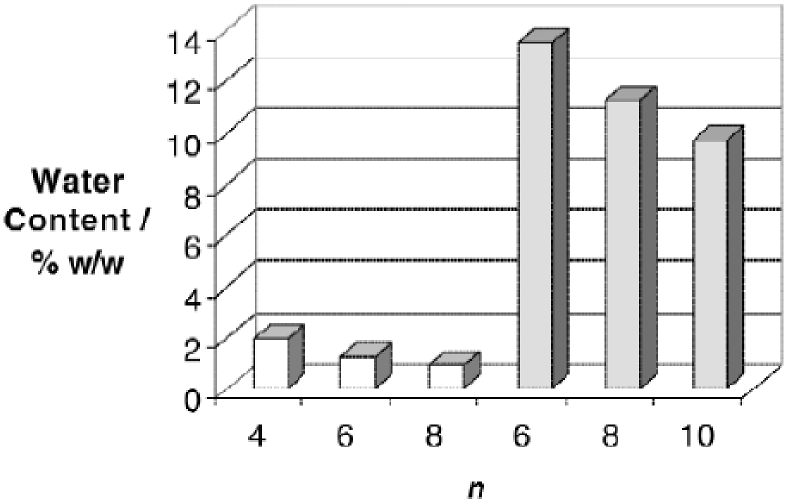


Figure 2.4: Water Content on Saturation at Ambient Temperature (22 °C) for [$C_n$mim][PF_6] (n = 4 to n = 8) (white) and for [$C_n$mim][BF_4] (n = 6 to n = 10) (gray)

2.8 The Effect of Water on the Viscosity of Ionic Liquids

The same group of researchers, (Seddon et al. , 2000) also studied the effect of water on the viscosity of ionic liquids. In general, ionic liquids are miscible with liquids of medium- to high-dielectric constant and immiscible with liquids with low-dielectric constant. For example, [C_4mim][BF_4] is completely miscible with ethanenitrile (ε = 35.94), 2-propenenitrile (ε = 33), methanol (ε = 32.66), dichloromethane (ε = 8.93), or 1,2-dimethoxyethane (ε = 7.2), whereas toluene (ε = 2.38) is only miscible to up to 50 mol % and 1,4-dimethylbenzene (ε = 2.27) up to 25 mol %. The effect of water and other solvents (ethanenitrile, trimethylethanenitrile, 2-propenenitrile, 1-methylimidazole, toluene, 1,4-dimethylbenzene, and 1,2-dimethoxyethane) on the viscosity of [C_4mim][BF_4] and [C_4mim][PF_6] has been investigated.

When the viscosity of the ionic liquid–cosolvent mixtures is plotted against the molar fraction of cosolvent (refer Figure 2.5), the studied solvents appear to have a surprisingly similar effect on the viscosity of the ionic liquid. In fact, a single exponential equation can be fitted to this data, which can be used for estimation of viscosity at 20 °C of such mixtures, with correlation coefficients >0.97.

In other words, $\eta = \eta_s \exp(-x_{cs}/a)$ can be used to predict the viscosity of a reaction mixture as a function of the concentration of the dissolved reactants and/or products, independent of their polarity. In the equation, η_s is the viscosity of the pure ionic liquid at 20 °C, x_{cs} is the mole fraction of the cosolvent and a is a constant with values 0.23 for [C_4mim][BF_4] ($r^2 = 0.98$) and 0.19 for [C_4mim][PF_6] ($r^2 = 0.97$).

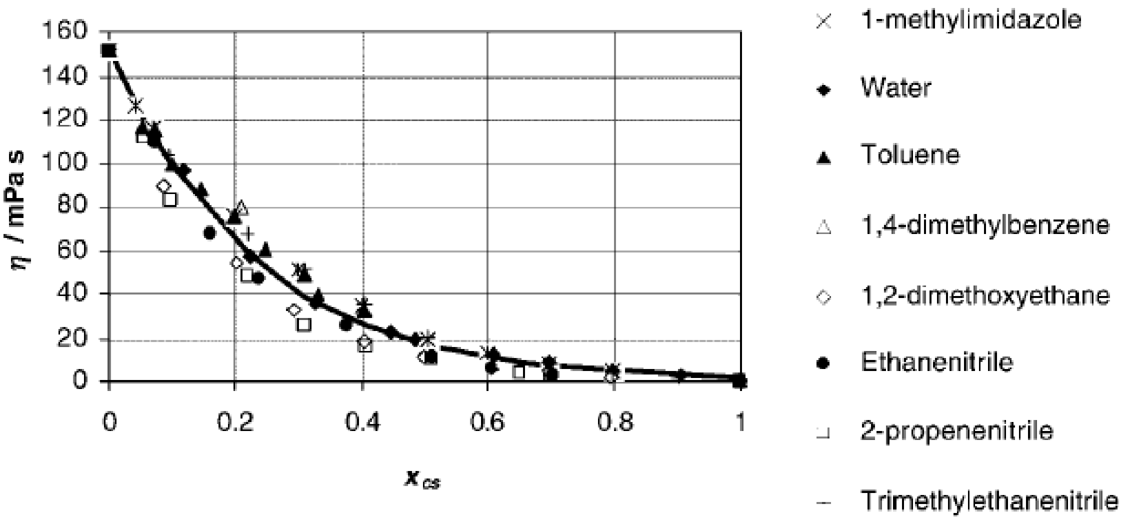


Figure 2.5: Viscosity at 20 °C of cosolvents-[C_4mim][BF_4] mixtures vs. mole fraction of cosolvent; the solid line represents the theoretical fit of these data to eq. 1, $r^2 = 0.98$

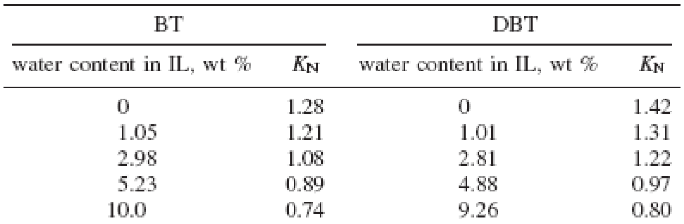
Based on the graph, it shows that the presence of water will reduce the viscosity of the ionic liquids. Interesting water-ionic liquid interactions have been identified and discussed. The structural change at the equimolar concentration of water and ionic liquid indicates the possible formation of a hydrogen-bonded complex with water.

2.9 Effect of Water Content in IL on Sulfur Partition Coefficients

A group of researchers studied the effect of water in IL on the sulfur partition coefficient, K_N, (Gao et al. , 2008). Based on the data shown in Table 2.1, it suggests that the water content in the IL plays an important role in determining the values of the sulfur partition coefficient K_N between [HPy][BF_4] and diesel; even 1% water content in an IL can result in about 8% lowering of extractive ability of [HPy][BF_4] for DBT from diesel.

This implies that, with the increase of water content in an IL, the solubility of sulfur compounds in IL decreases drastically. This also indicates that sulfur compounds dissolved in the used IL can be precipitated by a water dilution process.

Table 2.1: Influence of Water Content in IL on K_N between [HPy][BF_4] and Diesel



BT		DBT	
water content in IL, wt %	K_N	water content in IL, wt %	K_N
0	1.28	0	1.42
1.05	1.21	1.01	1.31
2.98	1.08	2.81	1.22
5.23	0.89	4.88	0.97
10.0	0.74	9.26	0.80

As seen in Figure 2.6, the values of the sulfur partition coefficient K_N between [HPy][BF_4] and diesel reached nearly zero when 80% water was added to the sulfur compound-saturated [HPy][BF_4] system. Therefore, IL saturated with sulfur compounds could be regenerated by water dilution process.

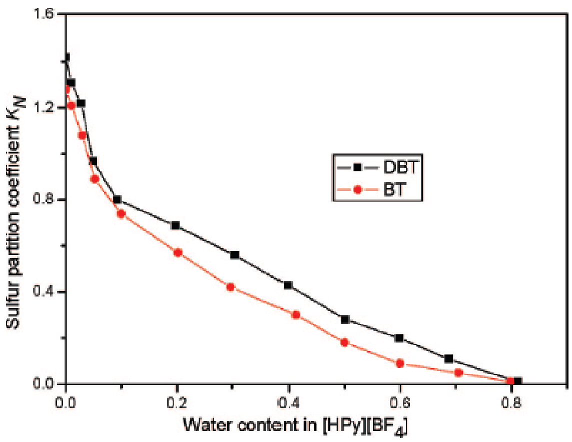


Figure 2.6: Sulfur partition coefficients between [HPy][BF4] and diesel at different water contents.

Both of the group of researchers (Seddon et al. , 2000; Gao et al. , 2008) agreed that water content in IL gives a crucial impact on the efficiency of IL to remove sulfur, and alter its physical properties.

2.10 Partition Ratio, K_D Calculation

The percentage of DBT (or other sulfur compounds) extracted and partition ratio of DBT to the ionic liquid were calculated by difference from the integral of the dibenzothiophene signal using the equation, (Holbrey et al. , 2008):

$$K_D = [\text{DBT}]\text{ionic liquid}/[\text{DBT}]\text{dodecane}$$

$$K_D = \frac{[\text{DBT}]_{\text{IL}}}{[\text{DBT}]_{\text{dodecane}}}$$

which reduces, when the phase volumes are equal, to

$$K_D = [\text{Iinitial}–\text{Idodecane}]/[\text{Idodecane}]$$

$$K_D = \frac{[I_{\text{initial}} - I_{\text{dodecane}}]}{[I_{\text{dodecane}}]}$$

where I is the peak integral analysed by GC-MS.

2.11 Ionic Liquid Characteristic and Performance Analysis

Several methods can be used to determine the water content and the sulfur removal of the IL Water content in ionic liquid could be determined by Karl Fischer Titration. On the other hand, CHNS analyzer is used to investigate the performance of ionic liquid in removing sulfur from model oil.

2.11.1 Karl Fisher Titration

Karl Fischer titration is a classic titration method in analytical chemistry that uses coulometric ovolumetric titration to determine trace amounts of water in a sample. The popularity of the Karl Fischer titration is due to several practical advantages that it holds over other methods of moisture determination, including:

- High accuracy and precision
- Selectivity for water
- Small sample quantities required
- Easy sample preparation
- Short analysis duration
- Nearly unlimited measuring range (1ppm to 100%)
- Suitability for analyzing solid, liquid and gas
- Independence of presence of other volatiles
- Suitability for automation

The most important advantage of Karl Fischer titration method over conventional loss on drying (LOD) thermal methods of moisture determination is its specificity for water. Loss on drying will detect the loss of *any* volatile substance.

2.11.2 CHNS Analyzer

A CHNS Analzer is a scientific instrument which can determine the elemental composition of a sample. The name derives from the three primary elements measured by the device: carbon (C), hydrogen (H), nitrogen (N) and Sulfur (S).

The analyzer uses a combustion process, where the sample is combusted in an oxygen-rich environment at 975° C, to break down substances into simple compounds which are then measured.

This will result in the determination of four elements simultaneously. It works based on the principle of "Dumas method" which involves the complete and instantaneous oxidation of the sample by "flash combustion". The combustion products are separated by a chromatographic column and detected by the thermal conductivity detector (T.C.D.), which gives an output signal proportional to the concentration of the individual components of the mixture.

The resulting reaction products for sulfur are converted to sulfur dioxide. All of the reaction products including nitrogen, carbon dioxide, water, and sulfur dioxide are then separated and detected. It will find the greatest utility in finding out percentages of C, H, N and S in organic compounds.

Key components of CHNS are auto sampler, combustion reactors, chromatographic column, and T.C.D. detector.

CHAPTER 3

METHODOLOGY

3.1 Ionic Liquids Used

Here is the list of ionic liquids used in the experiment:

Table 3.1: List of Ionic Liquids which being used

Nomenclature	Ionic Liquid
Bmim $OcSO_4$	1-butyl-3-methylimidazolium octylsulfate
Bmim OTf	1-butyl-3-methylimidazolium trifluoromethanesulfonate
Hmim NTf_2	1-hexyl-3-methylimidazolium bis {(trifluoromethyl) sulfonyl} amide
Mmim DMP	1-methyl-3-methylimidazolium dimethylphosphate
Emim DEP	1-ethyl-3-methylimidazolium diethyl phosphate
Bmim DBP	1-butyl-3-methylimidazolium-dibutyl-phosphate

3.2 Inspection of Water Content in the Ionic Liquids

1. 10 ml of each ionic liquid is filled up into a bottle.
   Take note: This step is carried out inside a glove bag (Figure 3.1) to make sure no water (from the surroundings) being absorbed into the ionic liquids.

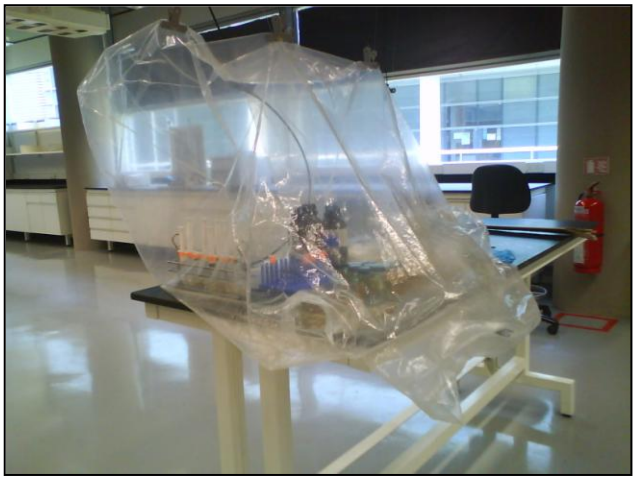


Figure 3.1: Glove Bag

2. All ionic liquids (Figure 3.2) are labeled accordingly.

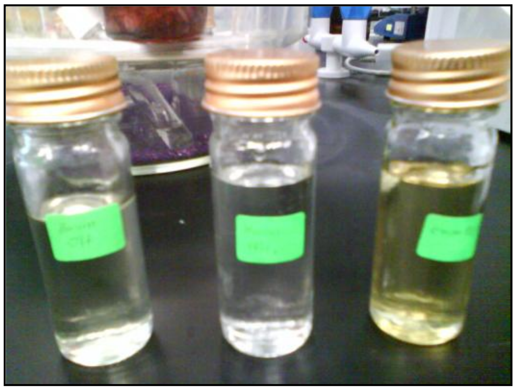


Figure 3.2: (From left) Bmim OTf, Hmim NTf_2 *and Emim DEP*

3. The cap bottles of each ionic liquid are opened for four hour.

4. For each hour, 0.2 ml of ILs are taken by syringe to check the water content by Karl Fisher Titration, (Figure 3.3).

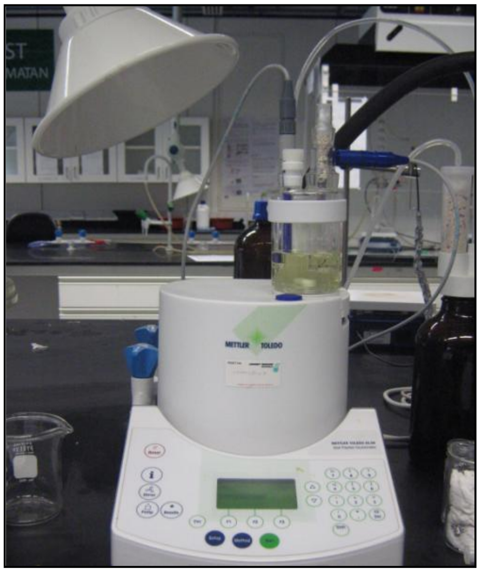


Figure 3.3: Karl-Fischer Titration

5. Mass of the ILs are weighted first, and the temperature and humidity of the surroundings are taken, (Figure 3.4 and 3.5).

Figure 3.4: (From left) Before weighing, After weighing Hmim NTf_2

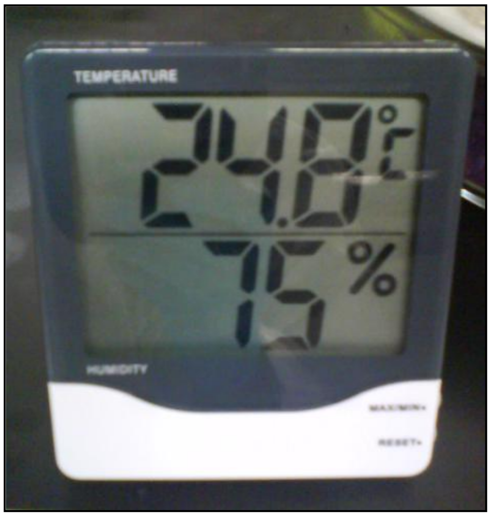


Figure 3.5: Temperature and Humidity of Hmim NTf$_2$

6. 2 ml of each ionic liquid (IL) from the bottle are transferred into a new syringe for each hour for extraction purpose.

7. Reading for each hour is taken, and procedure 1 and 2 are repeated accordingly.

3.3 Extraction and Analysis

1. 2 ml of each ionic liquid (IL) are prepared in a syringe based on previous procedure.

2. All ionic liquids are labeled accordingly

3. 2 ml of 4% Benzothiophene in n-Dodecane (Figure 3.6) is added into each syringe.

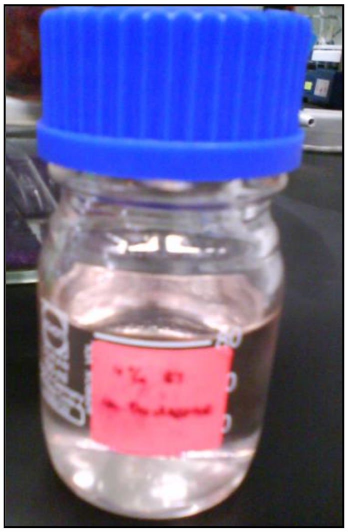


Figure 3.6: 4% Benzothiophene in n-Dodecane

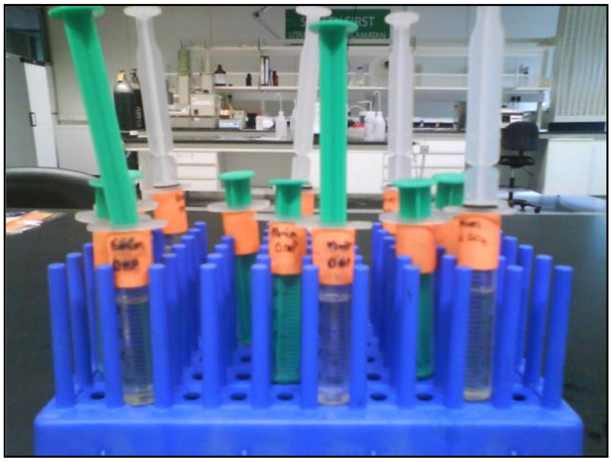


Figure 3.7: Ionic Liquids and 4% Benzothiophene in n-Dodecane in each Syringe

4. All syringes are placed onto the vortex mixer, (Figure 3.8). Each syringe is mixed for 1 minute with 2500 rpm.

Figure 3.8: Vortex Mixer with IL

5. Then, all syringes are centrifuged (Figure 3.9) at 2500 rpm for 1 minute. From this, there are two visible clear phases, which are ionic liquid (at the bottom layer) and model oil (at the top layer).

Figure 3.9: (From left) Centrifuge inside view, Centrifuge front view

6. Each phase is separated into small bottles with label, (Figure 3.10).

Figure 3.10: Separated IL and Model Oil

7. All samples are taken for CHNS (Figure 3.11 and 3.12) analysis.

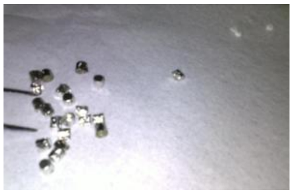


Figure 3.11: CHNS Samples Preparation

Figure 3.12: CHNS Analyzer

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Water Content Analysis

4.1.1 Emim DEP Water Content Analysis

Based on below graph (Figure 4.1), it shows that as the time increasing from zero hour until fourth hour, the water content in Emim DEP increased too. The water content which is initially 2355.7447 ppm at zero hour, increased to 11699.5467 ppm when it reached the fourth hour.

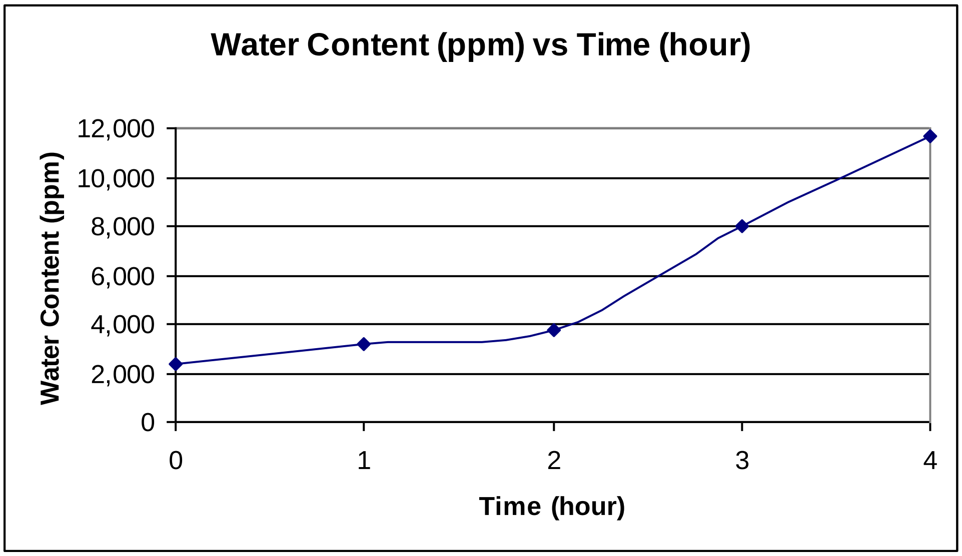


Figure 4.1: Emim DEP Water Content (ppm) vs Time (hour)

4.1.2 Hmim NTf_2 Water Content Analysis

Based on below graph (Figure 4.2), it shows that as the time increasing from zero hour until fourth hour, the water content in Hmim NTf_2 increased too. The water content which is initially 445.1529 ppm at zero hour, increased to 2613.5003 ppm when it reached the fourth hour.

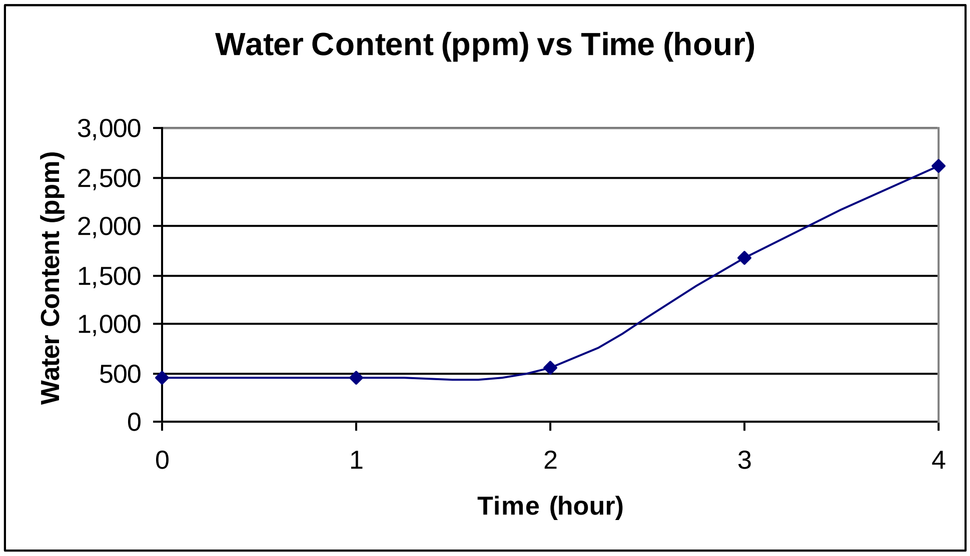


Figure 4.2: Hmim NTf_2 Water Content (ppm) vs Time (hour)

4.1.3 Bmim Otf Water Content Analysis

Based on below graph (Figure 4.3), it shows that as the time increasing from zero hour until fourth hour, the water content in Bmim Otf increased too. The water content which is initially 665.2335 ppm at zero hour, increased to 8600.5533 ppm when it reached the fourth hour.

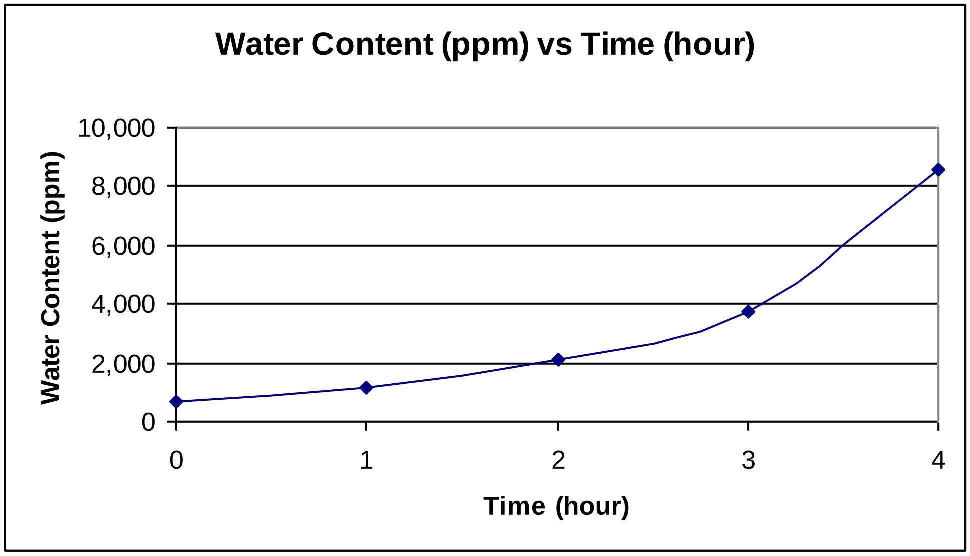


Figure 4.3: Bmim Otf Water Content (ppm) vs Time (hour)

4.1.4 Bmim $OcSO_4$ Water Content Analysis

Based on below graph (Figure 4.4), it shows that as the time increasing from zero hour until fourth hour, the water content in Bmim $OcSO_4$ increased too. The water content which is initially 6514.6330 ppm at zero hour, increased to 8871.9427 ppm when it reached the fourth hour.

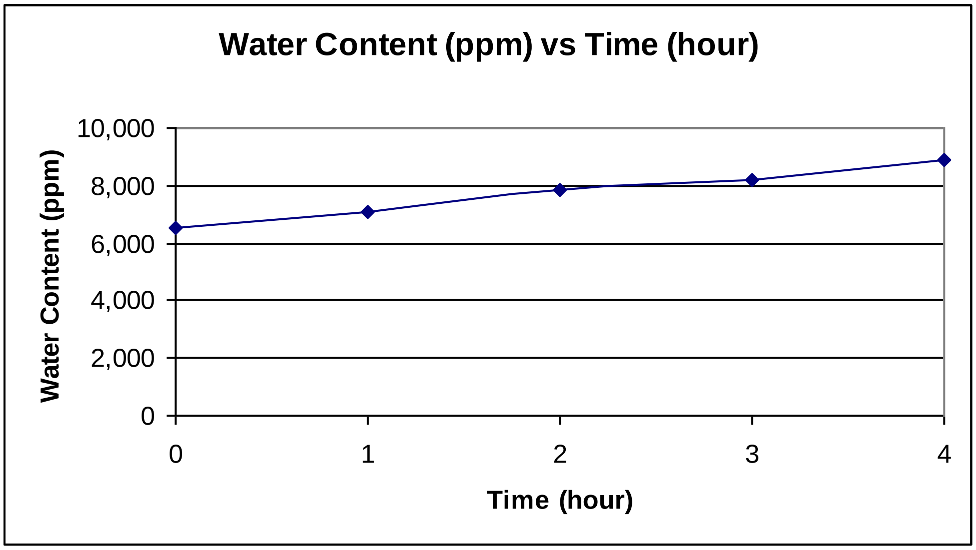


Figure 4.4: Bmim $OcSO_4$ Water Content (ppm) vs Time (hour)

4.1.5 Bmim DBP Water Content Analysis

Based on below graph (Figure 4.5), it shows that as the time increasing from zero hour until fourth hour, the water content in Bmim DBP increased too. The water content which is initially 17402.3333 ppm at zero hour, increased to 24974.0000 ppm when it reached the fourth hour.

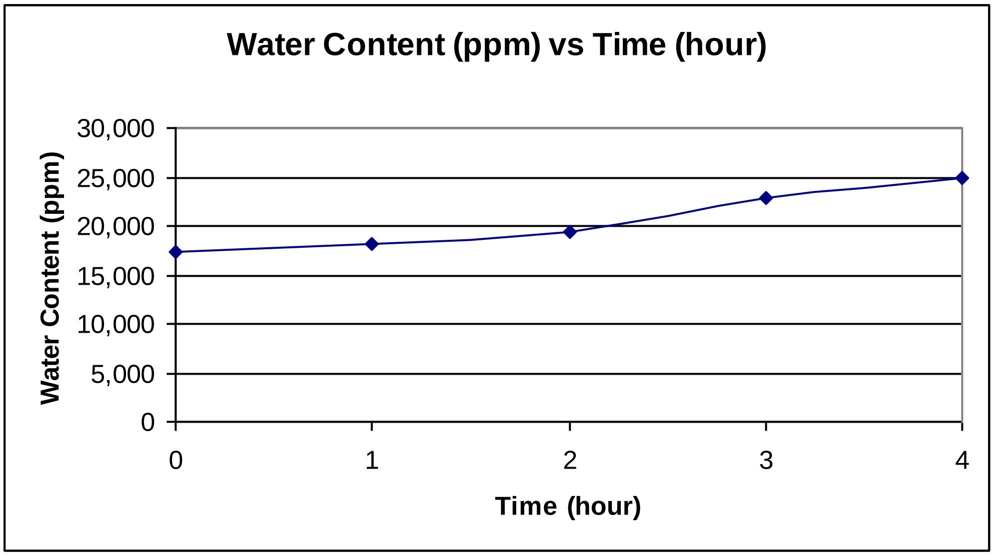


Figure 4.5: Bmim DBP Water Content (ppm) vs Time (hour)

4.1.6 Mmim DMP Water Content Analysis

Based on below graph (Figure 4.6), it shows that as the time increasing from zero hour until fourth hour, the water content in Mmim DMP increased too. The water content which is initially 2985.0500 ppm at zero hour, increased to 9304.8977 ppm when it reached the fourth hour.

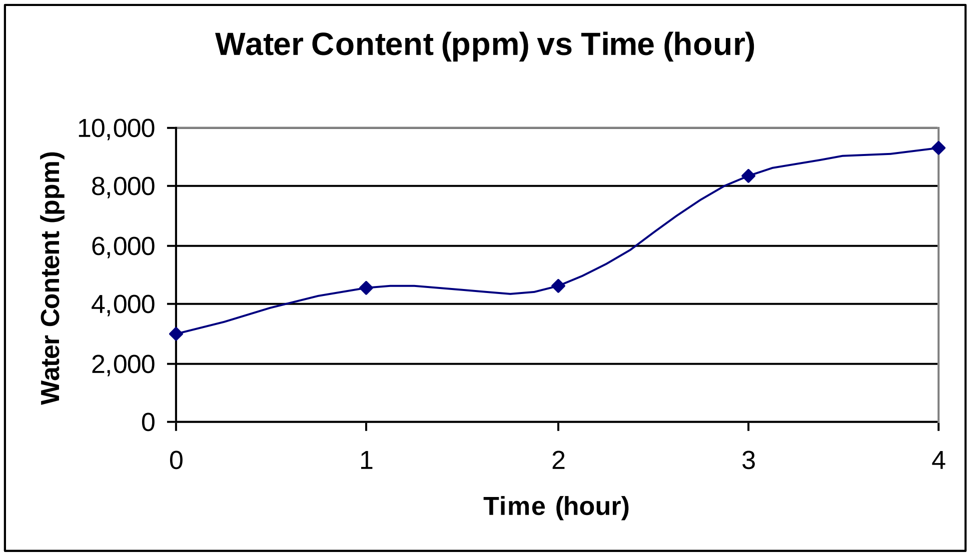


Figure 4.6: Mmim DMP Water Content (ppm) vs Time (hour)

4.1.7 Overall Water Content Analysis

Based on below graph (Figure 4.7), it shows that all ionic liquids will be affected after being exposed to the surroundings. After four hours of exposing, the water content for all the ionic liquids increased. The highest increment shown by Bmim Otf which is 1192.8623%. While for the lowest increment, shown by Bmim $OcSO_4$ with 36.1848%. In the next page, the overall water content increment can be seen.

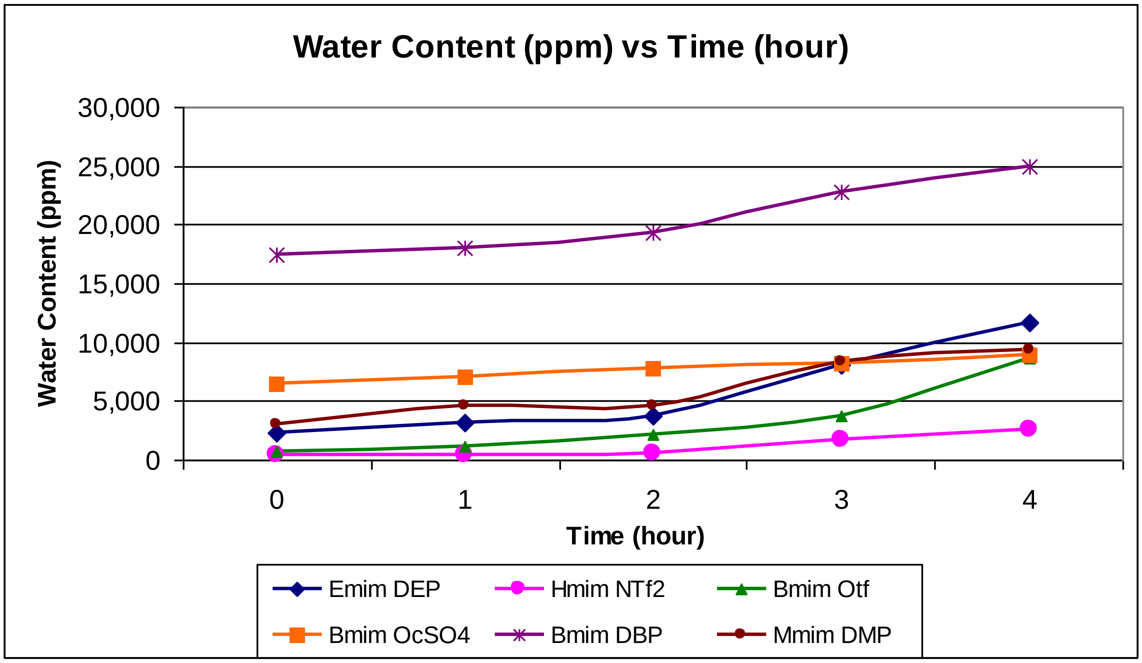


Figure 4.7: Overall Ionic Liquids Water Content (ppm) vs Time (hour)

Sample of calculation of water content increment are shown in Appendix B

Table 4.1: Overall Water Content Increment for each Ionic Liquids in Ascending Orders

Ionic Liquids	**Initial Water Content(ppm)**	**Final Water Content(ppm)**	**Difference (ppm)**	**Percentage Increment (%)**
Bmim $OcSO_4$	6514.6330	8871.9427	2357.3097	36.1848
Bmim DBP	17402.3333	24974.0000	7571.6667	43.50949
Mmim DMP	2985.0500	9304.8977	6319.8477	211.7166
Emim DEP	2355.7447	11699.5467	9343.8020	396.6390
Hmim NTf_2	445.1529	2613.5003	2168.3474	487.1017
Bmim Otf	665.2335	8600.5533	7935.3198	1192.8623

Based on above table (Table 4.1), it showed that the overall water content increase throughout time. It is seen from the table that, even though Bmim $OcSO_4$, Bmim DBP and Bmim Otf are all have the same cation chain which is $[Bmim]^+$ but the anion chain has major impact on the water content. As said in the literature review, (Seddon et al. , 2000) anion chain has major impact on water in ionic liquid compare to cation chain. Bmim Otf has the highest impact on water thus, explains the highest increment of water after 4 hours of exposure.

4.2 Sulfur Removal Efficiency

All ILs are taken to the CHNS analyzer to identify the amount of carbon, hydrogen, nitrogen and sulfur components in a chemical mixture. Fresh model oil with no impurities in it is also examined with CHNS analyzer. This will indicate the initial percentage of sulfur compound. The percentage of sulfur remained in the model oils were examined in order to calculate the amount of sulfur removal. The initial percentage of sulfur content in the fresh model oil is listed as below (Table 4.2):

Table 4.2: Initial Percentage of Sulfur Content in Fresh Model Oil

Model Oils	**Sulfur Percentage (%)**
4% of Benzothiophene in dodecane	3.125
Dodecane without Benzothiophene content	0.026

At the same time, the ionic liquid efficiency of sulfur removal of the ionic liquid can be determined by the above data. This can be done by applying the following equation:

$$\text{Ionic liquid efficiency} = \frac{\text{Initial Sulfur Content (\%)} - \text{Final Sulfur Content (\%)}}{\text{Initial Sulfur Content (\%)}}$$

By using the equation, the performance of the ionic liquid to remove sulfur compounds can be determined. Thus, the comparisons of ionic liquid efficiency at different time from 0th hour until 4th hour are shown below in Table 4.3 and Figure 4.8. Sample of calculations are shown in Appendix C.

Table 4.3: Ionic Liquid Efficiency of Sulfur Species Removal

IL	**Exposure time (hr)**	**Sulfur content in Model Oil (%)**		**% Sulfur Removal**
		Before Extraction	**After Extraction**	
Emim DEP	0	3.125	0.167	**94.66**
	4	3.125	0.767	**75.46**
Hmim NTf_2	0	3.125	0.580	**81.44**
	4	3.125	1.430	**54.24**
Bmim Otf	0	3.125	0.951	**69.57**
	4	3.125	0.985	**68.48**
Bmim $OcSO_4$	0	3.125	1.128	**63.90**
	4	3.125	1.346	**56.93**
Bmim DBP	0	3.125	1.278	**59.10**
	4	3.125	1.377	**55.94**
Mmim DMP	0	3.125	1.014	**67.55**
	4	3.125	1.082	**65.38**

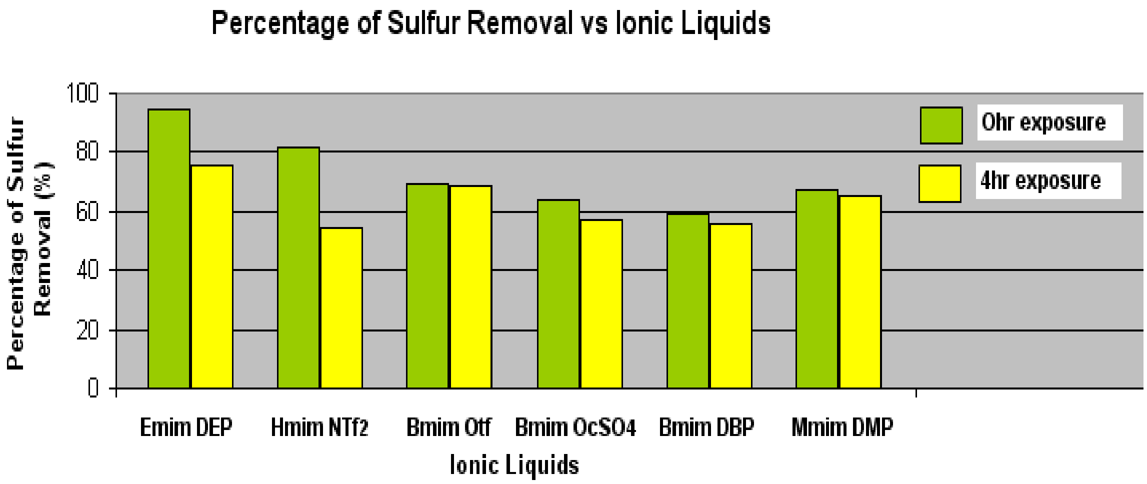


Figure 4.8: Comparison of Sulfur Species Removal Efficiency of Different ILs for 0 hour and 4 hour of Exposure to the Environment

Here are the summary of the ILs efficiency on sulfur species removal:

Table 4.4: Summary of Ionic Liquids Efficiency

Ionic Liquids	**At 0th Hour (%)**	**At 4th Hour (%)**
Emim DEP	**94.66**	**75.46**
Hmim NTf_2	**81.44**	**54.24**
Bmim Otf	**69.57**	**68.48**
Bmim $OcSO_4$	**63.90**	**56.94**
Bmim DBP	**59.10**	**55.94**
Mmim DMP	**67.55**	**65.38**

From the previous graph, all ionic liquids showed the same effect when the presence of water content increased. This proves the early literature review that, as water content increases, the efficiency of sulfur species removal by the ionic liquids will decrease, (Gao et al. , 2008).

After four hours of exposure, all ionic liquids are having increment in their water content. As water content increase, the viscosity of the ionic liquids will be decreasing, (Seddon et al. , 2000). The reductions of viscosity make the ionic liquids lost the capability to remove sulfur, thus reducing the efficiency of sulfur species removal.

Investigation on which ionic liquid has the highest drop of efficiency throughout 4th hour time (Table 4.5) was carried out. Calculations are referred in Appendix D.

Table 4.5: Ionic Liquid Efficiency Drops

Ionic Liquids	**Efficiency Drops (%)**
Emim DEP	25.45
Hmim NTf_2	33.40
Bmim Otf	1.564
Bmim $OcSO_4$	10.92
Bmim DBP	5.36
Mmim DMP	3.22

The lowest efficiency drop after 4 hour is Bmim Otf. It is then follows by Mmim DMP, Bmim DBP, Bmim $OcSO_4$, Emim DEP and Hmim $NTf_{2.}$ Based on the result, anion phosphate has the smallest impact on the water content in the ionic liquids, where by two out of three anion phosphates (Mmim DMP and Bmim DBP) has the efficiency drop less than 10%. After four hours of exposure, the efficiency of sulfur removal is almost the same as before exposure. Different cations do not really make a huge impact on the water content in the ionic liquid sulfur removal efficiency as the water is attracted more to anion, (Seddon et al. , 2000).

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

From all the experiments conducted on six different ionic liquids, all results showed an increment in water content (in ppm) after being exposed to the atmosphere for four hours. Based on the result, it shows that by exposing the ionic liquid to the surroundings, it will affect severely the water content in the ionic liquids. Water content in ionic liquids is preferably to be low, so that the efficiency in sulfur removal could be better.

From the experiment, the highest increment of the water content after four hours is Bmim Otf with 1192.8623 %. It is then followed by Hmim NTf_2 with 487.1017 %, Emim DEP with 396.6390 %, Mmim DMP with 211.7166 % and Bmim DBP with 43.50949 %. While Bmim $OcSO_4$ has the lowest increment with 36.1848 %. Even though Bmim $OcSO_4$, Bmim DBP and Bmim Otf are all have the same cation chain which is $[Bmim]^+$ but the anion chain has major impact on water in ionic liquid compare to cation chain.

Based on the literature review, it shows that water affecting the efficiency of ionic liquid to remove sulfur compound. The presence of water will reduce the viscosity of ionic liquid. As the water content in an IL increase, the solubility of sulfur compounds in IL will be decreases drastically.

While for the efficiency of sulfur removal, all ionic liquids showed that as water content increases, the efficiency of sulfur removal by the ionic liquids will decrease. Anion chain has major impact on water in ionic liquid compare to cation chain, where by two out of three anion phosphates (Mmim DMP and Bmim DBP) have the smallest efficiency drop. After four hours of exposure, Bmim Otf, Bmim DBP and Mmim DMP all showed less than 10% of efficiency drop to remove sulfur from crude oil models.

5.1 Recommendations

Here are some of the recommendations and future works that the author suggested:

- Make an initiative to reduce the initial water content of each ionic liquids (make it almost the same for every ILs). So that, the increment within a fraction of time, can be easily monitored.

- Instead of exposing the ionic liquids to the atmosphere, conducts an experiment on spiking water into the ionic liquids to check on the removal efficiency of sulfur-containing compounds.

- Since Bmim Otf showed the highest increment in water content after four hours of exposure yet has the smallest efficiency drop, further work or experiment can be conducted to test on the capability of Bmim Otf to remove sulfur with the presence of water.

CHAPTER 6

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APPENDICES

APPENDIX A

Water Content Observation

Table 1: Emim DEP Observation from 0 hour until 4th hour

Sample Num	Ionic Liquid	Time (hour)	Temperature (°C)	Humidity (%)	Mass (gram)	Water Content (ppm)	Mean of Water Content (ppm)
1	Emim DEP	0	25.4	75	0.2763	2334.461	2355.7447
2	Emim DEP	0	25.5	74	0.2549	2295.894	
3	Emim DEP	0	25.7	75	0.2604	2436.879	
1	Emim DEP	1	26.2	73	0.3070	3316.954	3211.9217
2	Emim DEP	1	26.2	72	0.2857	2848.314	
3	Emim DEP	1	26.2	72	0.2763	3470.497	
1	Emim DEP	2	26.4	61	0.2761	3501.940	3749.1497
2	Emim DEP	2	26.4	61	0.4814	3419.402	
3	Emim DEP	2	26.4	60	0.3136	4326.107	
1	Emim DEP	3	25.1	74	0.2761	8404.618	8033.3550
2	Emim DEP	3	25.2	74	0.2741	7815.469	
3	Emim DEP	3	25.3	74	0.2672	7879.978	
1	Emim DEP	4	24.8	71	0.2826	10715.68	11699.5467
2	Emim DEP	4	24.9	72	0.2896	10574.96	
3	Emim DEP	4	24.5	71	0.2757	13808.00	

Table 2: Hmim NTf_2 Observation from 0 hour until 4th hour

Sample Num	Ionic Liquid	Time (hour)	Temperature (°C)	Humidity (%)	Mass (gram)	Water Content (ppm)	Mean of Water Content (ppm)
1	Hmim NTf_2	0	25.7	74	0.3537	451.4372	445.1529
2	Hmim NTf_2	0	25.8	75	0.3155	466.1437	
3	Hmim NTf_2	0	25.9	76	0.3289	417.8778	
1	Hmim NTf_2	1	26.2	68	0.4367	380.6503	447.9272
2	Hmim NTf_2	1	26.3	65	0.3400	491.0588	
3	Hmim NTf_2	1	26.2	65	0.3040	472.0724	
1	Hmim NTf_2	2	26.4	60	0.3066	735.2794	555.5870
2	Hmim NTf_2	2	26.4	59	0.3299	331.7975	
3	Hmim NTf_2	2	26.5	59	0.4748	599.6841	
1	Hmim NTf_2	3	25.3	74	0.3521	1255.013	1669.8657
2	Hmim NTf_2	3	25.1	70	0.3378	1497.957	
3	Hmim NTf_2	3	25.0	70	0.3463	2256.627	
1	Hmim NTf_2	4	24.5	72	0.3421	2712.774	2613.5003
2	Hmim NTf_2	4	24.8	75	0.3413	3067.507	
3	Hmim NTf_2	4	24.8	75	0.3247	2060.220	

Table 3: Bmim Otf Observation from 0 hour until 4th hour

Sample Num	Ionic Liquid	Time (hour)	Temperature (°C)	Humidity (%)	Mass (gram)	Water Content (ppm)	Mean of Water Content (ppm)
1	Bmim Otf	0	26.0	74	0.3131	640.5302	665.2335
2	Bmim Otf	0	25.9	75	0.3203	698.0175	
3	Bmim Otf	0	26.1	74	0.3346	657.1528	
1	Bmim Otf	1	26.2	64	0.3276	775.7631	1189.6090
2	Bmim Otf	1	26.3	63	0.3112	1623.956	
3	Bmim Otf	1	26.3	62	0.2448	1127.859	
4	Bmim Otf	1	26.3	62	0.1912	1230.858	
1	Bmim Otf	2	26.5	59	0.2152	1582.265	2130.2023
2	Bmim Otf	2	26.5	57	0.1332	2845.508	
3	Bmim Otf	2	26.5	57	0.3531	1962.834	
1	Bmim Otf	3	24.9	70	0.3147	3432.062	3740.0257
2	Bmim Otf	3	25.0	70	0.3476	3941.321	
3	Bmim Otf	3	24.9	70	0.3075	3846.694	
1	Bmim Otf	4	24.9	75	0.2648	11862.70	8600.5533
2	Bmim Otf	4	24.9	75	0.3238	7426.704	
3	Bmim Otf	4	24.9	75	0.3080	6512.256	

Table 4: Bmim $OcSO_4$ Observation from 0 hour until 4th hour

Sample Num	Ionic Liquid	Time (hour)	Temperature (°C)	Humidity (%)	Mass (gram)	Water Content (ppm)	Mean of Water Content (ppm)
1	Bmim $OcSO_4$	0	25.4	68	0.2724	5512.482	6514.6330
2	Bmim $OcSO_4$	0	25.4	68	0.2227	5676.994	
3	Bmim $OcSO_4$	0	25.5	70	0.3052	8354.423	
1	Bmim $OcSO_4$	1	25.6	70	0.2425	6550.722	7058.1623
2	Bmim $OcSO_4$	1	25.5	68	0.2534	7612.806	
3	Bmim $OcSO_4$	1	25.6	64	0.2622	7010.959	
1	Bmim $OcSO_4$	2	25.0	73	0.3523	9099.328	7825.4727
2	Bmim $OcSO_4$	2	25.1	73	0.3722	7287.507	
3	Bmim $OcSO_4$	2	25.1	74	0.2664	7089.583	
1	Bmim $OcSO_4$	3	25.9	70	0.2559	9305.302	8215.1550
2	Bmim $OcSO_4$	3	25.8	68	0.2619	7349.427	
3	Bmim $OcSO_4$	3	26.0	69	0.2578	7990.736	
1	Bmim $OcSO_4$	4	26.2	67	0.3325	7713.353	8871.9427
2	Bmim $OcSO_4$	4	26.3	66	0.3403	10972.17	
3	Bmim $OcSO_4$	4	26.3	66	0.3434	7930.305	

Table 5: Bmim DBP Observation from 0 hour until 4th hour

Sample Num	Ionic Liquid	Time (hour)	Temperature (°C)	Humidity (%)	Mass (gram)	Water Content (ppm)	Mean of Water Content (ppm)
1	Bmim DBP	0	25.4	70	0.2587	16353.50	17402.3333
2	Bmim DBP	0	25.5	71	0.3686	16981.02	
3	Bmim DBP	0	25.5	70	0.3534	18872.48	
1	Bmim DBP	1	25.2	73	0.2658	15745.69	18065.8867
2	Bmim DBP	1	25.2	73	0.3263	19229.36	
3	Bmim DBP	1	25.3	73	0.3835	19222.61	
1	Bmim DBP	2	25.4	62	0.2462	19639.99	19301.4200
2	Bmim DBP	2	25.5	62	0.2628	18744.33	
3	Bmim DBP	2	25.5	65	0.2585	19519.94	
1	Bmim DBP	3	26.1	70	0.2606	21536.45	22847.1800
2	Bmim DBP	3	26.1	69	0.2588	23018.55	
3	Bmim DBP	3	26.2	69	0.2544	23986.54	
1	Bmim DBP	4	26.3	66	0.3372	24138.86	24974.0000
2	Bmim DBP	4	26.3	65	0.3254	25269.20	
3	Bmim DBP	4	26.3	65	0.3195	25513.94	

Table 6: Mmim DMP Observation from 0 hour until 4th hour

Sample Num	Ionic Liquid	Time (hour)	Temperature (°C)	Humidity (%)	Mass (gram)	Water Content (ppm)	Mean of Water Content (ppm)
1	Mmim DMP	0	25.5	69	0.2852	2551.262	2985.0500
2	Mmim DMP	0	25.6	71	0.4037	3873.190	
3	Mmim DMP	0	25.6	70	0.3365	2530.698	
1	Mmim DMP	1	25.2	69	0.2848	6543.738	4557.3043
2	Mmim DMP	1	25.3	70	0.4436	3590.652	
3	Mmim DMP	1	25.4	71	0.4877	3537.523	
1	Mmim DMP	2	25.6	65	0.3096	5153.758	4596.7837
2	Mmim DMP	2	25.6	65	0.3082	4290.006	
3	Mmim DMP	2	25.6	65	0.3199	4346.587	
1	Mmim DMP	3	26.3	68	0.3108	9656.692	8335.9920
2	Mmim DMP	3	26.3	69	0.3160	7918.755	
3	Mmim DMP	3	26.2	67	0.3068	7432.529	
1	Mmim DMP	4	26.4	64	0.3564	8028.269	9304.8977
2	Mmim DMP	4	26.4	64	0.3152	9370.654	
3	Mmim DMP	4	26.5	64	0.3931	10515.77	

APPENDIX B

Sample of Calculation on Water Content Increment

For Emim DEP

Initial Water Content = 2355.7447 ppm

Final Water Content = 11699.5467 ppm

Difference = Final Water Content - Initial Water Content

= (11699.5467 -2355.7447) ppm

= 9343.8020 ppm

$$\text{Percentage Increment} = \frac{\text{Final Water Content - Initial Water Content}}{\text{Initial Water Content}} \times 100\%$$

$$= \frac{(11699.5467 - 2355.7447)\ \text{ppm}}{2355.7447\ \text{ppm}} \times 100\%$$

= **396.6390 %**

For Hmim NTf_2

Initial Water Content = 455.1529 ppm

Final Water Content = 2613.5003 ppm

Difference = Final Water Content - Initial Water Content

= (2613.5003 -455.1529) ppm

= 2168.3474 ppm

$$\text{Percentage Increment} = \frac{\text{Final Water Content - Initial Water Content}}{\text{Initial Water Content}} \times 100\%$$

$$= \frac{(2613.5003 - 455.1529)\ \text{ppm}}{455.1529\ \text{ppm}} \times 100\%$$

= **487.1017 %**

For Bmim Otf

Initial Water Content = 665.2335 ppm
Final Water Content = 8600.5533 ppm
Difference = Final Water Content - Initial Water Content
= (8600.5533 - 665.2335) ppm
= 7935.3198 ppm

$$\text{Percentage Increment} = \frac{\text{Final Water Content - Initial Water Content}}{\text{Initial Water Content}} \times 100\%$$

$$= \frac{(8600.5533 - 665.2335)\ \text{ppm}}{665.2335\ \text{ppm}} \times 100\%$$

$$= \mathbf{1192.8623\ \%}$$

For Bmim $OcSO_4$

Initial Water Content = 6514.6330 ppm
Final Water Content = 8871.9427 ppm
Difference = Final Water Content - Initial Water Content
= (8871.9427 - 6514.6330) ppm
= 2357.3097 ppm

$$\text{Percentage Increment} = \frac{\text{Final Water Content - Initial Water Content}}{\text{Initial Water Content}} \times 100\%$$

$$= \frac{(8871.9427 - 6514.6330)\ \text{ppm}}{6514.6330\ \text{ppm}} \times 100\%$$

$$= \mathbf{36.1848\ \%}$$

For Bmim DBP

Initial Water Content = 17402.3333 ppm

Final Water Content = 24974.0000 ppm

Difference = Final Water Content - Initial Water Content

= (24974.0000 - 17402.3333) ppm

= 7571.6667 ppm

Percentage Increment = $\frac{\text{Final Water Content - Initial Water Content}}{\text{Initial Water Content}} \times 100\%$

= $\frac{(24974.0000 - 17402.3333)\text{ ppm}}{17402.3333\text{ ppm}} \times 100\%$

= **43.5095 %**

For Mmim DMP

Initial Water Content = 2985.0500 ppm

Final Water Content = 9304.8977 ppm

Difference = Final Water Content - Initial Water Content

= (9304.8977 - 2985.0500) ppm

= 6319.8477 ppm

Percentage Increment = $\frac{\text{Final Water Content - Initial Water Content}}{\text{Initial Water Content}} \times 100\%$

= $\frac{(9304.8977 - 2985.0500)\text{ ppm}}{2985.0500\text{ ppm}} \times 100\%$

= **211.7166 %**

APPENDIX C

Sample of Calculation on Ionic Liquid Efficiency of Removal of Sulfur Species

For Emim DEP

at 0th hour

$$\text{Ionic Liquid Efficiency} = \frac{\text{Initial Sulfur Content (\%)} - \text{Final Sulfur Content (\%)}}{\text{Initial Sulfur Content (\%)}}$$

$$= \frac{3.125 - 0.167}{3.125} \times 100\ \%$$

$$= \mathbf{94.656\ \%}$$

at 4th hour

$$\text{Ionic Liquid Efficiency} = \frac{\text{Initial Sulfur Content (\%)} - \text{Final Sulfur Content (\%)}}{\text{Initial Sulfur Content (\%)}}$$

$$= \frac{3.125 - 0.767}{3.125} \times 100\ \%$$

$$= \mathbf{75.456\%}$$

For Hmim NTf_2

at 0th hour

$$\text{Ionic Liquid Efficiency} = \frac{\text{Initial Sulfur Content (\%)} - \text{Final Sulfur Content (\%)}}{\text{Initial Sulfur Content (\%)}}$$

$$= \frac{3.125 - 0.580}{3.125} \times 100\ \%$$

$$= \mathbf{81.440\ \%}$$

at 4th hour

$$\text{Ionic Liquid Efficiency} = \frac{\text{Initial Sulfur Content (\%)} - \text{Final Sulfur Content (\%)}}{\text{Initial Sulfur Content (\%)}}$$

$$= \frac{3.125 - 1.430}{3.125} \times 100\ \%$$

$$= \mathbf{54.240\ \%}$$

For Bmim Otf

at 0th hour

$$\text{Ionic Liquid Efficiency} = \frac{\text{Initial Sulfur Content (\%)} - \text{Final Sulfur Content (\%)}}{\text{Initial Sulfur Content (\%)}}$$

$$= \frac{3.125 - 0.951}{3.125} \times 100\ \%$$

$$= \mathbf{69.568\ \%}$$

at 4th hour

$$\text{Ionic Liquid Efficiency} = \frac{\text{Initial Sulfur Content (\%)} - \text{Final Sulfur Content (\%)}}{\text{Initial Sulfur Content (\%)}}$$

$$= \frac{3.125 - 0.985}{3.125} \times 100\ \%$$

$$= \mathbf{68.480\%}$$

For Bmim $OcSO_4$

at 0th hour

$$\text{Ionic Liquid Efficiency} = \frac{\text{Initial Sulfur Content (\%)} - \text{Final Sulfur Content (\%)}}{\text{Initial Sulfur Content (\%)}}$$

$$= \frac{3.125 - 1.128}{3.125} \times 100\ \%$$

$$= \mathbf{63.904\ \%}$$

at 4th hour

$$\text{Ionic Liquid Efficiency} = \frac{\text{Initial Sulfur Content (\%)} - \text{Final Sulfur Content (\%)}}{\text{Initial Sulfur Content (\%)}}$$

$$= \frac{3.125 - 1.346}{3.125} \times 100\ \%$$

$$= \mathbf{56.928\ \%}$$

For Bmim DBP

at 0th hour

$$\text{Ionic Liquid Efficiency} = \frac{\text{Initial Sulfur Content (\%)} - \text{Final Sulfur Content (\%)}}{\text{Initial Sulfur Content (\%)}}$$

$$= \frac{3.125 - 1.278}{3.125} \times 100\ \%$$

$$= \mathbf{59.104\ \%}$$

at 4th hour

$$\text{Ionic Liquid Efficiency} = \frac{\text{Initial Sulfur Content (\%)} - \text{Final Sulfur Content (\%)}}{\text{Initial Sulfur Content (\%)}}$$

$$= \frac{3.125 - 1.377}{3.125} \times 100\ \%$$

$$= \mathbf{55.936\ \%}$$

For Mmim DMP

at 0th hour

$$\text{Ionic Liquid Efficiency} = \frac{\text{Initial Sulfur Content (\%)} - \text{Final Sulfur Content (\%)}}{\text{Initial Sulfur Content (\%)}}$$

$$= \frac{3.125 - 1.014}{3.125} \times 100\ \%$$

$$= \mathbf{67.552\ \%}$$

at 4th hour

$$\text{Ionic Liquid Efficiency} = \frac{\text{Initial Sulfur Content (\%)} - \text{Final Sulfur Content (\%)}}{\text{Initial Sulfur Content (\%)}}$$

$$= \frac{3.125 - 1.082}{3.125} \times 100\ \%$$

$$= \mathbf{65.376\ \%}$$

APPENDIX D

Sample of Calculation on Drop of Efficiency Sulfur Removal of Ionic Liquids

For Emim DEP

$$\text{Efficiency drop} = \frac{\text{Initial Efficiency} - \text{Final Efficiency}}{\text{Initial Efficiency}}$$

$$= \frac{94.656 - 75.456}{94.656} \times 100\ \%$$

$$= \mathbf{25.45\ \%}$$

For Hmim NTf_2

$$\text{Efficiency drop} = \frac{\text{Initial Efficiency} - \text{Final Efficiency}}{\text{Initial Efficiency}}$$

$$= \frac{81.44 - 54.24}{81.44} \times 100\ \%$$

$$= \mathbf{33.40\ \%}$$

For Bmim Otf

$$\text{Efficiency drop} = \frac{\text{Initial Efficiency – Final Efficiency}}{\text{Initial Efficiency}}$$

$$= \frac{69.568 - 68.48}{69.568} \times 100\ \%$$

$$= \mathbf{1.564\ \%}$$

For Bmim $OcSO_4$

$$\text{Efficiency drop} = \frac{\text{Initial Efficiency – Final Efficiency}}{\text{Initial Efficiency}}$$

$$= \frac{63.904 - 56.928}{63.904} \times 100\ \%$$

$$= \mathbf{10.916\ \%}$$

For Bmim DBP

$$\text{Efficiency drop} = \frac{\text{Initial Efficiency} - \text{Final Efficiency}}{\text{Initial Efficiency}}$$

$$= \frac{59.104 - 55.936}{59.104} \times 100\ \%$$

$$= \mathbf{5.36\ \%}$$

For Mmim DMP

$$\text{Efficiency drop} = \frac{\text{Initial Efficiency} - \text{Final Efficiency}}{\text{Initial Efficiency}}$$

$$= \frac{67.552 - 65.376}{67.552} \times 100\ \%$$

$$= \mathbf{3.22\ \%}$$

APPENDIX E

Key Milestone for FYP I

No	Detail / Week	1	2	3	4	5	6	7	8	9		10	11	12	13	14
1	Selection of Project Topic	▨	▨								**Mid Sem Break**					
2	Preliminary Research Work		▨	▨	▨											
3	Submission of Preliminary Report				■											
4	Project Work (Literature Review)					▨	▨	▨	▨	▨						
5	Submission of Progress Report								■							
6	Seminar (Compulsory)								■							
7	Project Work Continues (Literature Review)											▨	▨	▨	▨	▨
8	Submission of Interim Report Final Draft														■	
9	Oral Presentation															■

▨ **Process**

■ **Suggested Milestone**

Key Milestone for FYP II

No	**Detail/Week**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**		**10**	**11**	**12**	**13**	**14**
1	Project work continues	▨	▨	▨							**Mid Sem Break**					
2	Submission of Progress Report 1				■											
3	Project work continues				▨	▨	▨	▨	▨	▨						
4	Submission of Progress Report 2								■							
5	Seminar (compulsory)								■							
6	Project work continues											▨	▨	▨	▨	
7	Poster exhibition											■				
8	Submission of Dissertation Final Draft															■
9	Oral Presentation											25 Nov – 4 Dec 2009				
10	Submission of Dissertation (hard bound)											7 Days After Oral Presentation				

▨ **Process**

■ **Suggested Milestone**