The Effect of Imidazolium Based Ionic Liquids (ILs) Structure Properties towards Desulfurization in Fuel Oils

by

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Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
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BACHELOR OF ENGINEERING (Hons)
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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.

Thor Vincy

ABSTRACT

This report is to provide the details of the study namely The Effect of Imidazolium Based Ionic Liquids (ILs) Structure Properties towards Desulfurization in Fuel Oils. ILs is a defined as new class of organic salts with low melting point, made of organic cations and organic or inorganic anions. ILs are well known as green organic solvent due to their negligible vapour pressure compare others organic solvents. It have a lots of potential in various fields due to its distinguishing properties, such as chemically and thermally stable, non-flammable, high ionic conductivity, ease of regeneration, low vapor pressure, non-toxic, high salvation ability and etc. In this study, we are focus on desulfurization in fuel oils.

All ILs attractive features make the ILs field worth to be further explored and studied, especially when it is still relatively a new field. Due to its relatively new presence in the chemical industry, many data still are not available to understand about the ILs, especially mechanism of ILs in extract sulfur from fuel oils. Hence, the objective of this project is to get more insightful view of the ILs in term of molecular forces and structural properties in desulfurization of fuel oils by using simple parameters. These parameters are employed to develop a relationship between the ILs structure property and their sulfur extractability along with the help of the literature review of ILs available.

During the literature review studied, a few parameters been identified that will help in understanding the relation of the ILs structure properties towards desulfurization in fuel oils. Such parameters are such as density (ρ), molecular weight (MW), refractive index (R_I), molar refraction (R_m), molar volume (V_m) and sulfur partition coefficient (K_N). The relationship that developed will provide an initial prediction on the efficiency of ILs chosen provided that parameters concerned are given. It also acts as preliminary screening tool for many ILs that available so far, particularly in fuel oils desulfurization.

Based on the critical analysis of various suggested parameters to develop relationship between the ILs structure property and their sulfur extractability, it has been found that the molar volume (Vm), molar refraction (Rm) and fefractive index (R_I) are able to predict the ILs efficiency in removing sulfur.

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CHAPTER 1

INTRODUCTION

1. BACKGROUND STUDY

Society nowadays is more concern about the natural resources exploitation. As a part of the ecological system, humans now emphasizes on maintaining and working towards the achievement of green environment. This can be proven by the fact that the researches at the early 21st century mentioned in T. Umecky et al. [1] paper which is focusing more on reduction the usage of harmful volatile organic compounds. Oils, as major natural resources and major energy provider are currently being harvested carefully and being refined to not produce any harm to the environment. Hence, present refineries are looking for an effective, efficient and economic feasible way to remove sulfur from the oils.

According to J.G. Speight [2], over the past three decades, the average quality of crude oil has declined as can be seen via the progressive decrease in API gravity (i.e., increase in density) and a rise in sulfur content, also known as heavy oil. This so called heavy oil causes pollution to the environment. The sulfur compounds of fuels are converted into SOx compounds during the combustion of fuel and contribute to the formation of acid rains and air pollution [3]. The sulfur source may come from the fuel [4]. C. E. B. Jr in his book stated clearly that fuels like heavy oil contain significant amounts of sulfur [4].

He also suggested a few methods to reduce the sulfur emission; one of it is removing the sulfur from the incoming fuel or raw materials [4]. As a result of the adverse impact of the fuel to the environment and also people, stringent law and regulation are enforced by the government all over the world as to limit the sulfur emission of the fuel, especially by transportation vehicles. This is because according B. Pawelec et al. [5], transportation vehicles 95% dependent on oil and accounts for almost half its global use.

In other words, the road transport is a major contribution to air pollution. Therefore, the heavy oil shall be treated to reduce the sulfur content prior to the fuel consumption for the sake of environment.

The conventional method of removing sulfur from fuel oil, also known as desulfurization is hydrodesulfurization (HDS). According to A.M. Dehkordi et al. [3], at present, HDS is the most widely used industrial process for reducing the total sulfur content of hydrocarbon fuels. However, this method has few major drawbacks, such as involve high capital cost due to high consumption of energy and hydrogen [6], operating at extreme condition, i.e. high temperature and pressure [7], as well as unable to remove aromatic sulfur such as thiophenic compounds such as dibenzothiophene(DBT), benzothiophene (BT), and their derivatives [3]. This is proven in the previous investigations revealed by A.M. Dehkordi et al. [3], the sulfur-containing compounds remaining in treated fuels after the hydrodesulfurization (HDS) process are typically thiophenic compounds such as dibenzothiophene(DBT), benzothiophene (BT), and their derivatives.

According to X. Jiang et al. [8], there are few alternatives that have been developed so far for desulfurization, for example, the approaches based on adsorption, extraction, oxidation and biodesulfurization etc [8]. Among these alternatives, extractive desulfurization (EDS) is favored due to the fact that the technology is well established and can be operated under ambient conditions [8]. Ionic Liquids (IL) is considered as an option for desulfurization in replace of conventional deep HDS as it is a good extractant by having features such as good extractive ability for the S compounds, ease of regeneration for the used extractant, free of contamination to the fuels, non-toxic and environment friendly [8]. In this present study, the scope of study is limited to imidazolium based ILs since it is most widely used in desulfurization.

2. PROBLEM STATEMENT

Due to difficulties to remove aromatic sulfur compounds, several attempts to change extreme operation conditions, i.e. high temperature and pressure of HDS [6, 7]. However, to carry out the deep HDS processes, the energy and hydrogen consumption increased and lead to high increase in capital expenditure [6]. Hence, ILs as extractant in EDS come into the picture since it is more economical compares to deep HDS. This is because ILs can be used under ambient conditions.

According to M. Deetlefs et al [9], the ILs continue to gain its popularity as an alternatives for traditional organic solvents due to their distinction of many possible combinations of cations and anions which determine their physical properties, such as density, viscosity, melting point, hydrophobicity, solvent power, solubility and etc. Due to this many possibility of combinations, there are wide range of ILs can be existed. However, their physical data available are too little or incomplete to understand the ILs behavior, particularly in desulfurization and its mechanism [9].

The common and scatter data available in literature review so far are such as density (ρ), molecular weight (MW), refractive index (R_I), molar refraction (R_m), molar volume (V_m) and sulfur partition coefficient (K_N). The external launch of the property database, named ILTHERMO by IUPAC specifically dedicated to ILs is available now. But noticed that the database have limited information on sulfur partition coefficient (K_N).

It is also been observed that from the literature so far besides IL THERMO, sulfur partition coefficient (K_N) of ILs is not much available. This project is aim to relate the sulfur partition coefficient (K_N) to the ILs structure property. It studied how ILs structure property, by interpret parameters such as refractive index (R_I), molar refraction (R_m), molar volume (V_m) which influence the sulfur extractability of the ILs.

3. Objectives and Scope of Study

Listed below are the objectives and scope of study of this research project.

1. Critical analysis of the available ILs literature reviews.
2. To collect the data from literature review such as density (ρ), molecular weight (MW), sulfur partition coefficient (K_N), refractive index (R_I) and also molar refraction (R_M).
3. To utilize established equation to find out others parameter which can be used to relate the ILs structure property with desulfurization efficiency.

4. To study how the ILs behave in such a manner that they are able to extract sulfur from hydrocarbons.
5. To study the relationship of the ILs structure towards the efficiency of the sulfur removal.

CHAPTER 2

LITERATURE REVIEW

1. Definition of Desulfurization

J.G. Speight [2] define desulfurization process is defined as upgrading heavy oil and residua. In other words, desulfurization is a process to remove sulfur from the heavy crude oils. According to A.M. Dehkordi et al. [3], at present, HDS is the most widely used industrial process for reducing the total sulfur content of hydrocarbon fuels.

According A. Flores et al. [11], the HDS process happened where the C-S bond is broken by hydrogenolysis to produce H_2S and sulfur-free hydrocarbons. However, side reactions occur during the process, such as, hydrogenation and cracking [11]. Therefore, high concentration of H_2 and drastic experimental conditions (over 350°C and 100 bar) are needed in order to eliminate considerable amounts of sulfur. [11].

As mentioned earlier, the disadvantages of HDS is high operating temperature, high operating pressure conditions that resulted in high energy cost [7]. In addition, HDS are unable to remove aromatic sulfur compounds such as dibenthiophene (DBT), benzothiophene (BT), and their derivatives due to lack of high performance catalyst specific to such series of sulfur compounds [8].

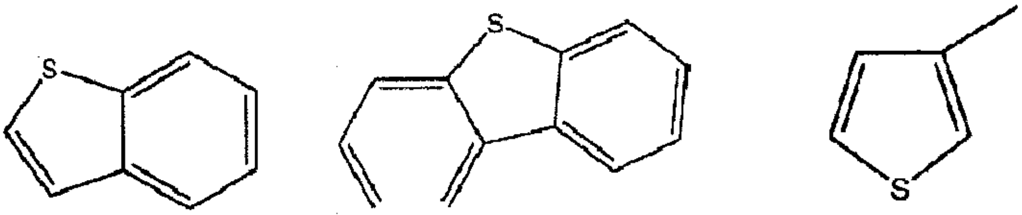
2. Types of Sulfur Compunds

According to B. Pawelec et al. [5], there are four types of sulfur that can be categorized based on their reactivities towards HDS. They are listed as below.

a. sulfur compounds dominated by alkyl benzothiophenes (BTs);
b. dibenzothiophenes (DBT) and alkyl dibenzothiophenes (DBTs) without alkyl substituents at the 4- and 6-positions;
c. alkyl DBTs with only one alkyl substituent at either the 4- or 6-position; and

d. alkyl substituents at the 4- and 6-positions.

They are also known as refractory sulfur compounds. Their low reactivity towards HDS is due to both the steric hindrance and electronic factors of the compounds. Studied has shown that the volume of catalysts used in HDS will needed to increases to cater the desulfurization via HDS [5]. In other words, using current HDS processes without changing the reactor volume since is not economic practical, means the refineries have to increase the catalysts activities (300-400%) [18] to meet the new requirement for the finish product. However, it is difficult to make this adjustment to the existing hydrotreating catalysts that have been established since past 50 years ago. Figure 2.1 below showed the structural formula of the aromatic sulfur concerned in this study.



BT DBT 3-MT

Figure 2.1: structural formula of the aromatic sulfur concerned in this study.

3. Hydrodesulfurization Process Description

According J.G. Speight [10], hydrodesulfurization (HDS) processes are used at several places in virtually every refinery. The purposes are to protect catalysts (since the catalyst represent a significant fraction of the costs of operating a hydrodesulfurization unit), and to meet product specifications.

J.G. Speight [10] described the hydrodesulfurization process is the reaction of hydrogen with a predominant hydrocarbon feedstock to produce a desulfurized hydrocarbon product and hydrogen sulfide. In a very simplified process (Figure 2.2), the feedstock is first pressurized to a pressure which is a little higher than that of the reactor section, mixed with hot recycle gas and preheated to the temperature of the reactor inlet. The hot feedstock (and the recycle gas) is then introduced to the catalyst in the reactor where temperatures on the order of 290 to 455°C (550 to 850°F) and pressures in the range 150 to 3000 psi prevail. Heat exchangers are employed to cool the reactor effluent and the desulfurized liquid product is separated from the recycle gas at a pressure somewhat lower than that of the reactor section. Hydrogen sulfide and any light hydrocarbon gases are removed from the recycle gas which is then mixed with fresh (makeup) hydrogen, compressed, and mixed with further hydrocarbon feedstock.

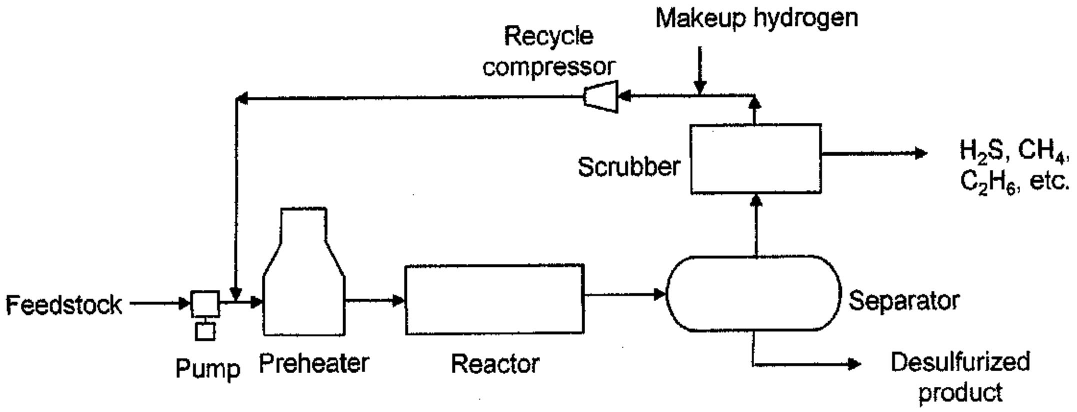


Figure 2.2: The HDS Process.

The disadvantages of HDS is high operating temperature (>300°C), high operating pressure (>4Mpa) and thus resulted in high energy cost [7]. Such severe operating conditions lead to rapid catalyst deactivation, shorter cycle times and reduced throughput [5]. In addition, HDS are unable to remove aromatic heterocyclic sulfur compounds such as dibenthiophene (DBT). Hence, there is a need to switch to another economically and technically feasible technology, which is desulfurization suing ILs.

4. Purposes of Desulfurization

4.1 Environmental Aspects

Concerns are raised related to the emissions of oxides of sulfur during combustion processes have resulted in the enactment of stringent emission standards requiring the application of costly process operations to ensure compliance i.e. sulfur emission to atmosphere [12]. The primary source of sulfur needed to produce SOx comes from the fuel. Emissions of SOx are also damaging to green plants, which are more sensitive than people and animals to SO_2. When SO_2 is released into the atmosphere, it can produce acid rain by combining with water to produce sulfuric acid (H_2SO_4) [9]. Acid rain is corrosive to the environment, particularly plant and aquatic life [9].

The regulation relates to sulfur emission is varies from country to country. According Pawelec et al. [5], in the USA, the acceptable level of sulfur in highway diesel was first reduced from 2000 ppm to 500 ppm by the Clean Air Act (CAA) amendments in the nineties, then to 350 ppm, 50 ppm and 15 ppm in the years 2000, 2005, and 2006, respectively (Figure 3.1). In the Europe (EU), Germany was the first country to adopt the 10 ppm sulfur limit for diesel as from January 2003. Other EU countries and Japan introduced diesel fuel with 10 ppm into the market from the year 2008. One of the specifications proposed for clean diesel by the Worldwide Fuel Charter (WWFC) is low sulfur content.

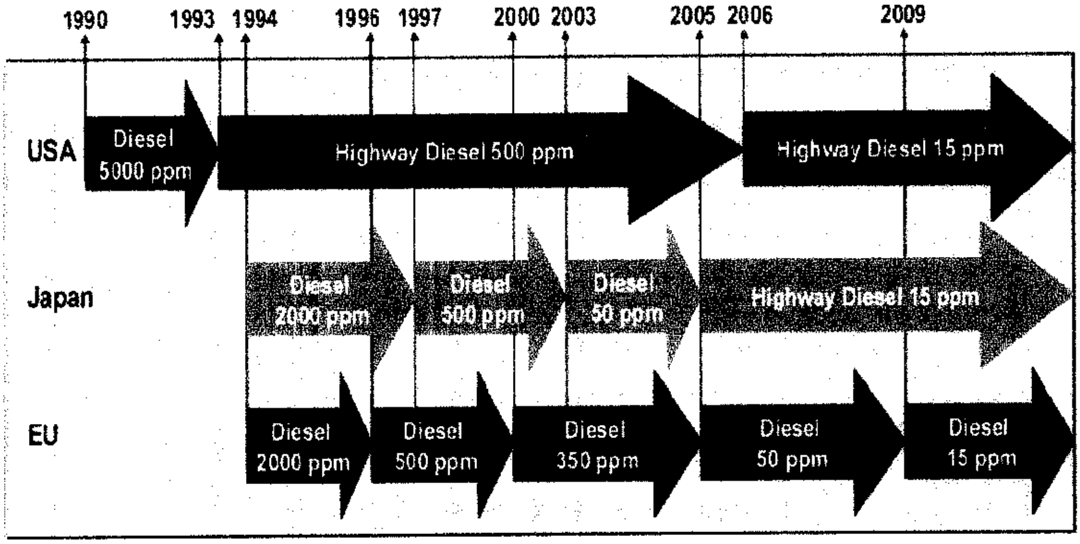


Figure 2.3: Trends in diesel sulfur fuel specifications for high way transportation vehicles [5].

For Malaysia, the sulfur content allowable is not more than 500ppm [13].

4.2 Quality of Petroleum Products

According to J. G. Speight [2], over the past three decades, the average quality of crude oil has declined as evidenced by a progressive decrease in API gravity (i.e., increase in density) and a rise in sulfur content as well as increase in viscosity, also known as heavy oil. Since the demand for light products is increasing at the expense of heavier fuels (e.g. heavy fuel oil), more crude conversion will be needed to upgrade the heavy crudes [5]. This has brought about a major focus in refineries on searching for the ways in which heavy feed stocks might be converted into low-boiling high-value products [2].

J. G. Speight [2] defined heavy oils and residua which have characteristics such as low API gravity (high density) and high viscosity, high initial boiling point, high carbon residue, high nitrogen content, high sulfur content and high metals content. In addition, the heavy feed stocks also have an increased molecular weight and a reduced of hydrogen content. This in turn led to low quality of the petroleum products produced [2]. There are several valid reasons for removing sulfur from petroleum fractions [2]. These include:

1. Reduction, or elimination, of corrosion during refining, handling, or use of the various products [2];
2. Production of products having an acceptable odor [2];
3. Increasing the performance (and stability) of gasoline [2];
4. Decreasing smoke formation in kerosene [2]; and
5. Reduction of sulfur content in other fuel oils to a level that improves burning characteristics and is environmentally acceptable [2].
6. To protect catalysts (since the catalyst represent a significant fraction of the costs of operating a HDS unit), and to meet product specifications [10].
7. To protect refinery equipment [14].

4.3 Ionic Liquids

4.3.1 Definition of Ionic Liquids

Ionic liquids (ILs) are a relatively a new class of solvents that have been under development since the early 1980s as environmentally friendly alternatives to organic solvents [15]. An IL is a salt composed of anions and cations that are poorly coordinated, with melting points typically under 100°C [15]. There are thousands known ionic liquids based on wide range of anions and cations, the combination of which defines the thermodynamic and physiochemical properties of the IL [15].

A distinguish feature of ILs is that they can be synthesized for a specific function based on the selection of anions and cations. Most of ILs have many attractive properties such as chemical and thermal stability, non-flammability, high ionic conductivity, wide range of potential window, low vapour pressure, high salvation ability, which may be the single most attractive property for their use as solvents [6].

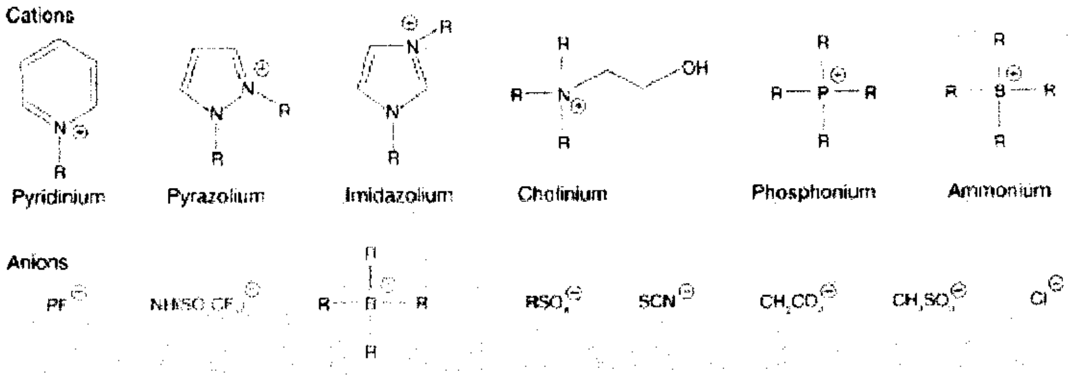
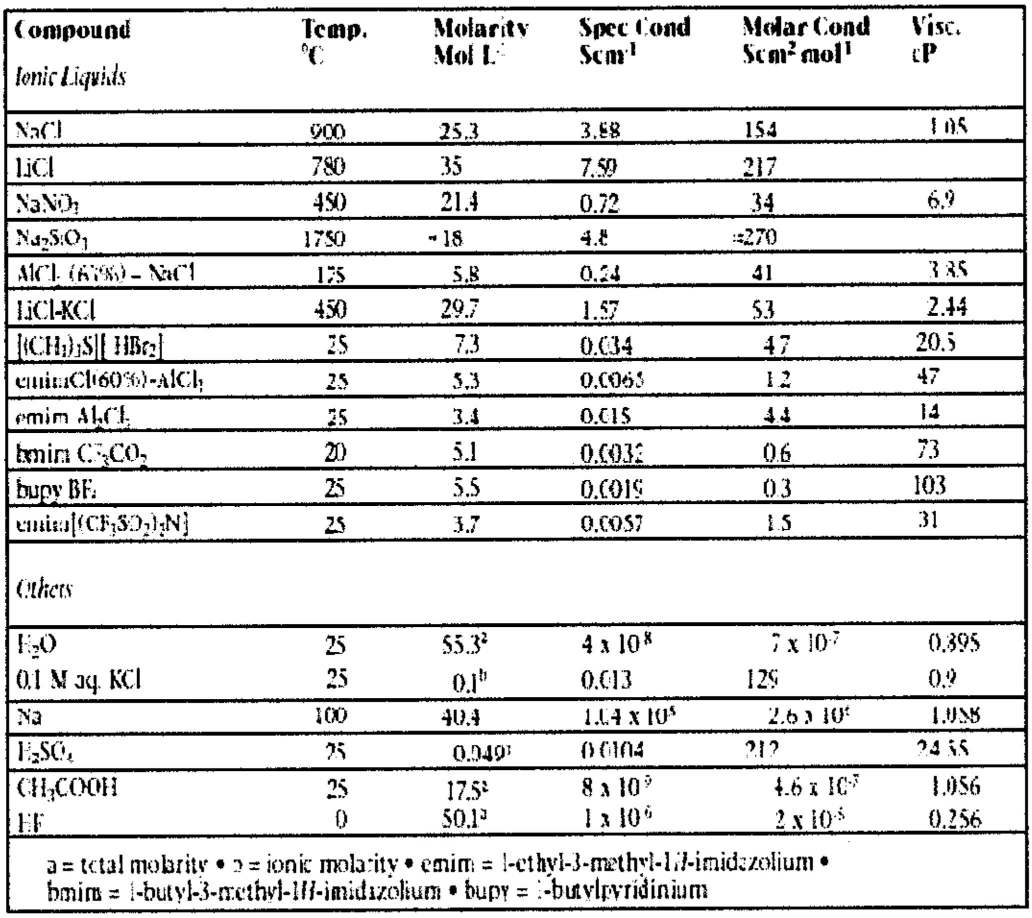


Figure 2.4: Some of the common cations and anions that compose ILs [19].

ILs has been demonstrated to be very effective in the fields of hydrogenation, esterification, nanomaterials synthesis, biocatalysis, and the selective extraction of aromatics [15]. The first commercial-scale applications of ILs have been appearing over the past eight years, such as BASF's biphasic acid scavenging utilizing ionic liquids (BASIL) project for photoinitiator precursors for use in UV-curable coatings [15]. The general properties of IL are shown in Figure 2.5.



Compound	Temp. °C	Molarity Mol L^{-1}	Spec Cond Scm^{-1}	Molar Cond Scm^2 mol^{-1}	Visc. cP
Ionic Liquids					
NaCl	900	25.3	3.88	154	1.05
LiCl	780	35	7.59	217	
$NaNO_3$	450	21.4	0.72	34	6.9
Na_2SiO_3	1750	~18	4.8	≈270	
$AlCl_3$ (67%) – NaCl	175	5.8	0.24	41	3.85
LiCl-KCl	450	29.7	1.57	53	2.44
$[(CH_3)_3S][HBr_2]$	25	7.3	0.034	4.7	20.5
emimCl(60%)-$AlCl_3$	25	5.3	0.0065	1.2	47
emim Al_2Cl_7	25	3.4	0.015	4.4	14
bmim CF_3CO_2	20	5.1	0.0032	0.6	73
bupy BF_4	25	5.5	0.0019	0.3	103
emim$[(CF_3SO_2)_2N]$	25	3.7	0.0057	1.5	31
Others					
H_2O	25	55.3^a	4 x 10^{-8}	7 x 10^{-7}	0.895
0.1 M aq. KCl	25	0.1^b	0.013	129	0.9
Na	100	40.4	1.04 x 10^5	2.6 x 10^6	1.058
H_2SO_4	25	0.049^b	0.0104	212	24.55
CH_3COOH	25	17.5^a	8 x 10^{-9}	4.6 x 10^{-7}	1.056
HF	0	50.1^a	1 x 10^{-6}	2 x 10^{-5}	0.256

a = total molarity • b = ionic molarity • emim = 1-ethyl-3-methyl-1*H*-imidazolium • bmim = 1-butyl-3-methyl-1*H*-imidazolium • bupy = 1-butylpyridinium

Figure 2.5: The general properties of ILs [16].

In summary, an ionic liquid is characterized by a specific conductivity in the mScm-1 range as a minimum, together with a molar conductivity probably exceeding 0.1 Scm^2 mol^{-1}. In addition, the liquid should only contain ions with lesser numbers of ion pairs or parent molecules. Ionic liquids tend to have low dielectric constant, which means they are not ionizing solvents [16].

4.3.2 Application of Ionic Liquids in Desulfurization

The traditional hydrodesulfurization (HDS) process faces various problems such as increased energy and hydrogen consumptions due to hydrogenation of aromatic sulfur compounds (S-compounds) such as benzothiophene (BT) and dibenzothiophene (DBT) as well as requires substantially improved reactivity and selectivity of the used catalyst [17]. In addition, undesired side reactions will also be induced to result in the decrease of the octane number of gasoline [17]. Not to mention the variations in feedstock sulfur content and the amount of cracked stock have a big influence in the process and operation conditions, which always required the change of operating condition to cater the desulfurization process. Therefore, it is critically important to develop new desulfurization technologies to minimize the negative health and environmental pollutions [17].

ILs attractive properties as mentioned above make it as a good extractant in desulfurization (deS). The use of ionic liquids in deep deS was first attempted by groups of Wasserscheid and Jess in 2001 [18]. The main reason using ILs in desulfurization is to minimize desulfurization energy requirements, and to decrease CO_2 production that is associated with other desulfurization processes such as HDS. ILs have advantages of low energy cost, mild operating conditions and facile of operation option [6].

Several other factors also contributed to the introduction of ILs as extractant in desulfurization. This includes the high operating cost of HDS which lead to significant investment of capital for a plant [19] and also property of ILs which is environmental friendly as extracting solvent and also the unique features of the ILs. Besides that, the difficulty to remove aromatic heterocyclic sulfur compounds such as dibenthiophene (DBT) also arises in HDS. But it is found from the several literature reviews [5-8, 17-19] that the ILs are proven to be able to remove the aromatic heterocyclic sulfur compounds effectively.

4.3.3 Ionic Liquids Desulfurization Mechanism

Most literature reviews reported that the ILs efficiency in sulfur removal is mainly due to the structure and size of anion or cation that compose the ILs [1, 6, 17, 21]. Some also said that the ability of ILs to remove sulfur is related to its cation head group [17]. Desulfurization happen when the π–π interaction between the unsaturated bonds of sulfur compounds and the imidazole ring of ILs form liquid clathrate [1]. As the alkyl substitute become larger or longer, the polarity and electrons disperse of the π-electrons rings increases. This leads to stronger the π–π interaction between the unsaturated bonds of sulfur compounds and the imidazole ring [8, 17]. In other words, the efficiency of ILs extract sulfur increases too.

In other paper, it stated that [20] the S-compounds with a conjugated structure, which is between the lone pairs on S atom and the π-electrons on aromatic ring, preferably insert into the dynamic molecular structure of the ILs. It is clearly that the aromatic π–π interaction and hydrogen bonding interaction maybe the dominant factors to influence the IL and sulfur interaction or in other words, desulfurization ability [22]. Some also mentioned that as cation size increases, columbic interaction between cation and anion get weaker. This then resulted that the π–π interaction between unsaturated sulfur and imidazole ring stronger, means can extract sulfur better [21].

CHAPTER 3

METHODOLOGY

1. Research Methodology

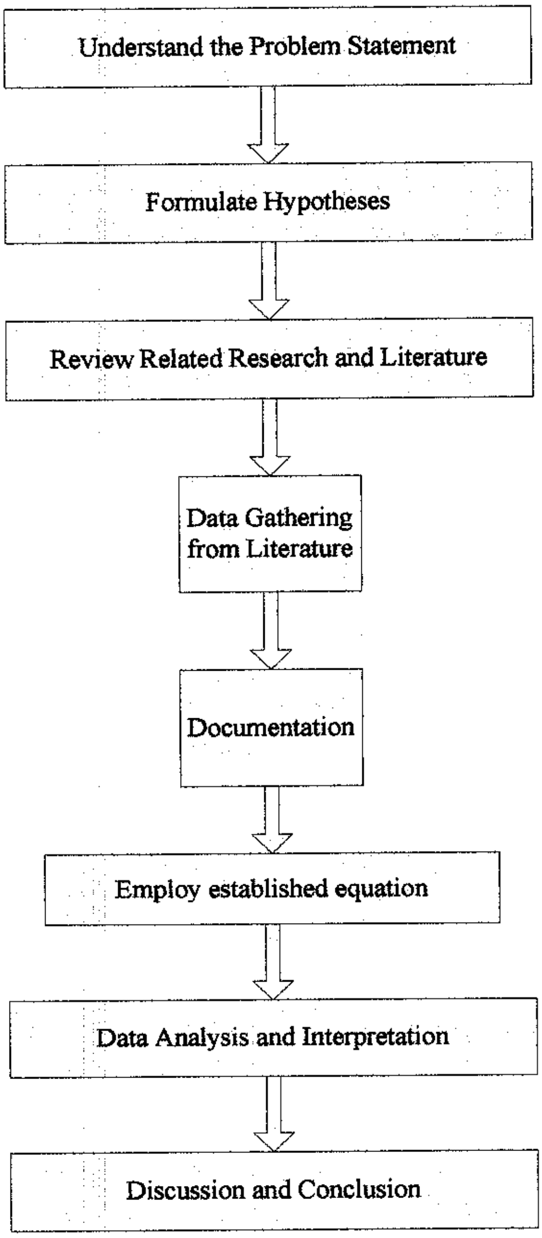


Figure 3.1: The Research Methodology.

2. Gantt Chart

Task	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	W11	W12	W13	W14	After Final
Project Work Continues	■	■	■	■	■	■	■								
Submission of Progress Report								■							
Project Work Continues								■	■	■	■	■			
Pre-EDX											■				
Submission of Draft Report												■			
Submission of Dissertation (soft bound)														■	
Submission of Technical Paper														■	
FYP 2 Oral Presentation															■
Submission of Project Dissertation (Hard Bound)															■

Table 3.1: Gantt Chart for FYP 2.

Key Activities:

1. FYP 2 Progress Report Submission: 13th July 2011
2. Pre-EDX: 4th August 2011
3. Submission of Final Report (Softbound) : 22nd August 2011
4. FYP 2 Oral Presentation: 12th – 15th Sept 2011
5. Submission of Final Report (Hardbound) :20th Sept 2011

CHAPTER 4

RESULTS AND DISCUSSION

1. Molar Volume (Vm)

Table 4.1: ILs Data of Vm and K_N.

No.	ILs	Vm (cm^3/mol)	K_N
1	[Emim][DCA]	167.18	1.3
2	[Mmim][DMP]	174.95	0.46
3	[Emim][DMP]	185.99	1.17
4	[Emim][$EtSO_4$]	188.41	0.8
5	[Bmim][BF_4]	188.45	0.7
6	[Bmim][DCA]	193.64	2.28
7	[Bmim][$MeSO_4$]	206.65	1.1
8	[Bmim][PF_6]	208.39	0.9
9	[Emim][DEP]	229.79	1.27
10	[Bmim][$OcSO_4$]	303.6	1.9
11	[Bmim][DBP]	329.85	1.59

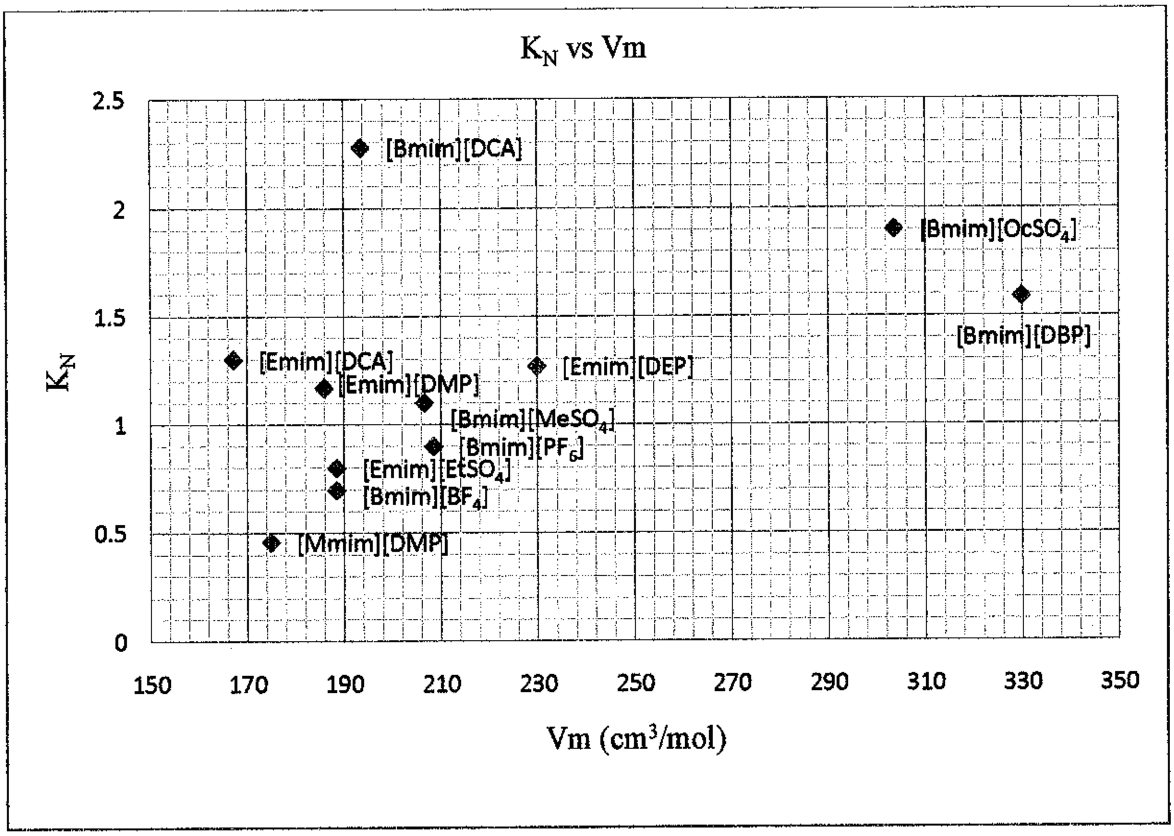


Figure 4.1: Graph of sulfur partition coefficient (K_N) vs molar volume (Vm).

Sulfur partition coefficient (K_N) is defined as the ratio of S-concentration in IL to S concentration in gasoline. [8]

$$K_N = \frac{[S]_{IL}}{[S]_{Gasoline}} \quad (1)$$

Hence, higher K_N means the better the desulfurization performance of an IL.

Desulfurization by ILs are mainly due to the dispersion forces of the π-electron of the cation rings of the imidazolium. The dispersion force of the π-electron can be achieved through the alkyl substitute of the cation or anion. In other words, anion or cation size effect contribute to the desulfurization ability of ILs by weaken the bonding between the cation and anion of the ILs. By weaken this bond, cation are more readily to be attached by sulfur compounds.

The Lorenz-Lorentz equation [23] expressed below can be used to explain well the relation of the efficiency of ILs extract sulfur with the refractive index (R_I), molar volume (Vm) and molar refraction (Rm).

$$R_m = \frac{N_A \alpha_e}{3\varepsilon_o} = \left(\frac{n^2-1}{n^2+2}\right) V_m \tag{2}$$

where Rm= molar refraction,

Vm = molar volume,

N_A =Avogadro's constant,

α_e = electronic polarizability,

ε_o = permittivity of free space,

n = refractive index.

Equation (2) stated that as molar volume (Vm) and molar refraction (Rm) increases, the polarity of the IL is high and have strong dispersion forces, which is the key of ILs to extract sulfur. The strong dispersion force allows stronger interaction between the sulfur compounds and the imidazolium cation.

The hypothesis here is that as the molar volume (Vm) increases, the K_N value should increases as well. Data above listed the available data for ILs that been found on the literature so far. From the data above, it can be seen that the K_N value for [Mmim] ILs is lowest compare others. This is probably due to the reason that the alkyl substitute of the cation is the shortest causing the interaction force between the cation and anion is strong. In addition, the molar volume of [Mmim][DMP] also considered lowest, i.e. 174.98 cm^3/mol among the ILs listed above. It agrees wells with the hypothesis; low molar volume should have low value of K_N.

However, [Emim][DCA] with lowest molar volume, 167.18 cm^3/mol have a K_N value of 1.3, considerable good in extracting sulfur as compare to [Mmim][DMP] with molar volume, 174.98 cm^3/mol and K_N value of 0.46.This is probably due to the anion, [DCA] that poses higher electron density compared to [DEP] as well as longer alkyl substitute of [Emim][DCA] compare to [Mmim][DMP]. A triple bond, i.e. [DCA] are made of one σ bond and two π bonds compare to double bond, i.e. [DMP] that consists of one σ bond and one π bond. Figure 1 below showed the ILs structure of [Mmim][DMP] and [Emim][DCA].

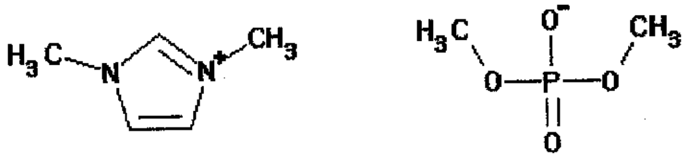


Figure 4.2: [Mmim][DMP] Structure.

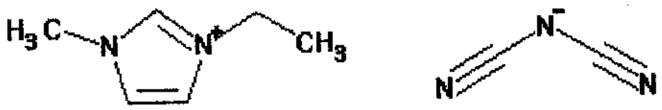


Figure 4.3: [Emim][DCA] Structure

Another interesting observation also can be found, the anion [DCA] for both cation of [Emim] and [Bmim], have the significant K_N value of 1.3 and 2.28 even though the molar volume of both considerably low among the common cation family. This may be due to the high electron density of [DCA] as described earlier.

Few observations explained below based on the listed data above support the hypothesis that for the same family of anion or common anion, as the molar volume (Vm) increases, the ILs extract sulfur better.

For alkylsulfate ILs, the molar volume of alkylsulfate ILs in increasing order, [Emim][EtSO$_4$] , [Bmim][MeSO$_4$], [Bmim][OcSO$_4$] also having value of K_N in increasing order, 0.8, 1.1 and 1.9. It also can be seen that the cation alkyl chain also play a role in the K_N value. As mentioned in the literature review, an IL extract better if the alkyl substitute is longer. Hence, for these three ILs, [Emim] with shortest alkyl chain having the lowest value of K_N.

For fluorinated ILs, the rule of as volume increases, the K_N value increases can be applied as well. From above, [Bmim][BF$_4$] and [Bmim][PF$_6$], both fluorinated ILs having value molar volume, Vm of 188.49 cm^3/mol and 208.39 cm^3/mol respectively having K_N value of 0.7 and 0.9. It supported the hypothesis mentioned above.

For common anion of [DCA] shown in data above, [Emim][DCA] with Vm of 167.18 cm^3/mol, K_N of 1.3 and [Bmim][DCA] with Vm of 193.64 cm^3/mol, K_N of 2.28 also obey the hypothesis.

For alkylphosphate ILs, the efficiency of the ILs extract sulfur can be predicted provided the molar volume is given. The increasing order of Vm of alkylphosphate ILs is [Mmim][DMP], [Emim][DMP], [Emim][DEP] and [Bmim][DBP] with K_N value of 0.46, 0.9, 1.27 and 1.59. The hypothesis predicted well the ability of alkylphosphate ILs extract sulfur.

All this showed that, as long as the ILs are from same anion family or common anion, provided that molar volume, Vm is available, the ability of the ILs to extract sulfur can be predicted. Molar volume, Vm can be obtained via equation below [9].

$$V_m = \frac{F_w}{\rho} \tag{3}$$

where *Vm* = molar volume,

Fw = molecular weight,

ρ = density.

2. Molar Refraction (Rm)

Table 4.2: ILs Data of Rm and K_N.

No.	ILs	Rm (cm^3/mol)	K_N
1	[Emim][DCA]	12.32	1.3
2	[Bmim][BF_4]	45.57	0.7
3	[Bmim][PF_6]	51.46	0.9
4	[Emim][$EtSO_4$]	54.02	0.8
5	[Bmim][$MeSO_4$]	58.47	1.1
6	[Bmim][$OcSO_4$]	91.07	1.9

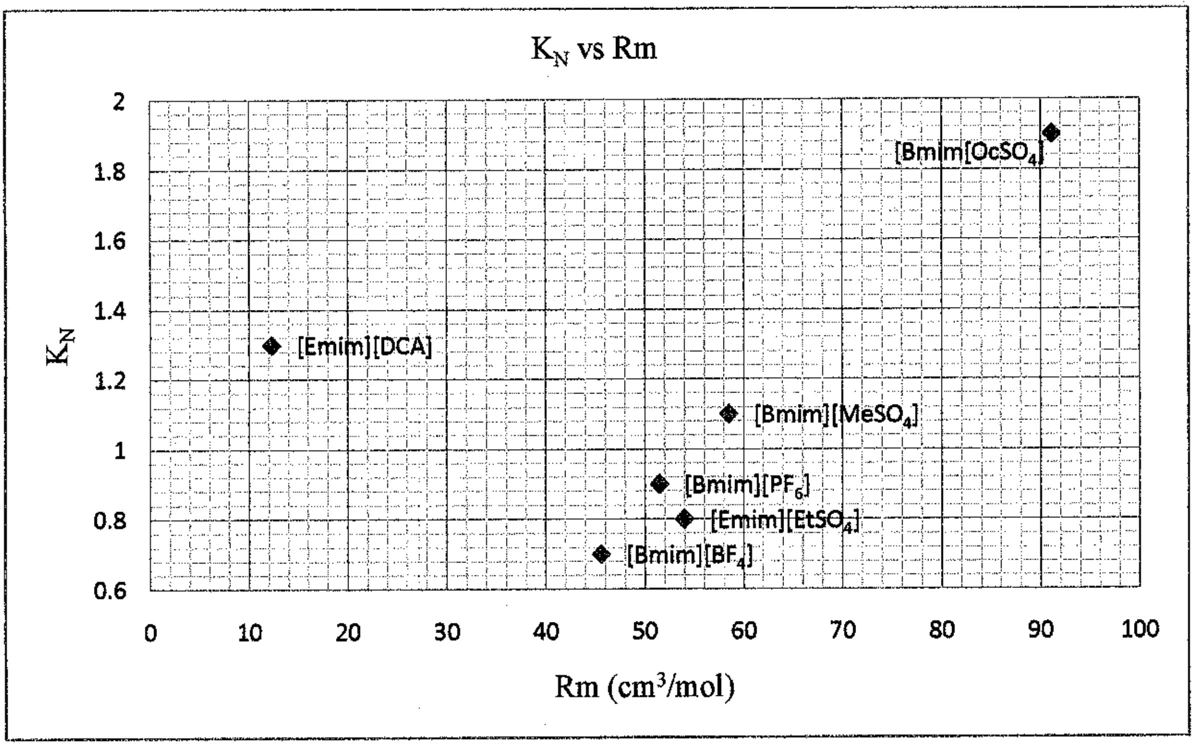


Figure 4.4: Graph of sulfur partition coefficient (K_N) vs molar refraction (Rm).

Besides molar volume (Vm), molar refraction (Rm) may be utilized to predict the desulfurization performance of ILs. Molar refraction, R_M defined as an approximate measure of the total volume (without free space) of the molecules in one mole of compound or in other words the hard core volume of one mole of molecule [9].

From the data above, again it showed that [Emim][DCA] having a significant value of K_N even though the molar refraction (Rm) of the ILs is the lowest, 12.32 cm^3/mol among the listed ILs above. This may be due to the high electron density of [DCA] as mentioned earlier. The K_N value of the [Bmim][BF_4], [Bmim][PF_6] and [Emim][$EtSO_4$] having almost similar of K_N value, 0.7, 0.9 and 0.8 respectively. This is most probably because they all having the same carbon number of 4.

Notice here that the [Bmim][PF_6] have K_N value of 0.9 higher that the [Emim][$EtSO_4$] with value of 0.8 even though the molar refraction of [Emim][$EtSO_4$], 54.02 cm^3/mol is higher than molar refraction of [Bmim][PF_6], 51.46 cm^3/mol. This is most likely due to the alkyl substitute on cation of [Bmim][PF_6] is longer than the alkyl substitute on cation of [Emim][$EtSO_4$].

The observations above showed that the alkyl substitute effect of cation overrides alkyl substitute effect of anion. Never the less, the alkyl substitute effect of anion still play a role to ILs in desulfurization. This is evidenced especially for a common cation but with anion of increasing alkyl substitute. For example, [Bmim][$OcSO_4$] and [Bmim][$MeSO_4$] with K_N value of 1.9 and 1.1.

Since the molar volume of [Bmim][PF_6] and [Emim][$EtSO_4$] are not much in different, they possess similar K_N value. Besides that, for fluorinated ILs, Figure 4.4 displayed that as molar refraction (Rm) increases, the K_N value increases as well. It is proven by the increasing order of molar refraction (Rm) value of [Bmim][BF_4], [Bmim][PF_6] having value K_N of 0.7 and 0.9 respectively.

For alkylsulfate ILs, the molar refraction (Rm) of alkylsulfate ILs in increasing order, [Emim][$EtSO_4$] , [Bmim][$MeSO_4$], [Bmim][$OcSO_4$] also having value of K_N in increasing order, 0.8, 1.1 and 1.9. These observations above demonstrated that if the molar refraction (Rm) of the ILs are available, it can be employed as a tool to predict the ILs desulfurization, i.e. as the molar refraction (Rm) increases, the value of K_N increases too.

3. Refractive Index (R_I)

Table 4.3: ILs Data of Rm and K_N.

No.	ILs	RI	K_N
1	[Emim][DCA]	1.113	1.3
2	[Bmim][PF_6]	1.40844	0.9
3	[Bmim][BF_4]	1.4215	0.7
4	[Bmim][CF_3SO_3]	1.4368	0.8
5	[Bmim][$OcSO_4$]	1.4699	1.9
6	[Bmim][$MeSO_4$]	1.4792	1.1
7	[Emim][$EtSO_4$]	1.4852	0.8

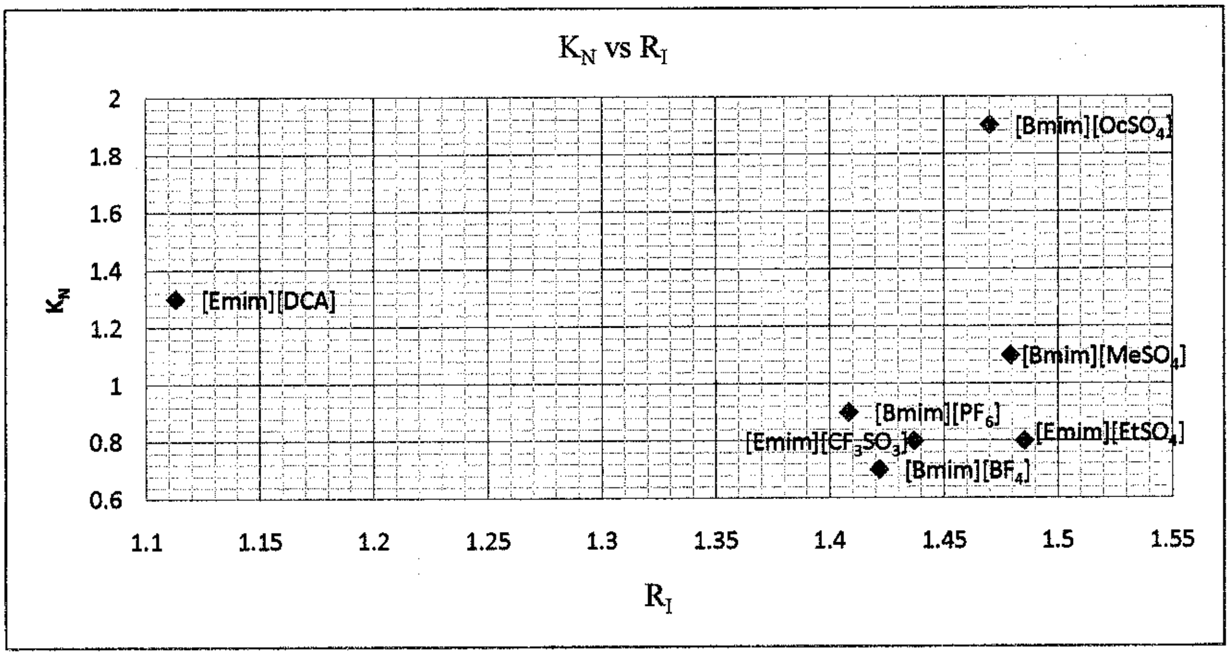


Figure 4.5: Graph of sulfur partition coefficient (K_N) vs refractive index (R_I).

The date above showed that the refractive index (R_I) can also be employed as a tool to predict imidazolium bases ILs ability to extract sulfur. Refractive index (R_I) defined as the ratio c_o/c, where c_o is the speed of light in vacuum and c is the speed of light in medium [9], which in this case in ILs. In other words, R_I describes the ability of the ILs to refract light as it moves from one medium to another medium. Higher value of R_I indicates more light is refracted.

In addition, M.Tariq et al. [23] mentioned that refractive index (R_I) can provide useful information when studying the forces between the molecules; but bear in mind that it shall not be generalized to explain the ILs behavior especially in desulfurization.

$$R_I{}^2 - 1 = 3\left(\frac{V_m}{R-1}\right)^{-1} \tag{4}$$

Equation 4 below tells that increasing the reduced molar volume reduces the refractive index. It also means that as the molar volume increases, the R_I should decreases as well.

This equation applies well on for fluorinated ILs, it can been observed that as the R_I increases from [Bmim][PF_6] to [Bmim][BF_4] with value of 1.40844 to 1.4215, the Vm value decreases too with value of 208.39 cm^3/mol for [Bmim][PF_6] and 188.45 cm^3/mol for [Bmim][BF_4]. The data for alkylsulfate ILs also displayed the same trend.

Another implication of R_I is that the higher the value of R_I, the compound is more tightly packed or dense. Hence, as the compound more tightly packed, the intermolecular forces of the cation and anion are stronger which leads to low ability to extract sulfur from fuel oils. Thus, [Bmim][PF_6] and [Bmim][BF_4] with value of R_I 1.40844 and 1.4215 respectively have K_N value of 0.9 and 0.7. Same explanation can be used to explain the alkylsulfate ILs too.

4. Relation between Density (ρ) and Refractive index (R_I).

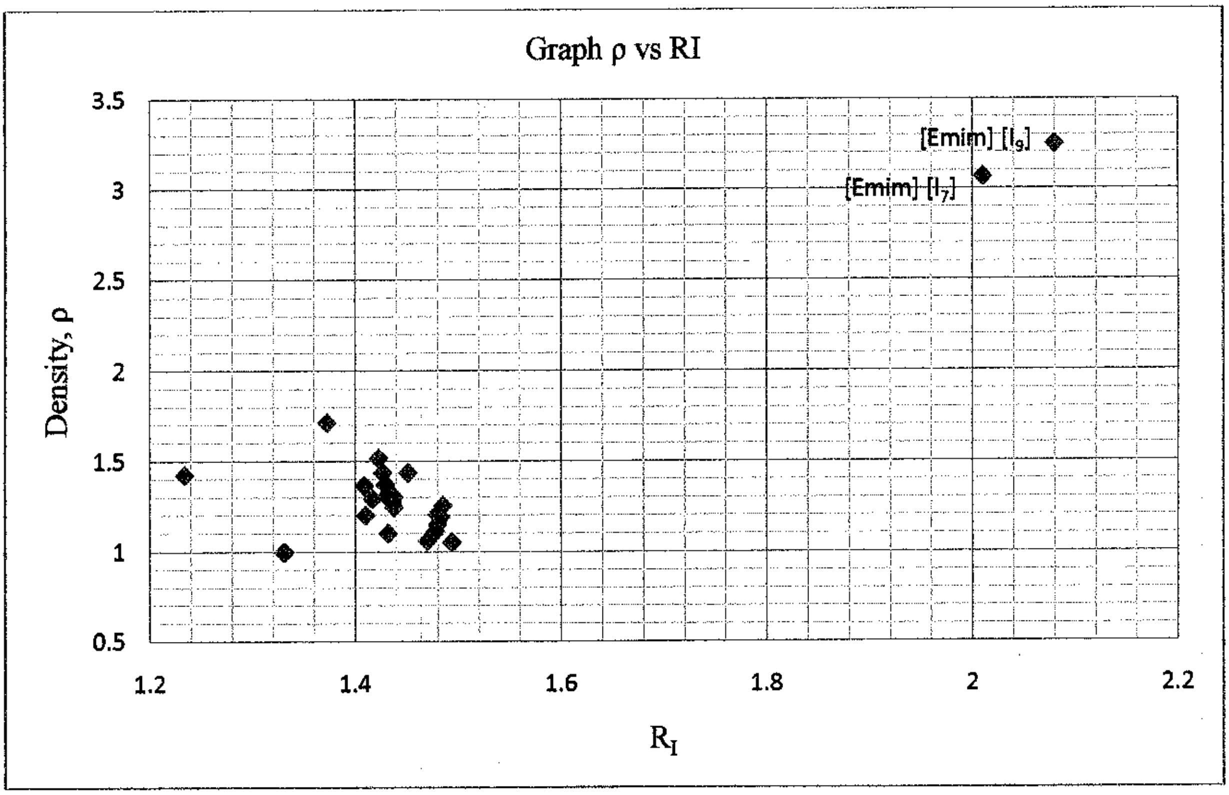


Figure 4.6: Graph of density (ρ) vs refractive index (R_I) of the ILs studied in this work.

Figure 4.6 displays the graph of density (ρ) vs refractive index (R_I) shows that the data are scatter. However, some of the data is correlated and can be explained well the graph. For example, the ILs such as [Emim][I_7] and [Emim] [I_9] as shown in the above graph. According to M. Deetlefs et al [9], as the halide content increases, the density of the ILs increase as well. Hence, the halide content and density increases in the order of [Emim][I_7] to [Emim] [I_9]. In this graph, only ILs that are correlated can be explained are shown.

The other ILs from the scatter data in Figure 4.6 that can be explained also is re-plotted in Figure 4.7 for further discussion.

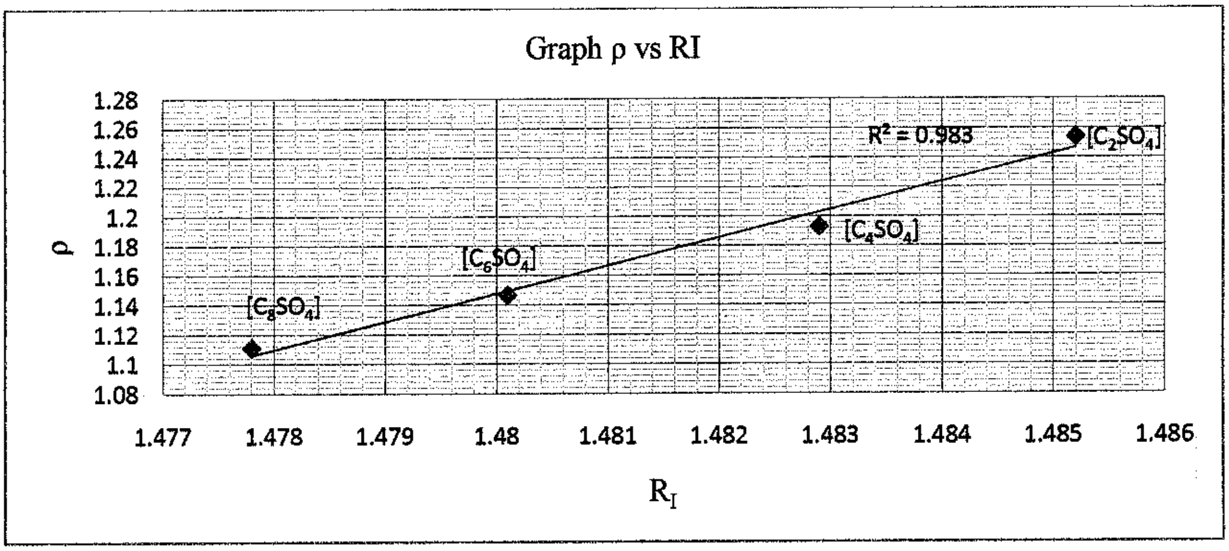


Figure 4.7: Graph of density (ρ) vs refractive index (R_I) of the [Emim] based ILs with anions of [C_2SO_4], [C_4SO_4], [C_6SO_4], [C_8SO_4] which extracted from Figure 4.8.

Figure 4.7 showed that for a common cation which in this case is [Emim], the refractive index increases as the density increases, the linear graph have a value of R^2 of 0.983. This happen because as the alkyl substitute of the anion increases, the ILs species is less packed, volume increases causes the density decreases as well. T. Umecky et al. [1] and M.Tariq et al. [23] both stated that as the alkyl chain increase, the density decreases which aligns with the result displayed by the graph presented above.

Besides that, the refractive index of the [Emim] based ILs increases as alkyl chain anion decreases. M. Deetlefs et al. [9] explained that higher refractive index indicates that more light are reflected which translate into tightly packing of the compounds, also means that the compound is denser. Hence, [Emim][C_2SO_4] which have the highest value of refractive index, 1.4852 also having highest value of density of 1.25412 among the ILs in concerned here.

5. Relation between Carbon Number Alkyl Substitute of ILs (CN) and Sulfur Partition Coefficient (K_N).

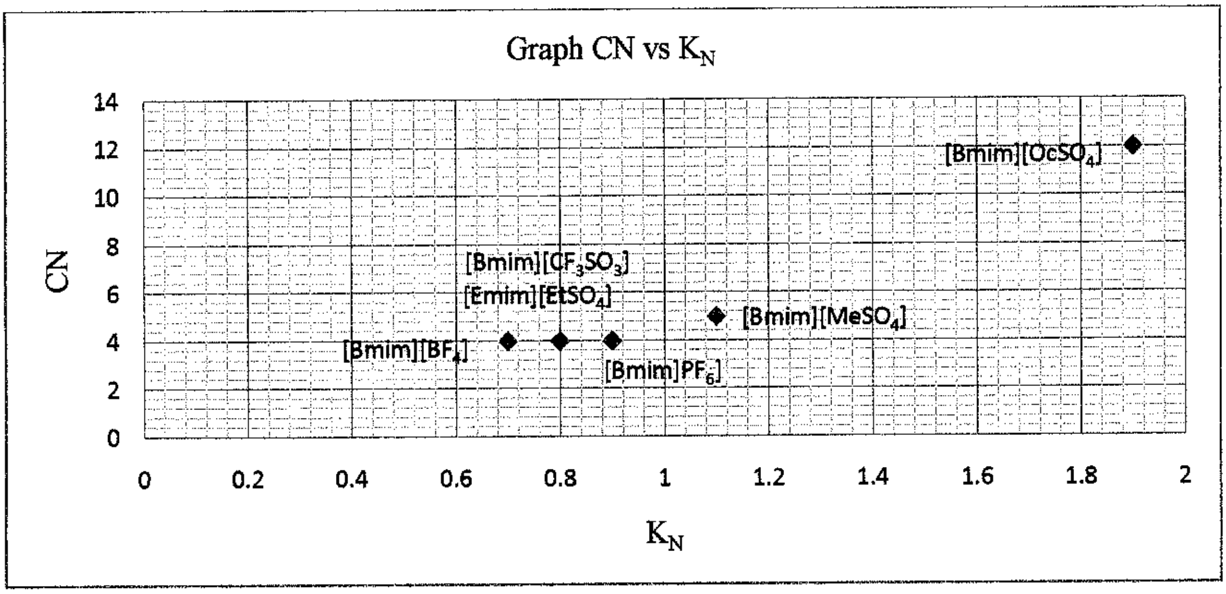


Figure 4.8: Graph of carbon number alkyl substitute of ILs (CN) vs sulfur partition coefficient (K_N).

Figure 4.8 displayed a graph of carbon number alkyl substitute of ILs, CN vs sulfur partition coefficient, K_N. The graph showed that as carbon number alkyl substitute of ILs, CN increases, the sulfur partition coefficient, K_N also increases. X. Jiang et al. [8], Chu et al. [17], Yi Nie et al. [21] explained that as the carbon number alkyl substitute of ILs increases, the polarity and the dispersion energy of π electrons of the cation increases as well.

A. P. Kumar et al. [24] discovered that as the carbon number alkyl substitute of ILs, CN increases, the Van Der Waals volume increases leads to bond between the cation and anion weaker. It then allows the imidazolium cation absorbs more sulfur compounds or in other words a stronger interaction π- π interaction of the sulfur and imidazolium cation.

In addition, the alkyl substitute can as well relate to the ILs size. As the ILs size increases, it leads to weaker interaction between cation and anion. Yi Nie et al. [21] and A. P. Kumar et al. [24] explained that as the columbic interaction between cation and anion gets weaker, it allows the cation to accommodate and extract the sulfur better.

Another observation from Figure 4.8 is that the ILs such as [Emim][EtSO$_4$], [Bmim][BF$_4$], [Bmim][PF$_6$] and [Bmim][CF$_3$SO$_3$] having the similar value of sulfur partition coefficient, K$_N$ 0.8, 0.7, 0.9, 0.8. This is because they having the same value of carbon number alkyl substitute i.e. 4.

6. Relation between Sulfur Partition coefficient (K_N) and Density (ρ).

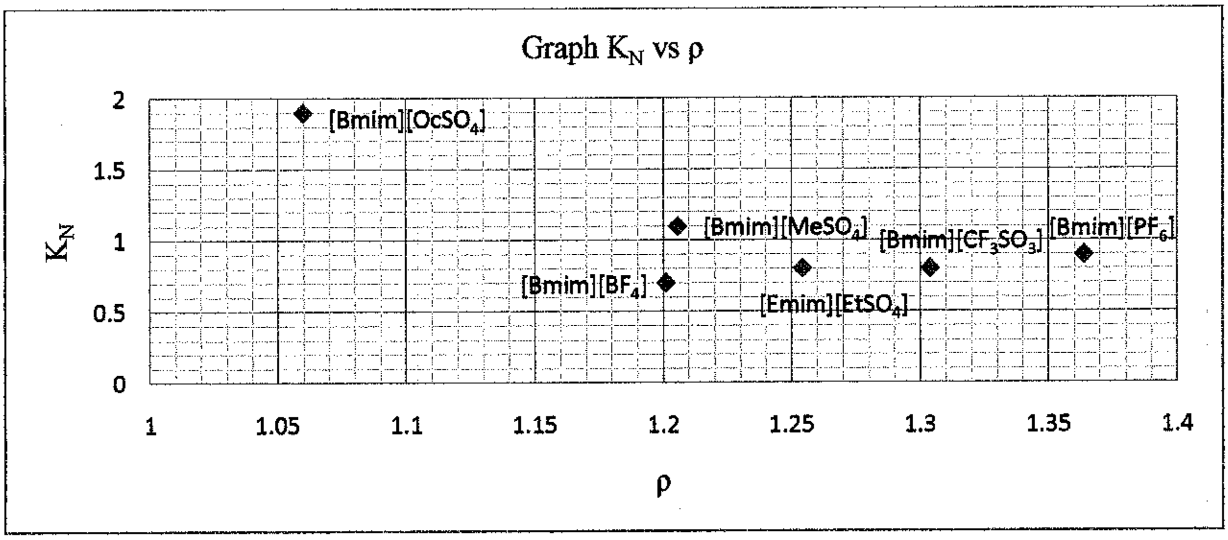


Figure 4.9: Graph of sulfur partition coefficient (K_N) vs density (ρ).

Figure 4.9 displayed the graph of sulfur partition coefficient (K_N) vs density (ρ). The graph showed that density is a poor correlation to sulfur partition coefficient (K_N).

7. Relation between Molar Refraction (Rm) and Refractive Index (R_I).

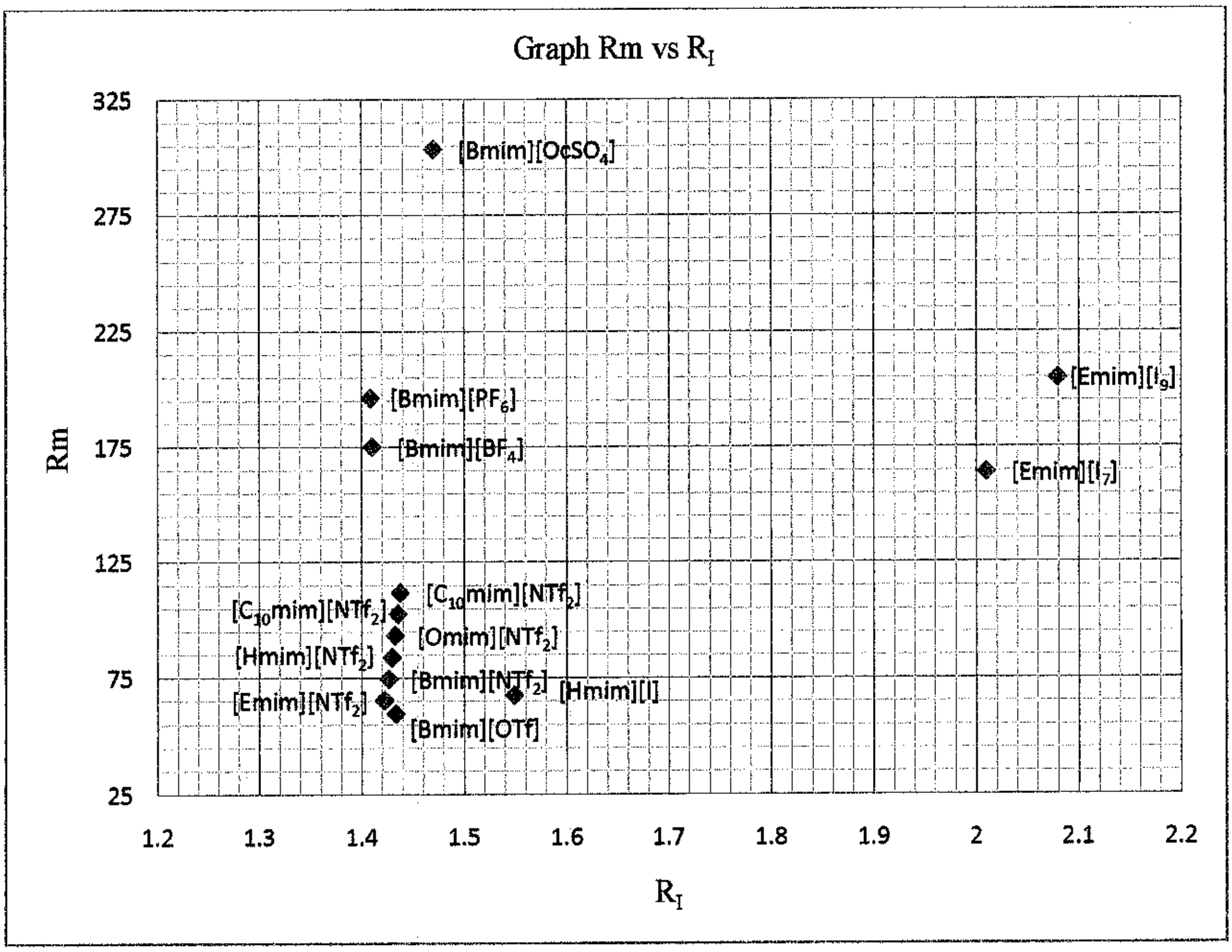


Figure 4.10: Graph of molar refraction (Rm) vs refractive index (R_I).

Figure 4.10 displayed a graph of molar refraction (Rm) vs Refractive Index (R_I). For the ILs of [Hmim][I], [Emim][I_7] and [Emim][I_9] shown above, as the refractive index increase, the hard core volume of the ILs, Rm increases as well. H. Machida et al. [25] stated that the hard core volume, i.e. Rm of ILs is related to the anion size. The series of ILs [Hmim][I], [Emim][I_7] and [Emim][I_9] in the graph shows that as the halide content increases, refractive index (R_I) increases, so is the molar refraction (Rm). It aligns with the finding in Figure 4.6 that as the halide content increases which applicable for [Hmim][I], [Emim][I_7] and [Emim][I_9] , the density of the ILs increases as well due to the increase of Rm.

The IL [Hmim][I] density data is not available from the literature done, but it can be predicted that the density in the increasing order is [Hmim][I], [Emim][I_7] and [Emim][I_9]

based on the theory of increasing of halide content supported by the graph above (Rm and R_I increases in the same order as well). [Bmim][PF_6] and [Bmim][BF_4] that having similar K_N value mentioned previously in Figure 4.8 having the similar value of R_I and Rm, 1.40844, 196.2 and 1.41, 175.3. [Bmim][$OcSO_4$] is having the highest value of molar refraction (Rm) of 303.6. This is due to the fact that H. Machida et al. [25] had proved the free volume of the [Bmim][$OcSO_4$] is much larger compare other studied ILs.

Besides that, some of the data are extracted from the Figure 4.10 and plotted in Figure 4.11 for further discussion.

8. Relation of Molar Refraction (Rm) and Refractive Index (R_I) for [NTf_2] Anion Based ILs with Different Cations.

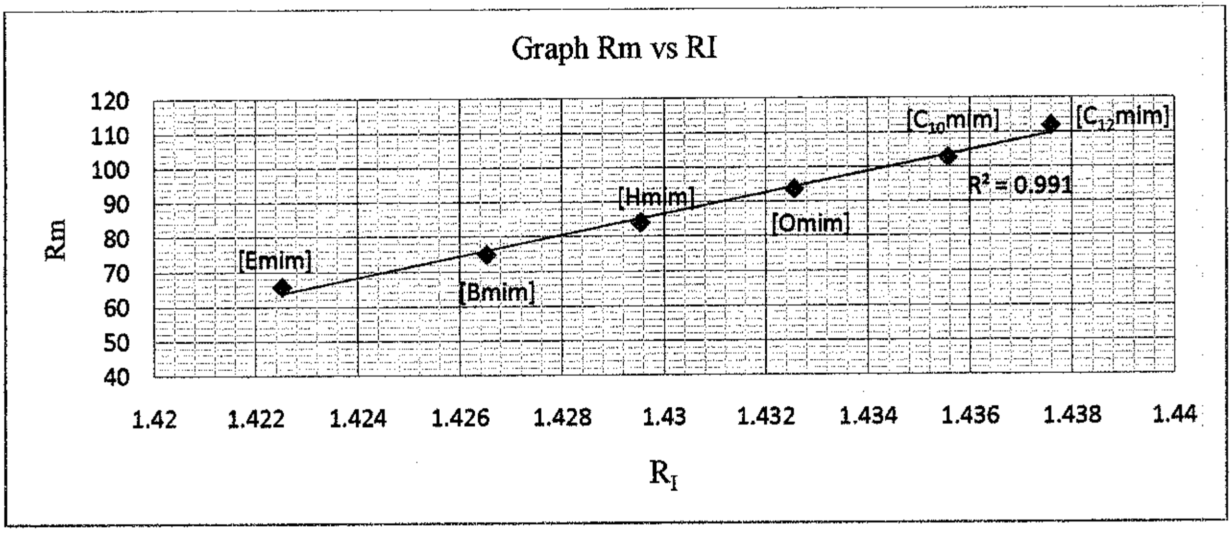


Figure 4.11: Graph of molar refraction (Rm) vs refractive index (R_I) for [NTf_2] anion based ILs with different cations.

Figure 4.11 displayed the graph of molar refraction (Rm) vs refractive index (R_I) for [NTf_2] anion based ILs with different cations. For a common anion based ILs, the refractive index (R_I) increases with the increase of molar refraction (Rm) and gives a value of R^2 of 0.991. According to the formula given by M. Deetlefs et al [9],

$$Rm = \left(\frac{F_W}{\rho}\right)\left(\frac{R_I^2-1}{R_I^2+2}\right) \tag{5}$$

where *Rm* = Molar refraction or hard core volume, *Fw* = formula weight,

ρ = density,

R_I = reflactive index.

Equation (5) proved that as refractive index (R_I) increases, the molar refraction (Rm) increases as well, which explains well the trend of the graph.

Another interesting point is displayed by Figure 4.11 as cation alkyl chain gets longer, the refractive index (R_I) increases and the molar refraction (Rm) increases too.

9. Relation between Density (ρ) and Refractive Index (R_I) for [NTf$_2$] Anion Based ILs with Different Cations.

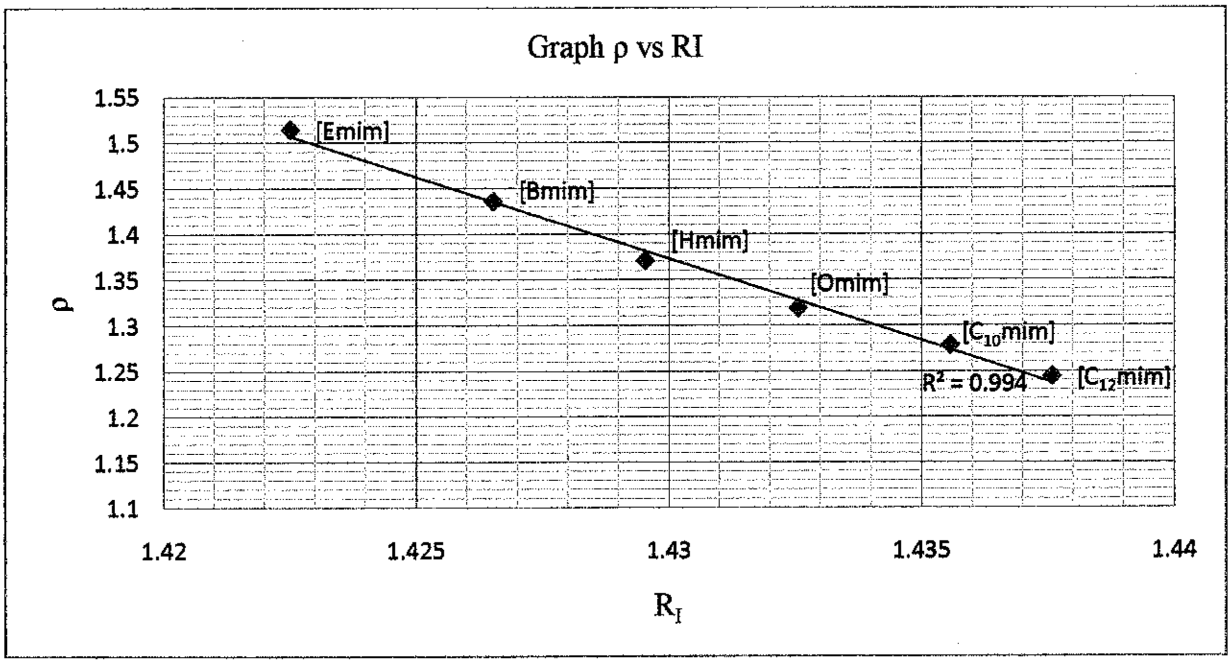


Figure 4.12: Graph of density (ρ) vs refractive index (R_I) for [NTf$_2$] Anion based ILs with different cations.

Figure 4.12 showed a graph of density (ρ) vs refractive index (R_I) for [NTf$_2$] anion based ILs with different cations. The graph proved that for a common anion ILs, as the alkyl chain gets longer, the refractive index increases but the density decreases. Combination of Figure 4.11 and Figure 4.12 clearly explains that as the alkyl chain increases, the hard core volume, Rm increases causing the density decreases. It is supported by T. Umecky et al. [1] that as the alkyl chain longer, the density decreases.

CHAPTER 5

CONCLUSION AND RECOMMEDATION

Based on Chapter 4 as well as supported by thorough literature review done, there is several general observations worth to be pointed out. Those observations are listed below.

1. For ILs are from same anion family or common anion, as molar volume (Vm) or the molar refraction (Rm) increases or the refractive index (R_I) decreases, the ability of the ILs to extract sulfur (K_N) increases as well.
2. Alkyl substitute effect of cation overrides alkyl substitute effect of anion.
3. As the alkyl substitute of the ILs increases or the ILs size increases, the ability of the ILs to extract sulfur (K_N) increases as well, can apply for alkyl substitute anion of common cation or alkyl substitute cation of common anion.
4. As the halide content of ILs increases, the density of the ILs increases, refractive index (R_I) increases, so is the molar refraction (Rm).
5. For a common cation and same anion family or common anion, the longer the alkyl chain of anion causes density (ρ) decreases.
6. For a common cation and common anion with decreasing of anion alkyl chain, the refractive index (R_I) increases as the density (ρ) increases.
7. Density is a poor correlation to sulfur partition coefficient, K_N.
8. For a common anion based ILs, as the cation alkyl chain longer, the refractive index (R_I) increases with the increase of molar refraction (Rm) but the density (ρ) decreases.

The outcome of this study outcome allows the preliminary screening of the various number of Imidazolium based ILs existing so far in the effort to select a good one that able to extract sulfur from fuel oils effectively. This screening can be done by just having parameters such as the molar volume (Vm), molar refraction (Rm) and refractive index (R_I) which can be easily obtained.

Perhaps molar volume (Vm) and molar refraction (Rm) and refractive index (R_I) can used as a primary tool to predict desulfurization of ILs provided they are from the same anion family or common anion. This is because molar volume (Vm) gives a big picture of the π-electron dispersion forces and molar refraction (Rm) which take into account the refractive index (R_I) of the ILs which provide the insightful view of the intermolecular forces of the cation an anion.

The hypothesis developed is as the molar volume (Vm), molar refraction (Rm) increases and refractive index (R_I) decreases the K_N value that measures the sulfur extractability of the ILs increases. This hypothesis allows predictions to be done on various ILs existing so far. No more trial and error that time consuming and no more uncertainty in the search of a good IL which extract sulfur well among the various ILs exists so far.

However, future works need to be conducted to establish a concrete and accurate finding. A ILs database that similar to periodic table of the elements is worth to be developed. This database can provide the researchers the necessary information in assisting the researches to understand the ILs either from the physical properties or till the intermolecular level. It also permits exploration more about the potential of the ILs.

It should be clearly emphasize here that the molar volume (Vm) and molar refraction (Rm) only provide the prediction or estimation of the ILs desulfurization ability. Others factors might as well affect the ILs desulfurization performance. Further insight study shall be done to understand better the ILs desulfurization ability.

Few measures can be taken to further improve the result obtained in this study. Researches can perform experiment on desulfurization on various ILs since in this scope of project, the focus is on imidazolium based ILs. Future work may be extended to pyridinium, pyrazolium, cholinium, phosphonium, ammonium based ILs etc to check if the hypothesis developed here applicable to them.

In addition, the hypothesis developed in this project is based on the ILs literature review exists so far. It can be further proven by experiment works that cover more ILs in desulfurization.

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APPENDIX

No.	ILs	RI	Density (g/cm^3)	MW (g/mol)	Rm (cm^3/mol)	Vm (cm^3/mol)	Type of S removed	K$_N$
1	[Mmim][DMP]		1.27 [1]	222.18 [1]		174.95 [2]	DBT BT 3-MT	0.46 [3] 0.47 [3] 0.059 [3]
2	[Mmim][MeSO$_4$]	1.48270 [18]	1.33 [4]	208.24 [4]	44.69 [5]	156.57 [2]		
3	[Emim][I]			238.07 [1]				
4	[Emim][I$_7$]	2.01 [6]	3.0660 [6]	999.50 [6]	164.33 [6], 164.08 [5]	325.99 [2]		
5	[Emim][I$_9$]	2.08 [6]	3.2464 ± 0.0014 [6]	1253.31 [6]	204.90 [6], 202.99 [5]	386.06 [2]		
6	[Emim][DEP]		1.150 [1]	264.26 [1]		229.79 [2]	DBT BT 3-MT	1.27 [3] 0.94 [3] 0.47 [3]
7	[Emim][OTf]	1.43320 [7]	1.386 [1]	260.24 [1]	48.82 [5]	187.76 [2]		
8	[Emim][TSO$_3$]			282.36 [1]				
9	[Emim][PF$_6$]		1.4218 [8]	256.13 [4]		180.15 [2]		
10	[Emim][BF$_4$]		1.34 [1]	197.97 [1]		147.74 [2]		
11	[Emim][FAP]		1.71 [1]	556.17 [1]		325.25 [2]		
12	[Emim][EtSO4]	1.4852 [9]	1.25412 [9]	236.29 [1]	54.02 [5]	188.41 [2]	DBT	0.8 [3]
13	[Emim][DMP]		1.27 [1]	236.21 [4]		185.99 [2]	DBT BT 3-MT	1.17 [3] 0.92 [3] 0.50 [3]
14	[Emim][NTf$_2$]	1.42251 [10]	1.5147 [10]	391.31 [1]	65.72 [10]	258.35 [10]		
15	[Emim][MeSO$_4$]	1.4852 [9]	1.28 [1], 1.25412 [9]	222.26 [1]	49.78 [5]	173.64 [2]		
16	[Emim][C$_4$SO$_4$]	1.4829 [9]	1.19311 [9]	264.34 [1]	63.26 [5]	221.56 [2]		
17	[Emim][C$_6$SO$_4$]	1.4801 [9]	1.14705 [9]	292.4 [1]	72.43 [5]	254.91 [2]		
18	[Emim][OcSO$_4$]	1.4778 [9]	1.11129 [9]	320.45 [1]	81.60 [5]	288.36 [2]		
19	[Emim][HSO$_4$]		1.38 [1]	208.24 [1]		150.90 [2]		
20	[Emim][Cl]		1.112 [4]	146.62 [1]		131.85 [2]		

21	[Emim][Br]	1.^{33048}[11]	0.99762 [11]	191.07 [1]	39.13 [5]	191.53 [2]		
22	[Emim][DCA]	1.113 [12]	1.060 [4]	177.21 [1]	12.32 [5]	167.18 [2]	DBT	1.3 [13]
23	[Emim][OAc]		1.027 [4]	170.21 [4]		165.75 [2]		
24	[Emim][SCN]	1.148 [12]	1.11 [1]	169.25 [1]	14.61 [5]	152.48 [2]		
25	[Pmim][BF4]		1.240 [19]	212		170.97 [2]		
26	[Bmim][OcSO4]	1.4699 [14]	1.060 [15] 1.0676 [14]	348.51 [1]	91.07 [5]	303.6 [15] 326.46 [14] 328.78 [2]	DBT	1.9 [3]
27	[Bmim][OTf]	1.433 [6] 1.43657 [10]	1.2968 ± 0.0008 [6] 1.2995 [10]	288.29 [6]	59.77 [6] 58.07 [10], 58.19 [5]	221.84 [10] 222.31 [2]		
28	[Bmim][FAP]	1.451 [2]	1.4363 ± 0.0011 [2]	584.23 [8]	108.98 [5]	404.76 [2]		
29	[Bmim][SCN]		1.070 [4]	197.30 [4]		184.39 [2]		
30	[Bmim][NTf$_2$]	1.42653 [10] 1.451 [6]	1.4360 [10] 1.4363 [6]	419.37 [6]	74.91 [10, 15] 79.83 [6]	292.04 [10] 292.04 [2]		
31	[Bmim][MeSO$_4$]	1.4792 [16] 1.47775 [10]	1.2057 [16] 1.2113 [10]	250.32 [1]	58.47 [10, 5]	206.65 [10] 207.61 [2]	DBT	1.1 [3]
32	[Bmim][BF$_4$]	1.410 [6] 1.33192 [11] 1.42150 [10] 1.4208 [14]	1.2011 ± 0.0002 [6] 0.9957 [11] 1.1994 [10] 1.2012 [14]	226.02 [6]	45.57 [6] 47.84 [10,2]	188.45 [10] 188.18 [2]	DBT	0.7 [3]
33	[Bmim][HSO$_4$]		1.277 [4]	236.29 [1]		185.04 [2]		
34	[Bmim][Cl]	1.33088 [11]	0.99922 [11]	174.68 [1]	35.75 [5]	174.82 [2]		
35	[Bmim][PF$_6$]	1.40844 [10]	1.3637 [10]	284.2	51.46 [10, 5]	208.39 [10] 208.40 [2]	DBT	0.9 [3]

36	[Bmim][DMP]						DBT BT 3-MT	1.59 [3] 1.37 [3] 0.59 [3]
37	[Bmim][DBP]		1.056 [4]	348.32 [4]		329.85 [2]	DBT BT 3-MT	1.59 [2] 1.37 [2] 0.59 [2]
38	[Bmim][$AlCl_4$]						DBT	4 [3]
39	[Bmim][CF_3SO_3]	1.4368 [16]	1.3038 [16]				DBT	0.8 [3]
40	[Bmim][OAc]	1.49381 [10]	1.0532 [10]	198.26 [4]	42.06 [10]	144.53 [10] 188.25 [2]		
41	[Bmim][I]	1.572 [17]	1.49 [1]	266.13 [1]	58.77 [5]	178.61 [2]		
42	[Bmim][I_3]	1.70 [6]	2.1468 ± 0.0037 [6]	519.92 [6]	91.83 [6], 93.60 [5]	242.18 [2]		
43	[Bmim][I_5]	1.91 [6]	2.5731 [6]	773.72 [6]	140.92 [6], 140.98 [5]	300.70 [2]		
44	[Bmim][I_7]	1.95 [6]	2.8642 ± 0.0001 [6]	1027.52 [6]	175.07 [6], 173.27 [5]	358.75 [2]		
45	[Bmim][Br]	1.33176 [11]	0.9996 [11]	219.13 [1]	44.94 [5]	219.22 [2]		
46	[Bmim][CSO_4]				207.26 [14]			
47	[Bmim][DCA]		1.06 [1]	205.26 [1]		193.64 [2]	DBT	2.28 [13]
48	[Hmim][BF_4]	1.42371 [20]	1.14 [1]	254.08 [1]	56.84 [5]	222.88 [2]		
49	[Hmim][OTf]		1.040 [4]	330.37 [4]		317.66 [2]		
50	[Hmim][FAP]		1.56 [1]	612.29 [1]		392.49 [2]		
51	[Hmim][NTf_2]	1.42954 [10]	1.371 [10]	447.42 [1]	84.23 [10, 5]	326.35 [10,2]		
52	[Hmim][PF_6]	1.41648 [10] 1.41787 [21]	1.2924 [3] 1.2937 [21]	312.2 [13] 312.24 [1]	60.69 [10, 5]	241.59 [10] 241.57 [2]		
53	[Hmim][Cl]	1.515 [17]	1.05 [1]	202.73 [1]	58.22 [5]	193.08 [2]		

54	[Hmim][I]	1.549 [6]	1.3814 ± 0.0004 [6]	294.17 [6]	67.07 [6], 67.74 [5]	212.95 [2]		
55	[Eeim][DEP]						DBT	1.61 [3]
56	[Beim][DBP]						DBT BT 3-MT	1.72 [3] 1.49 [3] 0.91 [3]
57	[Omim][NTf_2]	1.43251 [10]	1.3189 [10]	475.48	93.61 [10], 93.60 [5]	360.51 [10,2]		
58	[Omim][PF_6]	1.2340 [10]	1.2340 [10]	340.3 [13]	70.29 [10]	275.76 [10,2]		
59	[Omim][BF_4]	1.4319 [14]	1.1019 [14]	282.13	66.40 [5]	256.04 [2]		
60	[Omim][Cl]	1.505 [17]	1.000 [17]	230.78	68.45 [5]	230.78 [2]		
61	[C_{10}mim][NTf_2]	1.43557 [10]	1.2783 [10]	499.5	102.90 [10, 5]	393.88 [10], 390.75 [2]		
62	[C_{12}mim][NTf_2]	1.43758 [10]	1.2447 [10]	523.5	112.02 [10, 5]	427.07 [10]		
63	[C_{14}mim][NTf_2]	1.43456 [10]	1.2006 [10]	547.5	121.53 [10, 5]	466.14 [10]		
64	[Hmim][I]	1.549 [6]	1.3814 ± 0.0004 [6]	294.17 [6]	67.07 [6], 67.74 [5]	212.95 [2]		

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