Synthesis of Nitrile-Functionalized Sulphonium Ionic Liquids for the Desulfurization of Model Oil

by

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(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the

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Approved by,

…………………………………………………………
(Assoc Prof Dr. Mohamed Ibrahim Bin Abdul Mutalib)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
January 2014

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 excepts 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 HIDAYAH BINTI HASNAN

ABSTRACT

Ionic liquids are known as salt in liquid state and act as green solvents for synthesis, separation, chemical synthesis and electrochemistry. In the petroleum refining industry, one of the focused areas is to remove the sulfur in fuel because the sulfur contained in engine emissions would give negative impact to the environment. Besides, the current method of extracting sulfur compounds from crude oil have been used which is hydrodesulfurization (HDS). Unfortunately, the efficiency of HDS is very low and limited in treating the steric hindrance type of sulfur. Hence, this report contains the study on the Synthesis of Nitrile-Functionalized sulphonium ionic liquids for the desulfurization of model oil. The objective is to synthesis nitrile functionalized sulphonium ionic liquid and determines its performance in extractive desulfurization of model oil. In overall, the project scope and methodology involved mainly four stages; synthesis of the nitrile functionalized sulphonium ionic liquids, characterization of ionic liquids using ^{1}HNMR, FTIR and Anton Paar Viscometric, extraction of dibenzothiophene(DBT) from model oil (containing 500 ppm of DBT in dodecane)and determination of sulfur removal efficiency using Gas Chromatography.. The experiment went well and four ionic liquids were synthesized which are 1-Ethyl-tetrahydrothiophenium thiocyanate, 1-Ethyl-tetrahydro-thiophenium dicyanamide, 1-Butyltetrahydrothiophenium thiocyanate and 1-Ethyl-tetrahydrothiophenium dicyanamide. 1-Butyl-tetrahydro-thiophenium thiocyanate ionic liquid was used to extract sulfur compound, Dibenzothiophene (DBT), from model oil. The average percentage sulfur removal from model oil was 44.12%.

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SOx	Sulfur oxide
HDS	Hydrodesulfurization
Dibenzothiphene	DBT
ILs	Ionic Liquids
$[C_1mim][DMP]$	1-methyl-3-methylimidazolium diethyl phosphate
$[C_2mim][DEP]$;	1-ethyl-3-methylimidazolium diethyl phosphate
$[C_4mim][DBP]$	1-butyl-3-methylimidazolium dibutyl phosphate
$[C_4Py][BF_4]$	1-buylpyridinium tetrafluoroborate
$[C_6Py][BF_4]$	1-hexypyridinium tetrafluoroborate
$[C_8OPy][BF_4]$	1-octylpyridinium tetrafluoroborate
^{13}C-NMR	carbon-13 NMR
^{1}H-NMR	Proton NMR
FTIR	Fourier Transformer Infrared
GC	Gas Chromatography
ppm	Part Per Million
g	Gram
ml	Milliliter
MSDS	Material Safety Data Sheet

CHAPTER 1

INTRODUCTION

1.1 Background Study

The first discovery of oil in Sarawak in 1910 had provided the bedrock for the development of Malaysia's present oil and gas industry. Nowadays, the oil and gas industry had become one of the major industries in Malaysia and the demand from this industry has increased from year to year. Crude oil is the terms used for oil that is taken straight out of the ground which can be refined into various forms of energy such as gasoline, diesel fuel and heating oil. It is also a key component in a variety of chemical products such as plastics, detergents, paints and even medicines. Although crude oil assays evaluate various chemical properties of the oil, one of the most important properties determining the quality of the crude is its sulfur content. Crude oil is considered "sweet" if it is low in sulfur content or "sour" if the content of sulfur is high. It is important to remove sulfur as much as it can be removed because the combustion of sulfur species present in the crude lead to sulfur oxide (SOx) emission into the air and cause air pollution. Besides, sulfur dioxide oxidizes via several chemical pathways to form sulfur trioxide which then combines with water vapor or droplets to make sulfuric acid and causing acid rain. Due to stricter engineering regulations for the oil industry regarding the sulfur content, specifications of sulfur content are becoming more and more stringent worldwide.

With that, the project will covered about the method of removing sulfur from the crude oil by using ionic liquids. The title of the project is 'Nitrile-Functionalized Sulphonium Ionic Liquids for the Desulfurization of Model Oil'.

1.2 Problem Statement

1.2.1 Problem Identification

In the petroleum refining industry, hydrodesulfurization (HDS) is a catalytic chemical process that widely used to remove sulfur from refined petroleum products such as diesel fuel and fuel oils. The process basically involves catalytic hydrogenation of sulfur compounds to be converted into hydrogen sulfide by reacting crude oil fractions with hydrogen at reaction condition of 350 ^oC and 30 to 100 bar hydrogen pressure. Then, the hydrogen sulfide which is separated from the desulfurized oil is oxidized catalytically with air into elemental sulfur. This hydrodesulfurization process is highly effective for removing thiols, sulfides and disulfides. However, it is difficult to remove organic sulfur compounds with sterically hindered sulfur such as dibenzothiophene (DBT) because severe conditions are required in order to remove such compound. This will be resulted in large hydrogen consumption and making the operating process more expensive.

The refinery processing plant could have some problems if sulfur is not removed from the crude oil such as corrosion and leaking of the pipeline due to the presents of hydrogen sulphide. Sulfur compounds also produces sulfur dioxide (SO_2) from the burning of fuel by automotive vehicle as well as oil burning from power plant thus affecting the environment.

Therefore, an effective and easily applicable method needs to be importantly explored which can remove or lower down the amount of sulfur contents in the crude oil while not affecting the fuel properties themselves. The latest study also shows that ionic liquids have gained more interest over the past years due to its unique properties both as an extractant and also as a catalyst. By extracting these sulfur compound from the crude oil with ionic liquids could offer such a solution as an alternative to hydrodesulfurization.

1.2.2 Significant of the Project

The significant of the project is that by doing this project, it automatically offers an alternative method of removing sulfur from the model oil which is more environmental friendly.

1.3 Objective and Scope of Study

1.3.1 Objectives

The main purpose of this project is to find the alternative method for the sulfur removal in crude oil and environmentally friendly method by using the ionic liquids to extract sulfur from the model oil. The others main objectives of this project are also include:

- To synthesis and characterization of the nitrile-functionalized sulphonium ionic liquids
- To conduct the extractive desulfurization of the model oil using the nitrile-functionalized sulphonium ionic liquids
- To determine the extraction performance of the ionic liquids prepared

1.3.2 Scope of Study

Basically, the scope of this project includes determination of the efficiency of the nitrile-functionalized sulphonium ionic liquids in the desulfurization of crude oil. Once the ionic liquid was prepared, it was tested by using crude oil. The efficiency of the sulfur removal was evaluated by measuring the sulfur content in the model oil before and after the extraction with the synthesized ionic liquid.

1.4 The Relevancy of the Project

This project is relevant as from previous study it is proved that the ionic liquids are highly potential as an extractant. In addition, the project regarding the desulfurization of model oil is really related to the chemical industries especially to the oil and gas industries. Prevention and removal of sulfur from the crude oil is one of the important things to maintain the quality and quantity of productions. Hence, this research really helpful to understand the role of ionic liquids to remove sulfur in the crude oil.

1.5 Feasibility of the Project within the Scope and Time

Within almost 12 weeks of project completion, this project had accomplished due to the gantt chart and milestone that provided by supervisor and coordinator is followed strictly and accordingly. Nevertheless, some of the experiment and analysis was not being conducted yet and can be treated as future work. For the overall results from the experiment, the ionic liquids were synthesized and the extraction efficiency of the prepared ionic liquids in removing sulfur compounds from the crude oil was evaluated.

CHAPTER 2

LITERATURE REVIEW

In the era of the globalization, crude oil is still a vital source of energy for the world and will likely remain so for many decades to come. Most countries are significantly affected by developments in the crude oil market either as producers, consumers or both. In 2008, oil provided about 34% of the world's energy needs and in the future oil is expected to continue to provide a leading component of the world's energy mix (Natural Resources Canada, 2010). McGuigan (2003) stated that crude oil is a liquid found naturally in rock, containing mostly complex hydrocarbons with some additional organic material. It consists of carbon (83-87%), hydrogen (14%) and also of oxygen, nitrogen and sulfur (0.1-2%). Overall, crude oil consists of hydrocarbons, asphaltenes and resins, sulfur and ash. Paraffinic, naphthenic and aromatic hydrocarbon is the main group in crude oil.

Sulfur compounds are non-hydrocarbon contents of crude oil. Normally crude oil consists of three different types of sulfur compounds such as hydrogen sulphide (H_2S), elemental sulfur and aromatic sulfur compounds. Jiang *et al.* (2008) and Jian-long *et al.* (2007) discovered that aromatic sulfur compounds such as thiophenes and dibenzothiophenes are the most difficult sulfur compound to eliminate by using hydrodesulfurization (HDS) which is one of the desulfurization methods that have been recently used to eliminate certain type of sulfur compounds in crude oil. This problem is due to the low efficiency of catalyst to eliminate sulfur compounds. The structure of aromatic sulfur compounds that are satirically hindered causes the sulfur compounds cannot achieve high surface contact.

Failure to eliminate sulfur in crude oil will result in the released of SOx to the air and the emission of these oxides can cause serious respiratory diseases such as lung cancer if the person inhales the air. Stricter regulations are now being made compulsory in several nations and it is imposed on oil refineries to reduce sulfur contents to the range of 10-20 ppm (Asghar Molaei Dehkordi, March 2009). In 1993, the Clean Air prescribed the sales and supply of diesel oil with sulfur concentration more that 500 ppm.

In 1998, the European Union set the target for the year 2000 and 2005 for sulfur content in diesel fuel at the levels of 350 and 50 ppm respectively and in 2011 the sulfur content of free gasoline is under 10 ppm. New sulfur regulations took effect in Canada and the United States from June 1, 2006 to reduce the sulfur content in on-road diesel fuel and gasoline from 500 ppm to 350 ppm respectively. The maximum allowable sulfur content in diesel is targeted at 10 ppm by 2011 in the US. The sulfur content in gasoline will probably reach an average value of about 10 ppm in many countries by 2011 (Josef, Pavel and Michal, 2006).

2.1 Conventional Desulfurization Technology

On the other side, there are also technologies on non-conventional desulfurization processes which do not use hydrogen for the removal of sulfur compounds. The non-conventional desulfurization studies can be categorized into a few techniques such as adsorption. Desulfurization by adsorption is based on the ability of a solid sorbent to selectively adsorb sulfur compounds from the refinery stream. Based on the mechanism of the sulfur compound interaction with the sorbent, adsorption can be divided into two groups, adsorptive desulfurization and reactive adsorption desulfurization. Adsorptive desulfurization is based on the physical adsorption of sulfur compounds on the solid surface of the sorbent. Be washing the used sorbent with solvents (mixture of toluene and methanol), regeneration can be done and this result in high sulfur compound concentration flow (Yeon, et al., 2005). While for reactive adsorption desulfurization, chemical interaction between the sulfur compounds and the sorbent is applied. Sulfur is fixed on the sorbent, usually as sulfide and the S-free hydrocarbon is released into the purified fuel stream (Yeon, et al., 2005).

Regeneration of the spent sorbent results in sulfur elimination as H2s, S or SOx depending on the process applied. Efficiency of the desulfurization is mainly determined by the sorbent properties such as adsorption capacity, selectivity for the organosulfur compounds, durability and regenerability (Babich and Moulijn, 2003). The major distinction of this process from conventional hydrotreating is that the sulfur onto the catalyst after the feedstock-hydrogen mixture interacts with the catalyst. Thus the catalyst needs to be regenerated constantly. As for this project, the focused is applying the adsorption method of extracting the sulfur from the crude oil.

2.2 Ionic Liquids

This project proposes the use of ionic Liquids (ILs) as extracting agent in liquid-liquid extraction as an alternative for the desulfurization of refinery streams. Ionic liquids are purely ionic and molten salts with melting points at or below ambient temperature (melt below 100 ^{o} C) (Alonso and Arc, 2008). Ionic liquids consist of anions and cations. Most of the ionic liquids have the attractive properties including negligible vapour pressure, non-volatility, non-flammability, good thermal stability, great electrochemical stability, high ionic conductivity, adjustable miscibility make them as ideal solvents for extraction. In order to optimize the physicochemical properties, ionic liquids can be controlled by tailoring their cationic and anionic structures (Chu, et al. 2007). Based on the Nie, et al. (2006), the used of ionic liquids as an alternative to remove sulfur containing compounds is because of:

i. It is environmentally benign and designable
ii. It is virtually immiscible with fuels and hence free of cross-contamination
iii. It is nonvolatile and thermally stable over a wide range of temperature, as a result the used ionic liquids can be regenerated by distillation
iv. Many ionic liquids display desulfurization ability to a varying degree

Besides, ionic liquids are widely recognized as very suitable materials for separation processes such as extraction, gas cleaning and extractive distillations (Cheng, et al., 2008). This is due to their amazing combination of properties which differentiates them from molecular solvents. The properties are such as:

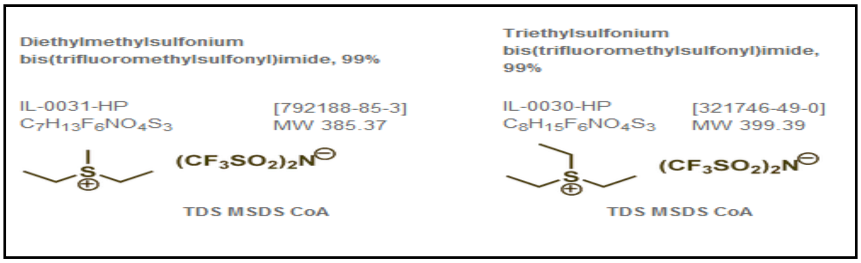
i. No measureable vapor pressure
ii. Non-flammable below their decomposition temperature
iii. Tunable properties
iv. Excellent salvation properties for variety of organic and inorganic compounds
v. High electric conductivities
vi. High thermal stabilities

With these properties, ionic liquids have been investigated as medium to replace current organic solvents used for many chemical reactions such as alkylation of naphthalene, alkylation of benzene, organocatalysis, extraction in the removal of sulfur compound and many more (Di-shun, et al., 2009).

Based on the Richard and Zhang, ionic liquids which act as solvents possess several advantages over conventional organic solvents, which make them environmentally compatible such as:

i. Ionic liquids have the ability to dissolve many different organic, inorganic and organo metallic materials
ii. Ionic liquids are highly polar
iii. Ionic liquids consists of loosely coordinating bulky ions
iv. Ionic liquids does not evaporate since they have very low vapor pressures
v. Ionic liquids are thermally stable, approximately up to 300ºC
vi. Most of ionic liquids have a liquid window of up to 200ºC which enables wide kinetic control
vii. Ionic liquids have high thermal conductivity and a large electrochemical window
viii. Ionic liquids are immiscible with many organic solvents
ix. Ionic liquids are nonaqueous polar alternatives for phase transfer processes
x. The solvent properties of ionic liquids can be tuned for a specific application by varying the anion cation combinations

Mainly, ionic liquids have nitrogen, sulfur and phosphorus as the central atoms of cationssuch as ammonium-based ionic liquids, imidazolium-based ionic liquids, piperidinium-based ionic liquids, pyridinium-based ionic liquids, pyrrolidinium-based ionic liquids, phosphonium-based ionic liquids, sulfonium-based ionic liquids.



Diethylmethylsulfonium bis(trifluoromethylsulfonyl)imide, 99%

IL-0031-HP [792188-85-3]
$C_7H_{13}F_6NO_4S_3$ MW 385.37

$(CF_3SO_2)_2N^{\ominus}$

TDS MSDS CoA

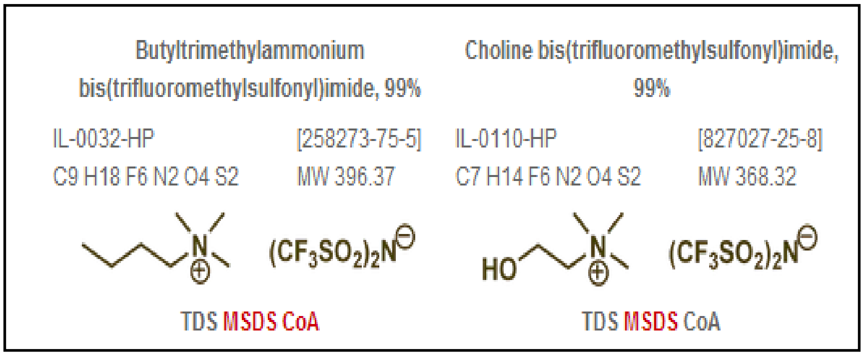
Triethylsulfonium bis(trifluoromethylsulfonyl)imide, 99%

IL-0030-HP [321746-49-0]
$C_8H_{15}F_6NO_4S_3$ MW 399.39

$(CF_3SO_2)_2N^{\ominus}$

TDS MSDS CoA

Figure 1 : Sulphonium-based Ionic Liquids



Butyltrimethylammonium bis(trifluoromethylsulfonyl)imide, 99%

IL-0032-HP [258273-75-5]
C9 H18 F6 N2 O4 S2 MW 396.37

$(CF_3SO_2)_2N^{\ominus}$

TDS MSDS CoA

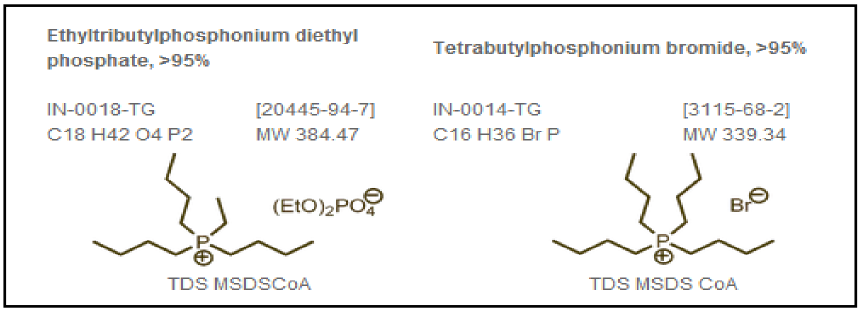
Choline bis(trifluoromethylsulfonyl)imide, 99%

IL-0110-HP [827027-25-8]
C7 H14 F6 N2 O4 S2 MW 368.32

$(CF_3SO_2)_2N^{\ominus}$

TDS MSDS CoA

Figure 2 : Ammonium-based Ionic Liquids



Ethyltributylphosphonium diethyl phosphate, >95%

IN-0018-TG [20445-94-7]
C18 H42 O4 P2 MW 384.47

$(EtO)_2PO_4^{\ominus}$

TDS MSDSCoA

Tetrabutylphosphonium bromide, >95%

IN-0014-TG [3115-68-2]
C16 H36 Br P MW 339.34

$Br^{\ominus}$

TDS MSDS CoA

Figure 3 :Phosphonium-based Ionic Liquids

2.3 Recent Development of Ionic Liquids as Solvent for Desulfurization Process

In order to overcome the problem of using of large amount of flammable and volatile organic compounds raises environmental and safety concerns, ionic liquids have become an alternative to replace these volatile organic solution.

There has been a lot of focus on using the imidazolium-based phosphate ionic liquids for extraction such as 1-methyl-3-methylimidazolium diethyl phosphate, [C_1mim][DMP]; 1-ethyl-3-methylimidazolium diethyl phosphate, [C_2mim][DEP]; and 1-butyl-3-methylimidazolium dibutyl phosphate, [C_4mim][DBP] which are advantageous as they are easy to manufacture in a commercial scale with very high yield (Nie, et al., 2006). Sulfur removal ability of phosphate ionic liquids have a potential in addition to high desulfurization ability, good stability, fluidity, non – toxicity and non-sensitivity moisture and air which also reported by (Nie et al, 2006).

Besides that, the pyridinium-based ionic liquids, 1-buylpyridinium tetrafluoroborate ([C_4Py][BF_4]), 1-hexypyridinium tetrafluoroborate ([C_6Py][BF_4]), an 1-octylpyridinium tetrafluoroborate ([C_8OPy][BF_4]) were found to be effective for the selective removal of aromatic heterocyclic sulfur compounds from diesel at room temperature (Gao, et al., 2008).

The extractive performance of ionic liquids also is affected by the structure and size of the cation (Gao, et al. 2008). The extractive performance using pyridinium-based ionic liquids is followed the order [C_4Py][BF_4]<[C_6Py][BF_4]<[C_8Py][BF_4] and for the sulfur removal selectivity of sulfur compounds followed the order benzotheophene (BT) <dibenzotheophene (DBT) under the same conditions.

Gao*et al.(*2008) reported that the extractive desulfurization process using ionic liquids can be a complementary technology for the hydrodesulfurization process. These studies indicate that the ionic liquids have high extraction ratios and greater selectivity compared to molecular solvents because of the unique solvent characteristics of ionic liquids.

The most important key for the best result of extractive desulfurization process is to find an effective ionic liquid that is nontoxic, chemically stable to moisture and air, low viscous and not expensive for commercial application and environmental friendly.

On the other side, it was stated by Liang Lu *et al*.(2007) that the sulfur removal of DBT containing model oil can reach 60 – 93 % under different reaction temperature for oxidative desulfurization in which ionic liquid [HMIm][BF_4] was used as a catalyst and solvent. The ionic liquid used was also recycled six times without a significant decrease in activity. This reaction was more superior to a simple extraction with ionic liquid alone.

In the presence of water, the performance of ionic liquids will be lowered. According to Xiaochua Jiang et al. (2008) even 1% of water content in ionic liquid can give rise to about 17 to 20% in lowering the extraction coefficient ability of ionic liquids. Therefore, this matter is taken seriously during synthesis of ionic liquids. The ionic liquids have undergone drying or heating process to make sure there is no or less water content in ionic liquids right after the synthesis.

2.4 Physichochemical Properties of Nitrile-Functionalized Ionic Liquids

Currently, there has been a focused on the nitrile-functionalized ionic liquids such as based in pyridinium, imidazolium and trimethyl ammonium salts because such ionic liquids have been shown to be suitable reaction media and ligands for catalytic reactions such as carbon-carbon coupling and could be promising electrolytes for lithium battery and dye-sensitized solar cells. Zhang et al.(2006) stated that a series of ionic liquids based on nitrile-functionalized imidazolium, pyridinium and quaternary ammonium as cations and chloride and tetraflouroborate, hexafluorophosphate, dicyanamide and bis(trifluoromenthanesulfonyl)imide as anions have been prepared and characterized. The physicochemical properties such as spectroscopic, thermal, solubility, electrochemical, tribological, and toxic properties were comparatively studied.

For the spectroscopic properties, NMR and FTIR spectroscopy were used to characterize the structures of ionic liquids. For all nitrile-functionalized ionic liquids, the main feature in the FTIR spectra was that the characteristic absorption of a CN group raging from 2237 to 2254/cm.

The replacement of a terminal methyl group with the CN group resulted in the disappearance of the aliphatic C-H vibrations at 2880 and 2940/cm. The absorption characteristics can be seen in the UV region which shown that th CN group have strong absorption below 300 nm and the absorption tail extends beyond 400 nm. The absorption intensity is at 250 – 260 nm and a new but weak absorption band is at 275 – 285 nm.

For the thermal properties, the phase behaviors of ionic liquids with a CN group such as melting and freezing points (T_m, T_f), crystal-crystal transition (T_{cc}), glass phase transition (T_g), melting enthalphy change (¢H_m) and the corresponding entropy change (¢S_m) as well as thermal decomposition temperatures (T_d) were investigated by DSC and thermo gravimetric analysis. Generally, incorporation of a CN group, the Tm, Tf, Tg and heat capacities are all increased. This may be attributed to the increased hydrogen-bonding interactions caused by the incorporation of a CN group. But for the melting enthalphy and entropy for the CN group ionic liquids is decreased. This may be attributed to the conformational changes in the nitrile-functionalized imidazolium groups and the enhancement in hydrogen-bonding interactions due to the incorporation of a CN group. Same goes to the Td of ionic liquids incorporation of a CN group which decreased remarkably.

Table 1 : Thermal Properties of Nitrile-Functionalized Ionic Liquids

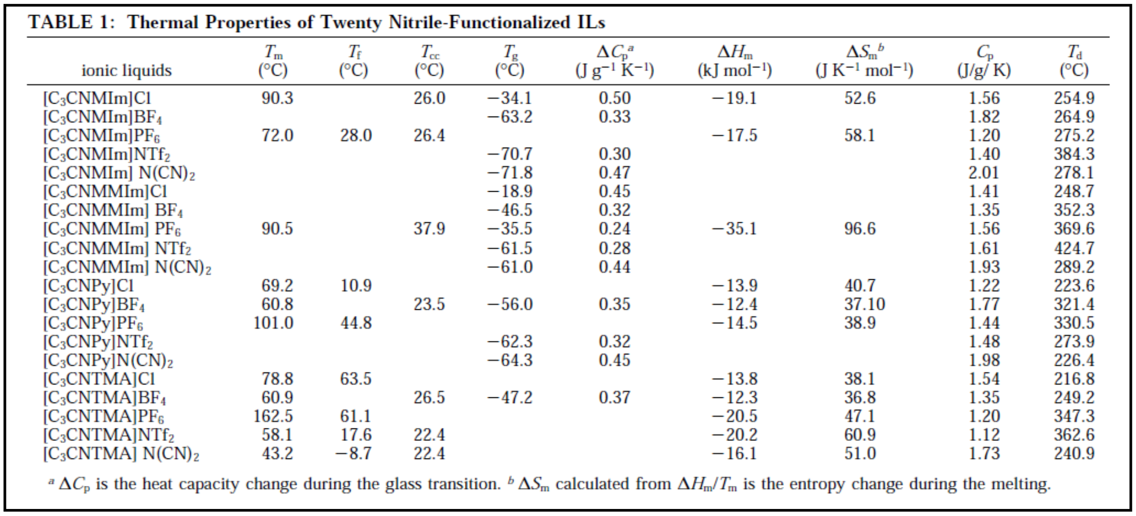


TABLE 1: Thermal Properties of Twenty Nitrile-Functionalized ILs

ionic liquids	T_m (°C)	T_f (°C)	T_{cc} (°C)	T_g (°C)	$\Delta C_p{}^a$ (J g^{-1} K^{-1})	ΔH_m (kJ mol^{-1})	$\Delta S_m{}^b$ (J K^{-1} mol^{-1})	C_p (J/g/ K)	T_d (°C)
[C_3CNMIm]Cl	90.3		26.0	−34.1	0.50	−19.1	52.6	1.56	254.9
[C_3CNMIm]BF_4				−63.2	0.33			1.82	264.9
[C_3CNMIm]PF_6	72.0	28.0	26.4			−17.5	58.1	1.20	275.2
[C_3CNMIm]NTf_2				−70.7	0.30			1.40	384.3
[C_3CNMIm] $N(CN)_2$				−71.8	0.47			2.01	278.1
[C_3CNMMIm]Cl				−18.9	0.45			1.41	248.7
[C_3CNMMIm] BF_4				−46.5	0.32			1.35	352.3
[C_3CNMMIm] PF_6	90.5		37.9	−35.5	0.24	−35.1	96.6	1.56	369.6
[C_3CNMMIm] NTf_2				−61.5	0.28			1.61	424.7
[C_3CNMMIm] $N(CN)_2$				−61.0	0.44			1.93	289.2
[C_3CNPy]Cl	69.2	10.9				−13.9	40.7	1.22	223.6
[C_3CNPy]BF_4	60.8		23.5	−56.0	0.35	−12.4	37.10	1.77	321.4
[C_3CNPy]PF_6	101.0	44.8				−14.5	38.9	1.44	330.5
[C_3CNPy]NTf_2				−62.3	0.32			1.48	273.9
[C_3CNPy]$N(CN)_2$				−64.3	0.45			1.98	226.4
[C_3CNTMA]Cl	78.8	63.5				−13.8	38.1	1.54	216.8
[C_3CNTMA]BF_4	60.9		26.5	−47.2	0.37	−12.3	36.8	1.35	249.2
[C_3CNTMA]PF_6	162.5	61.1				−20.5	47.1	1.20	347.3
[C_3CNTMA]NTf_2	58.1	17.6	22.4			−20.2	60.9	1.12	362.6
[C_3CNTMA] $N(CN)_2$	43.2	−8.7	22.4			−16.1	51.0	1.73	240.9

[a] ΔC_p is the heat capacity change during the glass transition. [b] ΔS_m calculated from $\Delta H_m/T_m$ is the entropy change during the melting.

The densities of corresponding ionic liquids increased after incorporation of a CN group and as expected the densities decreased linearly with increasing temperature. The strong dipole moment of the nitrile group may be responsible for the formation of a more ordered structure of cation and anion in the ionic liquid molecule and thus results in the increase of densities of ionic liquids. The viscosities of the ionic liquids after incorporation of a CN group also increased obviously. The increased hydrogen bonding interactions derived from a CN group may be responsible for the increases in the viscosity because the CN group is an electron donor and liable to form hydrogen bonding. The refractive indices and the surface tensions of ionic liquids with a CN group are higher than those of the corresponding ionic liquids without CN group (Zhang et al.,2006).

Besides that, what has been reported previously, the corresponding order of the solubilities could be methanol > benzene > hexane > cycloalkane > hexane. After incorporation of a CN group, the solubilites of methanol, benzene, hexane, cycloalkane and hexane in the ionic liquids decreased from a slight to a large extent. The hydrophobic properties also decreased indicating the ionic liquids with a CN group tended to be more hydrophilic because of the increased polarity of the cation.

In addition, for the tribological properties, the ionic liquids with a CN group showed much lower friction coefficients and this nitrile-fucntionalized ionic liquids have more excellent trobological properties. It is also can be seen that the electrochemical stabilities of ionic liquids after the incorporation of a CN group became much higher than that without a CN group while the incorporation of a CN group would remarkably decrease the toxicity of the ionic liquid.

Thus it can be concluded from the results showed that the incorporation of a CN group to a cation could result in remarkable changes in these properties such as enhanced electrochemical stabilities, remarkably decreased in toxicity and relatively complicated properties.

The study has been made on the ability one of the nitrile functionalized ionic liquids which is thiocyanate based task-specified ionic liquids for separataion of benzene and cyclohexane. Gonfa et al. (2013) found that it is difficult to separate cyclohexane and benzene which is one of the most important processes in the petrochemical industry due to their close boiling points and azeotrope formation. With that, this thiocynate ionic liquid was investigated as solvent for separation of benzene and cyclohecane using extractive distillation. From the results, it is shown that this ionic liquid can break the azeotropic mixture and increase the relative volatility of the cyclohexane to benzene. Thus it is showing that the nitrile-functionalized ionic liquids have the ability in separation and extraction such as separation of sulfur from crude oil.

Based on the Zhao et al. nitrile-functionalized ionic liquids are considerably more effective for the immobilization of palladium catalyst for the transfer of a vinyl group in Stille reactions with respect to alkyl-substituted ionic liquids as shown in Figure 4. Analysis of nanoparticles extracted from the ionic liquids provides evidence for the stabilizing effect exerted by the nitrile pendant group on the metal centre.

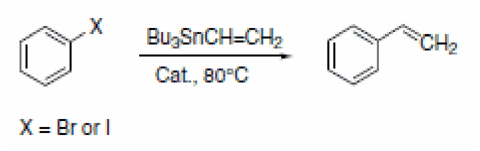


Figure 4 : Stille Reactions

While model substrates were used in the above examples, desulfitative Mizoroki-Heck-type arylation of alkenes using complex precursors can be performed efficiently in nitilefunctionalized ionic liquid as shown in Figure 5, again proving superior to the commonly used organic solvents and simple ionic liquids, add Zhao et al.

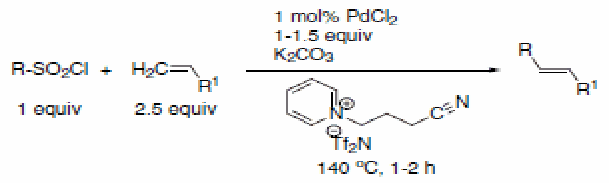


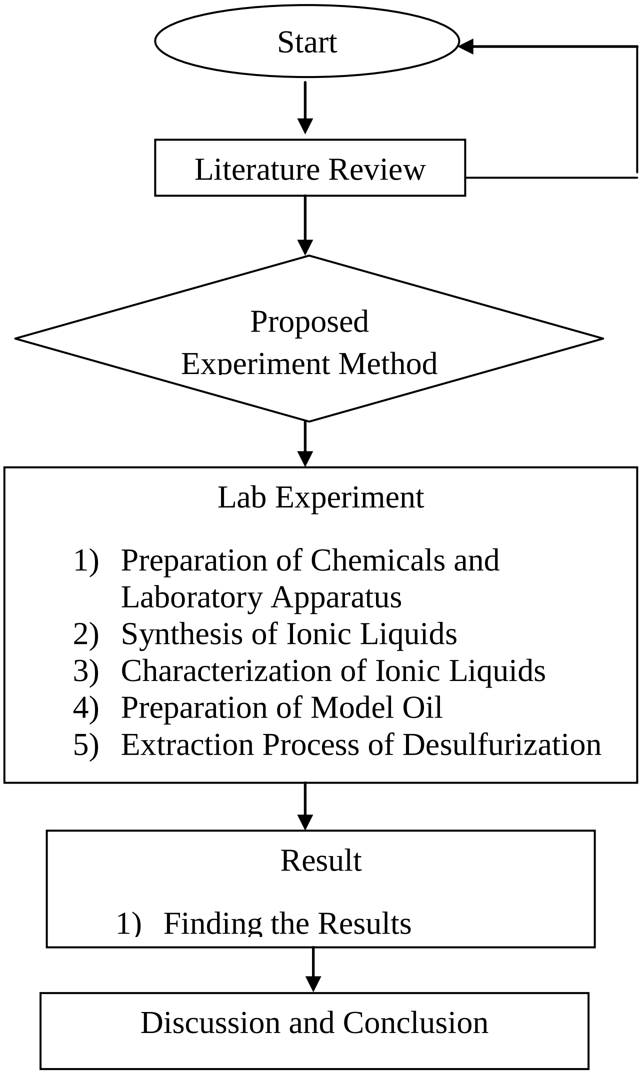
Figure 5 : Desulfitative Mizoroki-Heck-type Arylation of Alkenes

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

The research methodology is based on the process flow below:



3.2 Project Activities

Based on the guidance from literature review, the methods have been divided into four parts which are synthesis of ionic liquids, characterization of ionic liquids, preparation of model oils and application of the synthesized ionic liquids for extractive desulfurization process.

3.2.1 Chemicals and Laboratory Apparatus

Table 2 lists the chemicals and laboratory apparatus used throughout the synthesis of the ionic liquids.

Table 2 : Chemicals and laboratory apparatus used in the synthesis of ionic liquids

No.	Equipment	Quantity
1	Reflux condenser	1
2	Hot plate stirrer	1
3	Vacuum line	1
	Apparatus	Quantity
1	Round bottom 1 neck flask	5
2	Magnetic stirrer	2
3	Beaker	5
4	Conical flask	5
5	Measuring cylinder (100 ml)	2
6	Sample bottle (20 ml)	6
7	Pipette	5
8	Dropper	10
	Chemicals	Quantity
1	n - Dodecane	500 ml
2	1-Bromoethane	50 ml
3	1-Bromobutane	50 ml
4	Acetonitrile	300 ml
5	Tetrahydrothiophene	50 ml
6	Sodium Dicyanamide	50 g
8	Sodium Thiocyanate	50 g
9	1 - Dibenzothiophene	50 g
10	Dichloromethane	300 ml
11	N-Hexane	300 ml
12	1-Bromoethane	50 ml

Table 3 : Physical properties of the chemicals in the synthesis of ionic liquids

Chemical Name	Molar Mass (g/mol)	Density (g/ml)	Boiling Point (ºC)
n-Dodecane	170.33	0.780	214 - 218
Bromoethane	108.97	1.46	38 - 39
Bromobutane	137.02	1.27	99 - 103
Acetonitrile	41.05	0.786	81 -82
Tetrahydrothiphene	88.17	0.999	119
Sodium Dicyanamide	89.03	-	41.5
Sodium Thiocyanate	81.072	1.735	Decomposes
Dichloromethane	84.93	1.33	39.6
N-Hexane	86.18	0.6548	68 - 69

3.2.2 Synthesis of Nitrile-Functionalized Sulphonium Ionic Liquids

The nitrile-functionalized sulphonium ionic liquids are prepared by the quarternization of tetrahydrothiophene with the corresponding alkyl halides followed by the anion exchange reaction. Hence in overall, there are two different steps for the synthesis of ionic liquids.

In the first step Tetrahydrothiphene was treated with 1-Bromoethane in the presence of acetonitrile at a 40ºC for 72 hours (3 Days). The progress of the reaction was monitored using thin layer chromatography. When the reaction was completed, the solvent was evaporated using a rotary evaporator and the halide salt formed was further dried in a vacuum oven at 50 ºC for 24 hours. The second step is the anion exchange reaction, the halide salt was mixed with sodium thiocyanate (NaSCN) in dichloromethane for 24 hours. The solid formed was filtered off and the organic layer was washed with small amount of cold water. The dichloromethane was removed using a rotary evaporator and the ionic liquids formed were further dried in vacuum line at 50 ºC for 24 hours.

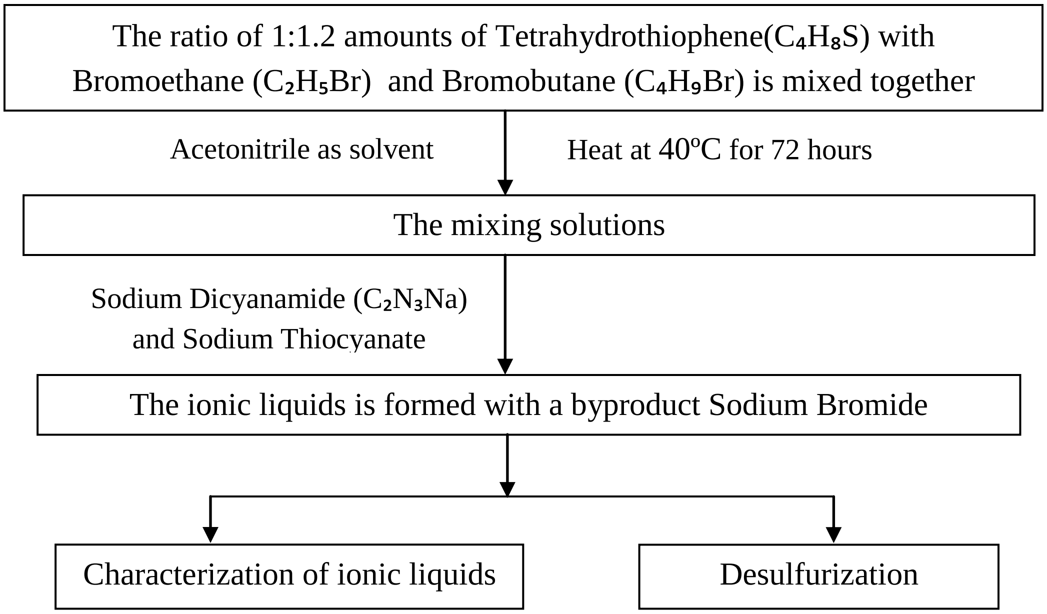


Figure 6 : Flow diagram of the synthesis of ionic liquids

Table 4: Quatrenization reaction for synthesis ionic liquids

Ratio amount of Starting Material (1 : 1.2)		Conditions	Ionic Liquids Synthesized
Tetrahydrothiophene (C_4H_8S)	1-Bromoethane (C_2H_5Br)	Heat at 40ºC for 72 hours	1-Ethyltetrahydro-thiopheniumbromide
Tetrahydrothiophene (C_4H_8S)	1-Bromobutane (C_4H_9Br)	Heat at 40ºC for 72 hours	1-Butytetrahydro-thiopheniumbromide

Table 5 : Reactant and condition for anion exchange reaction

Ratio amount of Starting Material (1 : 1.5)		Conditions
Cation	Anion	
1-Ethyltetrahydrothiopheniumbromide	Sodium Dicyanamide Na[N(CN)$_2$]	Stirred for 24 Hours
1-Butyltetrahydrothiopheniumbromide		
1-Ethyltetrahydrothiopheniumbromide	Sodium Thiocyanate (NaSCN)	Stirred for 24 Hours
1-Butyltetrahydrothiopheniumbromide		

a) <u>Synthesis of Sulphonium bromide</u>

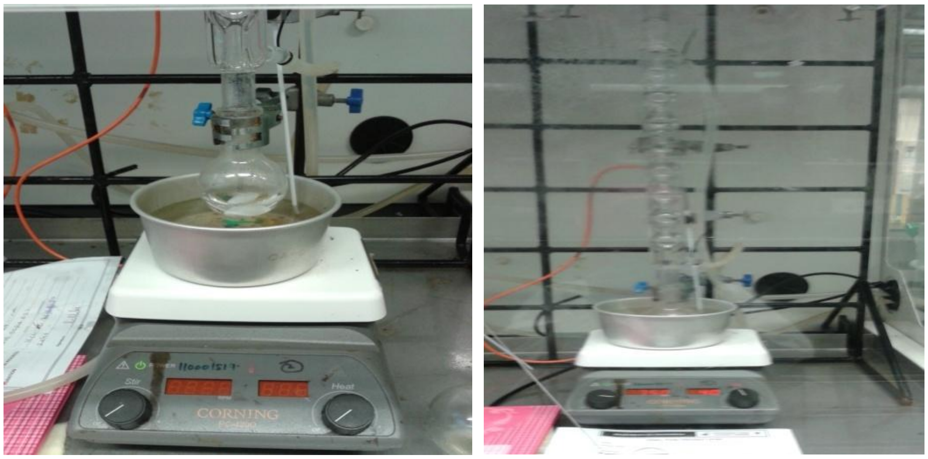


Figure 7 : Experiment setup for synthesis of ionic liquids

The experiment was set up as in Figure 7. The round bottom flask was flitted with a reflux condenser and an oil bath. To a solution of tetrahydrothiophene in acetonitrile (50 ml), 1-Bromoethane (10.17 ml) was added and the reaction mixture was stirred at 40ºC for 72 hours (3 Days). The progress of the reaction was monitored using thin layer chromatography (TLC).When the reaction was completed, the solvent was evaporated using rotary evaporator and the bromide salt formed was washed with hexane to remove the unreacted starting material. The ionic liquid formed was further dried in vacuum oven at 50 ºC for 24 hours. The product obtained as brown solid.

Monitor the Progress of Reaction by using TLC Method.

1) A very small amount of starting materials (Tetrahydrothiphene(C_4H_8S) and Bromoethane(C_2H_5Br) and the reaction mixture was spotted in a TLC paper. Then, the TLC paper is put in the Dichloromethane as shown in Figure 8.1.
2) After the Dichloromethane,DCM(CH_2Cl_2), have run through the TLC paper, it was developed in iodine chamber as shown in Figure 8.2.
3) The final result of the TLC paper as shown in the Figure 8.3. The blue circle is indicated the starting material while the red circle is indicated the product. If there is still a spot like in the blue circle above the red circle, it indicates that the reaction is not completed yet. While if there is nothing above the red spot, then the reaction is completed. At first the reaction was estimated to complete within 48 hours. Nevertheless, after 48 hours and the reaction mixture was tested with TLC, he result shown that the reaction is not completed. Hence the reaction continued for another 24 hours.

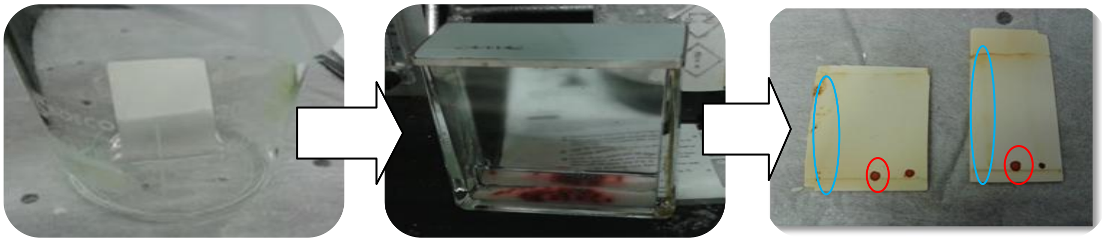


Figure 8.1 Figure 8.2 Figure 8.3

Figure 8 : TLC identification process

After the reaction is fully completed, the solvent was removed by rotary evaporation. Then, the remaining liquid in the flask is washed with n-Hexane (solvent) to remove any starting material left in the liquid. Finally, the solvent n-Hexane is removed by rotary evaporation again and dried by using the vacuum line to remove the trace amount of water and solvent. The reaction was repeated by replacing 1-Bromoethane with 1-Bromobutane.

Figure 9: Rotary evaporator and vacuum line

Figure 11.1: Mixture before synthesize

Figure 11.2 : Mixture after synthesize

Figure 10 : Product of ionic liquid mixture

b) Synthesis of Nitrile-Functionalized Sulphonium Ionic Liquids:Anion Exchange Reaction

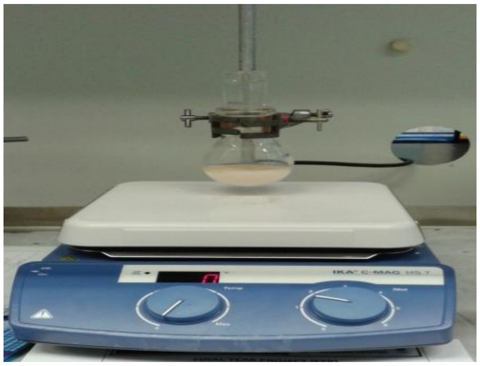


Figure 11: Stirring of mixture without heating

The experiment was set up as in Figure 11. To a solution of 1-Ethyltetrahydrothiopheniumbromide (2g, 0.01522 mol)in DCM (25 ml)Sodium thiocyanate (1.81 g, 0.02283) was added and the reaction mixture was stirred at room temperature for 24 hours. After 24 hours, the mixture was filtered in order to remove sodium bromide as shown in Figure 12 and the solvent dichloromethane was removed by rotary evaporation.

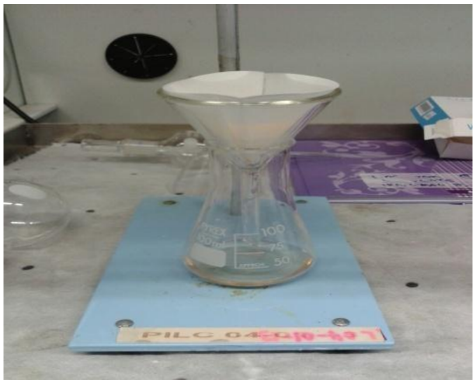


Figure 12: Filtration of ionic liquid and sodium bromide

Then, the remaining liquid in the flask was washed with n-Hexane (solvent) to remove any other contaminants left in the liquid. Finally, the solvent n-Hexane was removed by rotary evaporation again and dried by using the vacuum line to remove the trace amount of water and solvent. The steps are repeated by replacing the sodium thiocyanate with sodium dicyanamide.

3.2.3 Characterization of the Ionic Liquids

Characterization of the synthesized ionic liquids was carried out using the instruments shown in Table 6.

Table 6: Characterization of ionic liquids

Equipment	Testing
Proton NMR Spectroscopy	To determine the structure and purity of ionic liquids
Fourier transform infrared spectroscopy (FTIR)	To determine the functional group of ionic liquids
Anton PaarViscometric	To determine the density and viscosity of ionic liquids
Gas Chromatography (GC)	To determine amount of compound (dibenzothiophene) present

a) ^{1}H NMR or Proton NMR

For ^{1}H NMR measurement, 20 mg ionic liquid is dissolved in about 600 μL to 1000 μL of solvent. For 1-Ethyltetrahydrothiopheniumbromide and 1-Butyltetrahydrothiopheniumbromide, the solvent used is deuterated Chloroform ($CDCl_3$) while for 1-Ethyl-tetrahydrothipheniumthiocyanate the solvent used is deuteriated dimethyl sulfoxide (DMSO). After the ionic liquid has been dissolved it was transferred directly to NMR tube and the sample volume can be adjusted by adding the remaining solvent to the NMR tube so that the final sample volume is about 700 μL or a sample height about 4.5 cm is reached. This is followed by vigorous shaking of the sample to effectively dissolve the compound.

b) Fourier transform infrared spectroscopy (FTIR)

The sample of ionic liquids needs to be prepared before it can be tested using FTIR. Firstly, the sample is weighted about 1-3 mg. About 250 to 300 mg Potassium bromide, KBr, is weighted and measured using a small scoop. The sample is grounded with KBr together. The mixture of sample and KBr is transferred into a die set and is placed just enough to cover the bottom in pellet die. Die is placed into a hydraulic press and a vacuum is applied for 1 minute. Pressure is gradually increased to almost 10 tons. Wait for 1 minute. After 1 minute, the pressure and the vacuum are released. KBr pressed disc is removed and transferred onto a sample holder. Lastly, place the sample holder with KBr disc into FTIR unit for analysis as shown in Figure 14.

Figure 13: FTIR unit

c) Anton Paar Viscometric

Other important properties of the ionic liquid such as the density and viscosity were determined by using Anton Paar Viscometer. The density and viscosity of ionic liquid was measured with an Anton Paar, Oscillating U-tube density and viscosity meter, from 20 ºC to 100 ºC.

d) Gas Chromoratgraphy (GC)

Chromatography is a very important analytical tool because it allows the chemist to separate components in a mixture for subsequent use or quantification. Most samples that chemists want to analyze are mixtures. If the method of quantification is selective for a given component in the mixture, separation is not required. However, it is often the case that the detector is not specific enough, and a separation must first be performed. There are several types of chromatography depending on the type of sample involved. In this experiment, gas chromatography has been used. Gas Chromatography is a common type of chromatography used in analytical chemistry for separating and analyzing compounds that can be vaporized without decomposition. The gas chromatograph makes it possible to separate the volatile components of a very small sample and to determine the amount of each component present. In some situations, GC may help in identifying a compound. 4 samples of model oil contain dibenzothiophene (DBT) with concentration of 10 ppm, 100 ppm, 300 ppm and 700 ppm was prepared for calibration.

3.2.4 Preparation of Model Oil

The model oil used in this study was n-dodecane spiked with dibenzothiophene (DBT) as the sulfur containing compounds. Table lists the entire chemical used with their physical properties in preparing the model oil.

Table 7 : Sulfur Used with Their Physical Properties

Chemical Name	Purity (%)	Molar Mass (g/mol)	Density (g/cm3)	Boiling Point (ºC)
Dibenzothiopene	99.5	184.26	1.051	84

The model oil is prepared with a concentration of 500 ppm of sulfur using dibenzothiophene, DBT (0.05746 g) and then dissolved in n-dodecane (19.94254 g) in a volumetric flask. 500 ppm of DBT is equal to 0.2873 wt%. The model oil was then analyzed using the Gas Chromatography to record the dibenzothiophene content in model oil. Model oils with different volume of dibenzothiophene content (10 ppm, 100 ppm, 300 ppm and 700 ppm) were prepared for the calibration of the standard for Gas Chromatography.

Table 8: Calculation to prepare for the model oil with dibenzothiophene (DBT)

Volume of DBT (ppm)	Weight Percent of DBT in n-dodecane (wt %)	Amount of DBT (mg)	Amount of n-dodecane (g)
10	0.005746	0.5746	9.99943
100	0.057460	2.8730	4.99713
300	0.172400	8.6197	4.99138
500	0.287300	57.460	19.9425
700	0.402250	20.113	5.97990

3.2.5 Extractive Desulfurization Process

The next step of this project was the extraction of dibenzothiophene, DBT from model oil. The experiment was carried out by using the synthesized ionic liquid 1-Butyl-tetrahydrothiophenium thiocyanate. The extractive desulfurization experiment was conducted in sample bottles. The mass ratio of ionic liquid to model oil was 1:1.

First, 1.5 g of 1-Butyl-tetrahydro-thiophenium thiocyanate ionic liquid is added into a bottle sample followed by 1.5 g of model oil contains estimated of 500 ppm dibenzothiophene (DBT). Figure 14 shows that the mixture of the ionic liquid and model oil were forming two different layers. The above portion was oil phase and the below portion was ionic liquid phase. Next, the mixture was heated and stirred at 30 °C with a 500 rpm stirring for 30 minutes as shown in Figure 15. After the heating process, the mixture was then left to settle for 10 minutes before the oil layer and the ionic liquid layer were separated using syringe. All the steps were repeated for three times in order to get the accurate results.

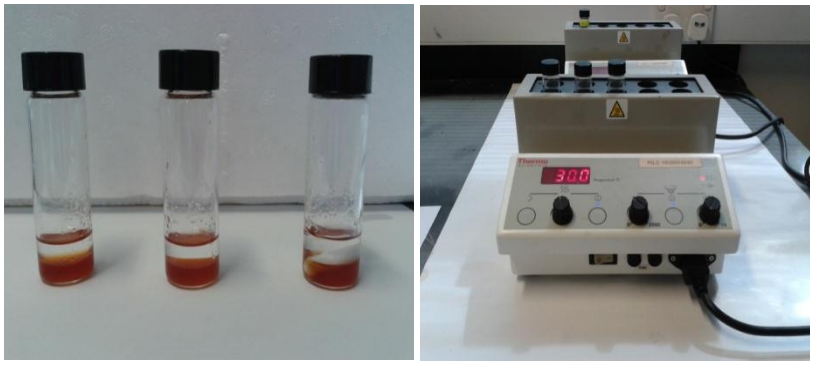


Figure 14: 2 layers of ionic liquid and model oil and extractive desulfurization process

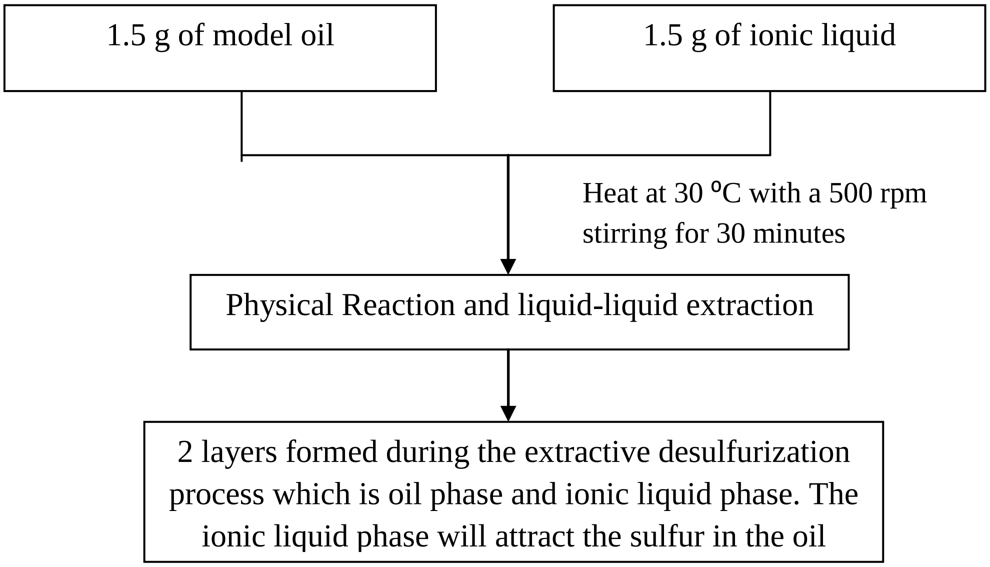


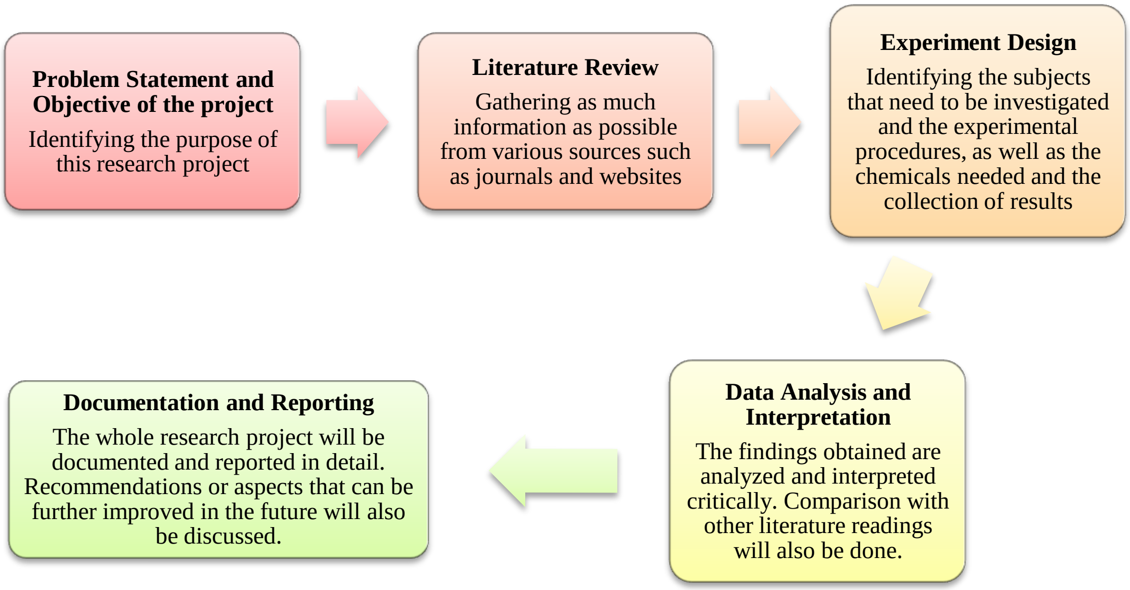
Figure 15 : Flow diagram of the extractive desulfurization process

3.2.6 Process of Determine Sulfur in Model Oil and Ionic Liquids

In order to determine the amount of dibenzothiophene (DBT) left in the model oil before and after extraction, the sample will be sent to Gas Chromatography (GC). This equipment will be used in order to compare the result.

3.3 Key Milestone

Several key milestones for this research project must be achieved in order to meet the objective of this project:



Problem Statement and Objective of the project

Identifying the purpose of this research project

Literature Review

Gathering as much information as possible from various sources such as journals and websites

Experiment Design

Identifying the subjects that need to be investigated and the experimental procedures, as well as the chemicals needed and the collection of results

Data Analysis and Interpretation

The findings obtained are analyzed and interpreted critically. Comparison with other literature readings will also be done.

Documentation and Reporting

The whole research project will be documented and reported in detail. Recommendations or aspects that can be further improved in the future will also be discussed.

<u>Milestone</u>

1) Literature Review and Research Works --Done
2) Proposal Defense ---Done
3) Preparation of Chemicals and Apparatus Laboratory ----------------------Done
4) Synthesis and Characterization of Ionic Liquids ---------------------------------Done
5) Preparation of Model Oil --Done
6) Extractive Desulfurization Process and Test ---------------------------------Done
7) Preparation for Pre-SEDEX ---Done
8) Preparation for Oral Presentation ---Week 12 FYP (II)
9) Report and Technical Paper Writing -----------------------------------Week 7 - 15 FYP (II)

3.4 Gant Chart

Table 9 : Timelines for FYP I and FYP II

Activities	WEEK																													
	FYP (I) MAY 2013															FYP (II) SEPTEMBER 2013														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	SEMESTER BREAK	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Confirmation of Project Title	🟩	🟩	🟩																											
Preliminary Research Work			🟩	🟩	🟩	🟩																								
Submission of Extended Proposal Defense																														
Proposal Defense								🟩	🟩																					
Project Work Continues						🟩	🟩	🟩	🟩	🟩	🟩	🟩																		
Submission of Interim Draft Report																														
Submission of Interim Report																														
Experiment													🟩	🟩		🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩					
Submission of Progress Report																							🟩							
Pre-SEDEX																										🟩				
Submission of Draft Report																											🟩			
Submission of Dissertation (Soft Bound)																												🟩		
Submission of Technical Paper																												🟩		
Oral Presentation																												🟩		
Submission of Dissertation (Hard Bound)																														🟩

Process 🟩

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Synthesis of Ionic Liquids

One of the objectives of this study is to synthesis the nitrile-functionalized sulphonium-based ionic liquids. There are two steps involved in the synthesis of ionic liquids. The first step is the synthesis of sulphonium salt by the reaction between tetrahydrothiophene (C_4H_8S) and 1-Bromoethane (C_2H_5Br) or 1-Bromobutane (C_4H_9Br). The second step is the introduction of the desired anion by the ion-exchange with different sodium salt of anions. Sodium thiocyanate (NaSCN) and Sodium dicyanamide $Na[N(CN)_2]$ were used.

4.1.1 Quartenization Reaction

a) <u>Synthesis of 1-Ethyl-tetrahydro-thiophenium; bromide</u>

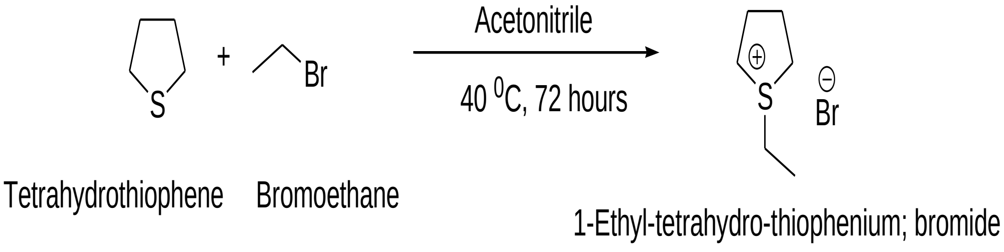


Figure 16: Synthesis of halide salt

Before synthesis of ionic liquid can be done, several parameters need to be determined.

Table 10: Calculation of parameter for synthesis of ionic liquid

Chemicals	Molecular Weight (g/mol)	Equilibrium	Mass (g)	Mol	Density (g/mL)	Volume (mL)
Tetrahydrothiophene (C_4H_8S)	88.10	1.0	10.00	0.1135	1.00	10.00
Bromoethane (C_2H_5Br)	108.97	1.2	14.84	0.1362	1.46	10.17

$$Mol = \frac{Mass}{Molecular\ Weight}$$

$$Density = \frac{Mass}{Volume}$$

For Tetrahydrothiophene (C_4H_8S),

$$Mol = \frac{10.00\ g}{88.10\ g/mol} = 0.1135\ mol$$

$$Volume = \frac{Mass}{Density} = \frac{10.00\ g}{1.00\ g/mL} = 10.00\ mL$$

For Bromoethane (C_2H_5Br),

$$Mol = 0.1135\ mol\ C4H8S \times \frac{1.2\ C2H5Br}{1.0\ C4H8S} = 0.1362\ mol$$

$$Mass = Mol \times Molecular\ Weight = 0.1362\ mol \times \frac{108.97g}{mol} = 14.84g$$

$$Volume = \frac{Mass}{Density} = \frac{14.84\ g}{1.46\ g/mL} = 10.17\ mL$$

b) Synthesis of 1-Butyl-tetrahydro-thiophenium; bromide

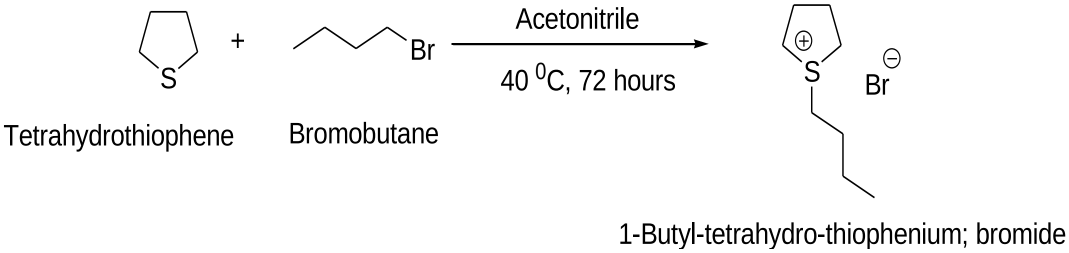


Figure 17: Synthesis of halide salt

Table 11: Calculation of parameter for synthesis of ionic liquid

Chemicals	Molecular Weight (g/mol)	Equilibrium	Mass (g)	Mol	Density (g/mL)	Volume (mL)
Tetrahydrothiophene (C_4H_8S)	88.10	1.0	14.00	0.1589	1.00	14.00
Bromobutane (C_4H_9Br)	137.02	1.2	26.13	0.1907	1.27	20.57

Figure 18: 1-Ethyltetrahydrothiophenium bromide and 1-Butyltetrahydrothiophenium bromide

4.1.2 Anion Exchange Reaction

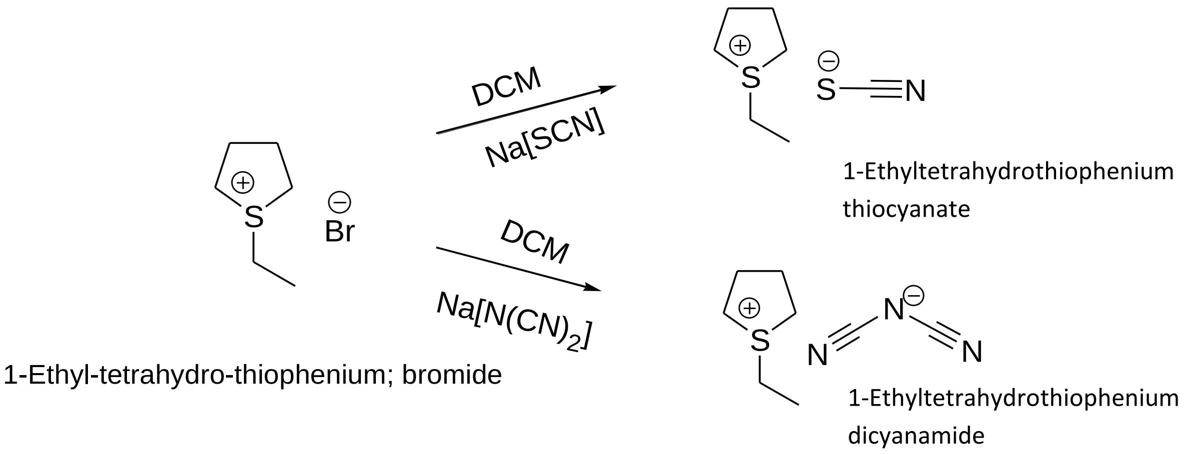


Figure 19: Synthesis of ionic liquids

Table 12: Calculation of Parameter for Synthesis of Ionic Liquid

Chemicals	Molecular Weight (g/mol)	Equilibrium	Mass (g)	Mol
1-Ethyl-tetrahydro-thiophenium;bromide	197.07	1.0	3.00	0.01522
Sodium Thiocyanate Na[SCN]	81.072	1.5	1.8512	0.02283
Sodium Dicyanamide Na[N(CN)$_2$]	89.03	1.5	2.0330	0.02283

The Figure 21 shows of the pictures of 1-Ethyl-tetrahydrothiophenium thiocyanate and 1-Ethyltetrahydrothiophenium dicyanamide ionic liquids.

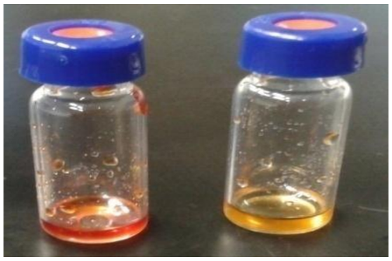


Figure 20: 1-Ethyltetrahydrothiophenium thiocyanate and 1-Ethyltetrahydrothiophenium dicyanamide

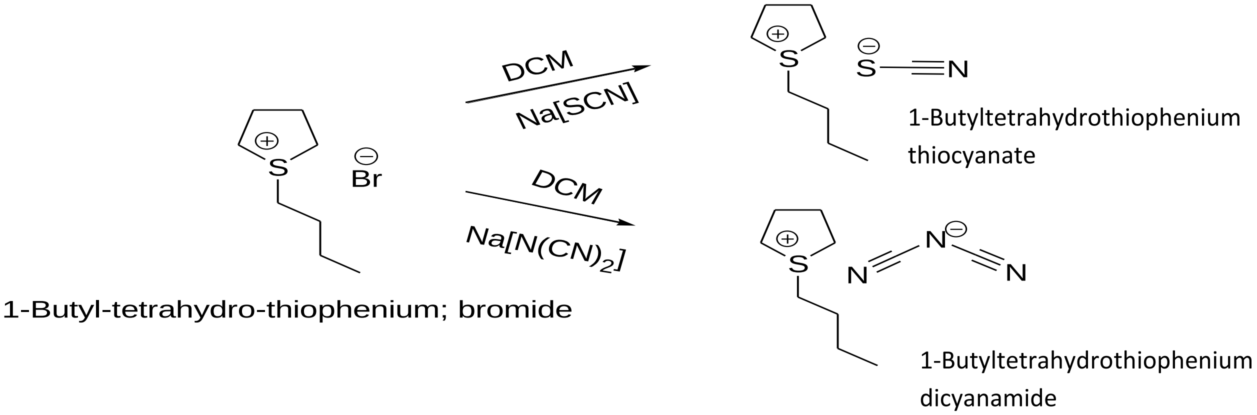


Figure 21: Synthesis of ionic liquids

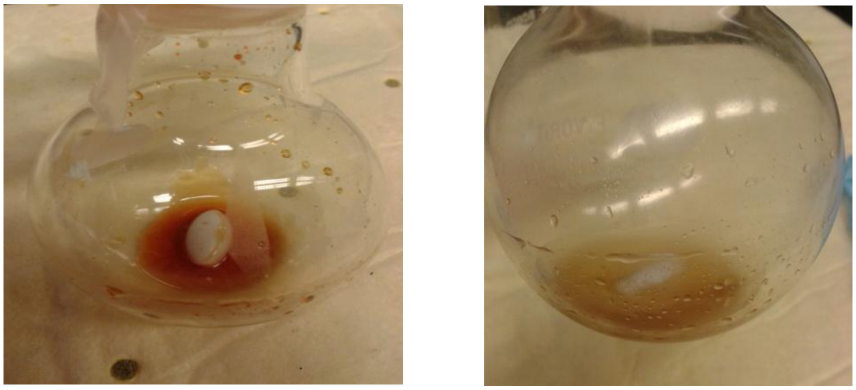


Figure 22: 1-Butyltetrahydrothiophenium thiocyanate and 1-Butyltetrahydrothiophenium dicyanamide

Table 13: Calculation of parameter for synthesis of ionic liquid

Chemicals	Molecular Weight (g/mol)	Equilibrium	Mass (g)	Mol
1-Butyl-tetrahydro-thiophenium;bromide	225.12	1.0	10.00	0.0444
Sodium Thiocyanate Na[SCN]	81.072	1.5	5.40	0.0666
Sodium Dicyanamide Na[N(CN)$_2$]	89.03	1.5	5.93	0.0666

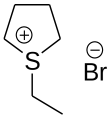
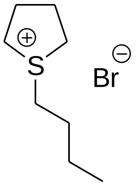
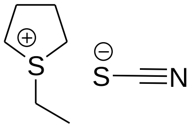
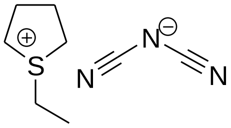
4.2 Characterization of Ionic Liquids

4.2.1 ^{1}H NMR or Proton NMR Analysis

Structure information of compounds can be obtained from an NMR spectrum. Much like using infrared (IR) spectroscopy to identify functional groups, analysis of an I D NMR spectrum provides information on the number and type of chemical entities in a molecule. ^{1}H NMR is the application of nuclear magnetic resonance in NMR spectroscopy with respect to hydrogen-1 nuclei within the molecules. In sample where natural hydrogen (H) is used, practically all of the hydrogen consists of the isotope ^{1}H for instance hydrogen-1 having a proton for a nucleus.

The ionic liquids were characterized by using proton NMR to determine their structures and purity. The results are as shown in Table 14. The ^{1}H NMR spectra are provided in Appendix B.

Table 14: ^{1}H NMR results of synthesized ionic liquids

Molecular Structure of Ionic Liquids	^{1}H NMR
 1-Ethyl-tetrahydro-thiophenium; bromide	2.007 (2H) 1.991 (2H) 2.066 (2H) 3.952 (4H) 3.000 (3H)
 1-Butyl-tetrahydro-thiophenium; bromide	2.008 (2H) 2.029 (2H) 1.995 (2H) 4.033 (4H) 2.003 (2H) 2.019 (2H) 3.000 (3H)
 1-Ethyltetrahydrothiphenium; thiocyanate	1.998 (2H) 1.967 (2H) 2.000 (2H) 3.958 (4H) 3.000 (3H)
 1-Ethyltetrahydrothiphenium dicyanamide	2.998 (3H) 3.980 (4H) 2.036 (2H) 12.87 (13H)

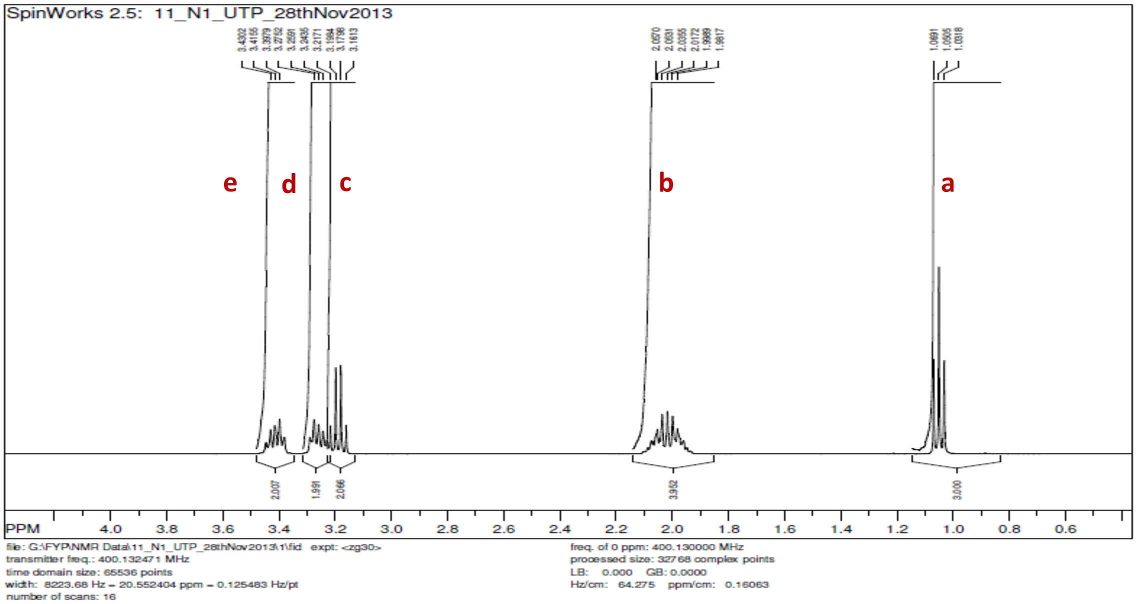


Figure 23: Proton NMR of 1-Ethyltetrahydrothiophenium bromide

The Figure 24 above shows that the result for the Proton NMR of 1-Ethyltetrahydrothiophenium bromide ionic liquid. Based on the figure, there are 5 peaks that were corresponding to the cation 1-Ethyltetrahydrothiophenium bromide ionic liquid. Table 15 shows the summary of the peaks in the spectrum.

Table 15: Summary number of protons at each peak for 1-Ethyltetrahydrothiophenium bromide

Peak	Molecular structure	Number of protons	Chemical shift (ppm)	Integrated value
a	CH_3	3	1.0	3.00
b	CH_2CH_2	4	2.0	3.952
c	CH_2	2	3.2	2.066
d	CH_2	2	3.2	1.991
e	CH_2	2	3.4	2.007

Based on Table 15, by dividing each integral by the smallest integral on the peak (1.991), it gives a ratio of 1.507/1.985/1.038/1/1.008 for the 5 signals. Then by multiplying with two gives the ratio of 3.014/3.97/2.076/2/2.016 which is closed to the integral numbers for the expected structure of a pure compound which consists of 3/4/2/2/2. Each peak represents approximately the same amount of protons as expected integrals. With that, it is proven that 1-Ethyltetrahydrothiophenium bromide ionic liquid has successfully been formed with the expected structure and it is almost pure and clean as there are no other peaks that formed except from the expected structure. Tetrahydrothiophene and Bromoethane are completely reacted to be an ionic liquid of 1-Ethyltetrahydrothiophenium bromide.

Next is to analyze the result of Proton NMR of 1-Butyltetrahydrothiophenium bromide ionic liquid as shown in the Figure 25. From the figure, there are 7 peaks that were corresponding to the cation 1-Butyltetrahydrothiophenium bromide ionic liquid. Table 16 shows the summary of the peaks in the spectrum.

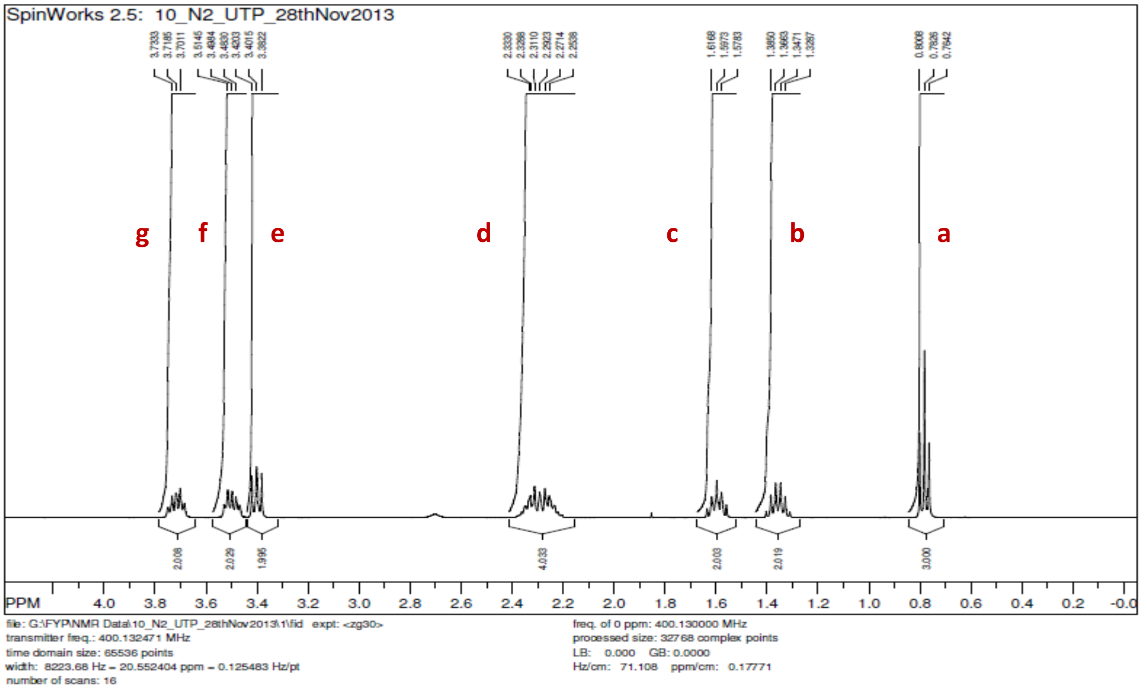


Figure 24: Proton NMR of 1-Butyltetrahydrothiophenium bromide

Table 16: Summary number of protons at each peak for 1-Butyltetrahydrothiophenium bromide

Peak	Molecular structure	Number of protons	Chemical shift (ppm)	Integrated value
a	CH_3	3	0.8	3.00
b	CH_2	2	1.4	2.019
c	CH_2	2	1.6	2.003
d	CH_2CH_2	4	2.5	4.033
e	CH_2	2	3.4	1.995
f	CH_2	2	3.5	2.029
g	CH_2	2	3.7	2.008

The data is analyzed same as previous result of Proton NMR. Based on Table 16, by dividing each integral by the smallest integral on the peak (1.995), it gives a ratio of 1.504/1.012/1.004/2.007/1/1.017/1.007 for the 5 signals. Then by multiplying with two gives the ratio of 3.008/2.024/2.008/4.013/2/2.034/2.013 which is closed to the integral numbers for the expected structure of a pure compound which consists of 3/2/2/4/2/2/2. Each peak represents approximately the same amount of protons as expected integrals. Hence, it is also proven that 1-1-Butyltetrahydrothiophenium bromide ionic liquid has successfully been formed with the expected structure and it is almost pure and clean as there are no other peaks that formed except from the expected structure.

Tetrahydrothiophene and Bromobutane are completely reacted to be an ionic liquid of 1-Butyltetrahydrothiophenium bromide.

After that, the result of Proton NMR for 1-Ethyltetrahydrothiophenium thicocyanate ionic liquid was analyzed as shown the Figure 26. Based on the figure, there are 5 peaks that were corresponding to the cation 1-Ethyltetrahydrothiophenium thicocyanate ionic liquid.

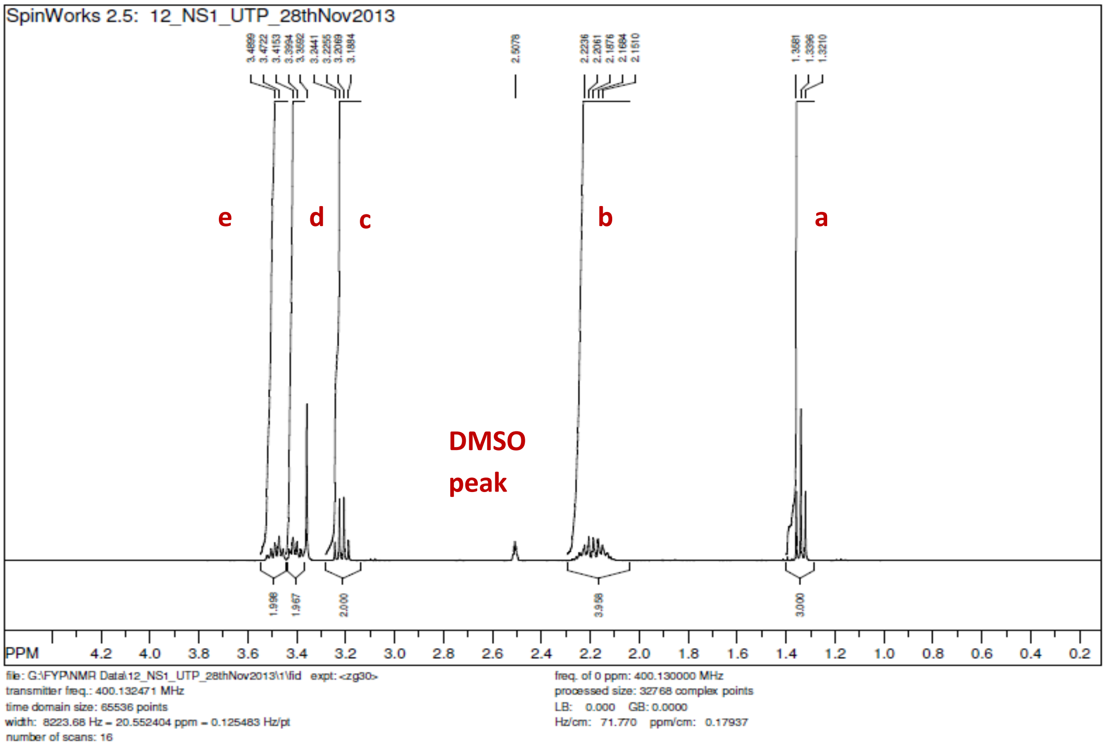


Figure 25: Proton NMR of 1-Ethyltetrahydrothiophenium thicocyanate

Table 17: Summary number of protons at each peak for 1-Ethyltetrahydrothiophenium thiocyanate

Peak	Molecular structure	Number of protons	Chemical shift (ppm)	Integrated value
a	CH_3	3	1.4	3.00
b	CH_2CH_2	4	2.2	3.958
c	CH_2	2	3.2	2.000
d	CH_2	2	3.4	1.967
e	CH_2	2	3.5	1.998

The spectrum of the 1-Ethyltetrahydrothiophenium thicocyanate and 1-Ethyltetrahydrothiophenium bromide is almost the same due to the cation that have been used is the same. The difference is only for 1-Ethyltetrahydrothiophenium thicocyanate, it has been introduced an anion exchange which is thiocyanate.

From the structure of thiocyanate, there is no other proton number that attached to thiocyanate. Hence, there are no peaks that will indicate for the present of thiocyanate. From the Table 17 which shows the summary of the peaks in the spectrum, it can be concluded that each peak represents approximately the same amount of protons as expected integrals. So, it is also proven that 1-Ethyltetrahydrothiophenium thicocyanate ionic liquid has successfully been formed with the expected structure and it is almost pure and clean as there are no other peaks that formed except from the expected structure and dimethyl sulfoxide-d6 (DMSO) peak which is the solvent peak used in this characterization.

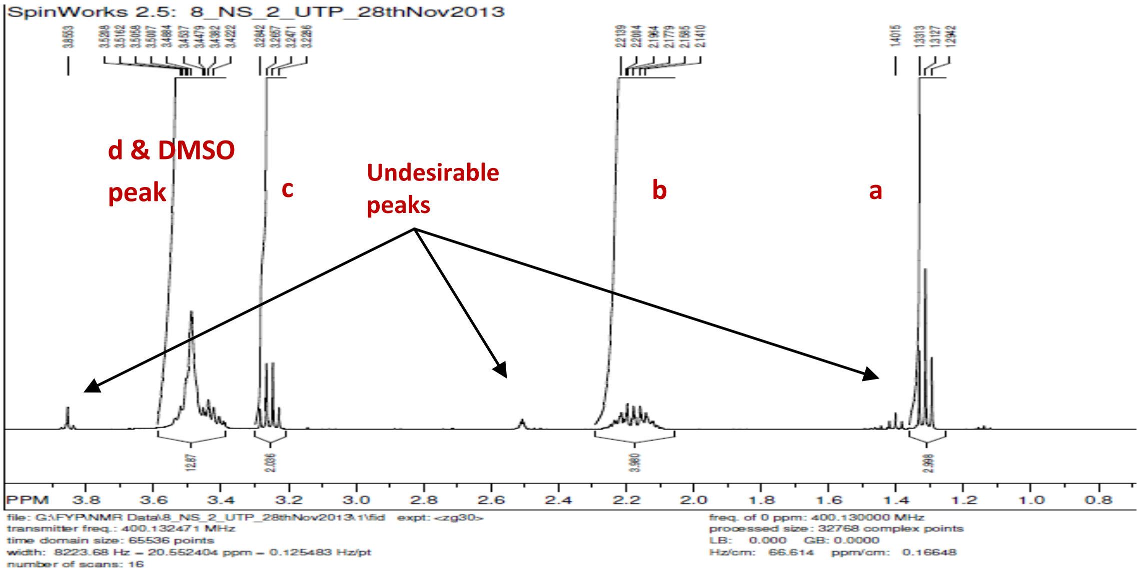


Figure 26: Proton NMR of 1-Ethyltetrahydrothiophenium dicyanamide

Table 18: Proton NMR of 1-Ethyltetrahydrothiophenium dicyanamide

Peak	Molecular structure	Number of protons	Chemical shift (ppm)	Integrated value
a	CH_3	3	1.4	2.998
b	CH_2CH_2	4	2.2	3.980
c	CH_2	2	3.2	2.036
d	CH_2 CH_2	4	3.4	12.87

Lastly, the Figure 27 above shows that the result of Proton NMR for 1-Ethyltetrahydrothiophenium dicyanamide ionic liquid. Same goes to 1-Ethyltetrahydrothiophenium dicyanamide ionic liquid, generally the spectrum is almost the same with the previous spectrum of 1-Ethyltetrahydrothiophenium bromide due to the same type and structure of the cation. But anion dicyanamide had been introduced to cation Ethyltetrahydrothiophenium bromide. Nevertheless, same as thiocyanate, the dicyanamide did not consist of proton number that attached to the structure so there are no peaks that will represent of dicyanamide. From the Table 18 which shows the summary of the peaks in the spectrum, it can be concluded that each peak represents approximately the same amount of protons as expected integrals and also dimethyl sulfoxide-d6 (DMSO) peak which is the solvent peak used in this characterization. Even so, it also can be seen that there are many undesirable peaks from the spectrum. All these undesirable peaks could be corresponds to the present of solvent in the ionic liquid. This is regardless to the failure of the vacuum line to function, hence not all the solvent has been successfully removed. Although the ionic liquid had been put into vacuum oven in replacing the vacuum line but the efficiency of the vacuum oven is not as good as vacuum line. So, it is proven that 1-Ethyltetrahydrothiophenium dicyanamide ionic liquid has also successfully been formed with the expected structure but not as pure and clean as previous ionic liquids that have been prepared properly according to the procedure.

4.2.2 Fourier Transform Infrared Spectroscopy, FTIR Analysis

FTIR is used to identify chemical compounds based on how infrared radiation is absorbed by the compounds chemical bonds. There is a reference known as infrared spectroscopy correlation table that lists some general absorption peaks for common types of atomic bond and functional group. FTIR analysis was done for the synthesized ionic liquids in order to determine the actual functional group that presents in the ionic liquid either it is corresponding to the expected structure or vice versa. The sample will exposed to electromagnetic radiation and the response is monitored as showed in the Figure 28, Figure 29 and Figure 30.

This is how to read FTIR spectrum. First of all, the very complex looking region below 1500 wave numbers is called the fingerprint region and can mostly be ignored. The fingerprint region contains bond stretches between backbone atoms and is usually too much of a mess to be any help. Instead, concentrate on the region between 1500-4000 wave numbers. This region contains peaks that correspond to stretches in functional groups, and is all that is usually needed to determine molecular structure. By finding the large peaks in the functional group region and seeing what functional group bond stretch they correspond to, a model of the molecule can begin to take shape. The depth of the peak correlates with how much of the substance is present in the sample.

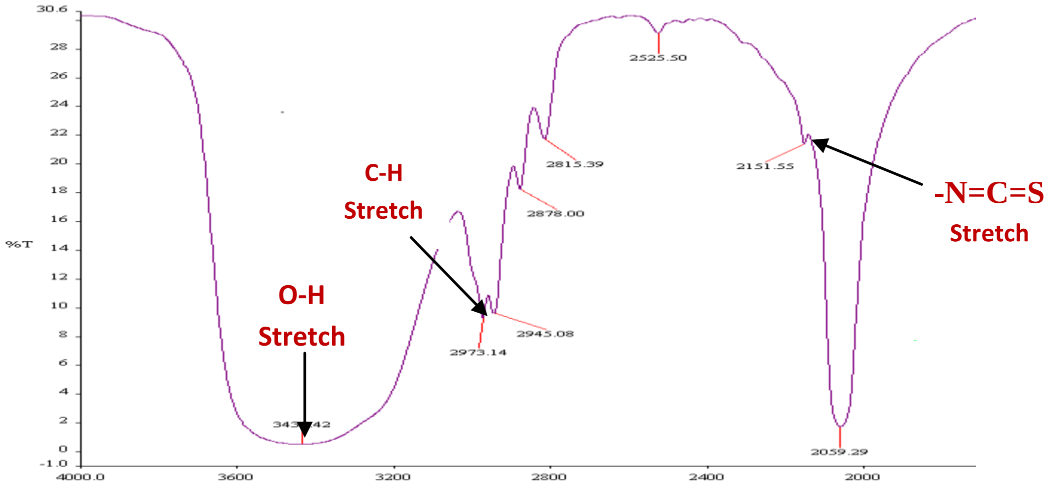


Figure 27: FTIR analysis of 1-Ethyl-tetrahydrothiophenium thiocyanate

The peaks of wave number indicate the types of the functional group in the ionic liquid. The types of functional group can be determined through the correlation table in Appendix. Based on the analysis of Figure 28, the 1-Ethyltetrahydrothiophenium thiocyanate ionic liquid contains of alkanes group (C-H bond) with wave number: 2800 – 2950 cm^{-1}; isothiocyanates group (-N=C=S) with wave number; ~2125cm^{-1} which represent the presence of nitrile; and alcohol group (O-H) with wave number; ~3650cm^{-1} which represent the presence of some water. Therefore, the analysis illustrate that the 1-Ethyl-tetrahydrothiophenium thiocyanate is verified.

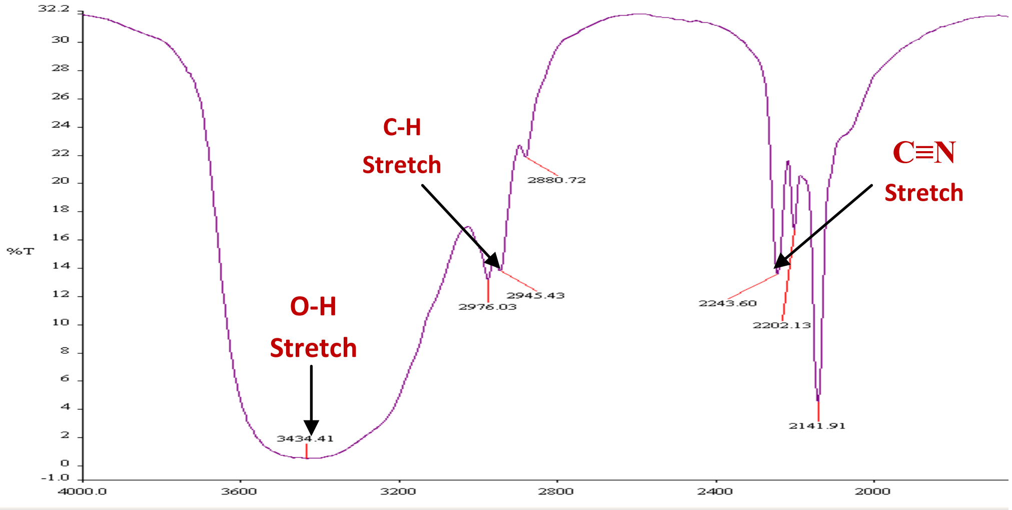


Figure 28: FTIR analysis of 1-Ethyltetrahydrothiophenium dicyanamide

Based on the analysis of Figure 29, the 1-Ethyltetrahydrothiophenium dicyanamide ionic liquid contains alkanes (C-H bond) with wave number: 2800 – 2950 cm^{-1}; nitriles group (C≡N) with wave number; ~2250cm^{-1}; and alcohol group (O-H) with wave number; ~3650 cm^{-1}which represent the presence of some water. Therefore, the analysis illustrate that the 1-Ethyl-tetrahydro-thiophenium dicyanamide is verified.

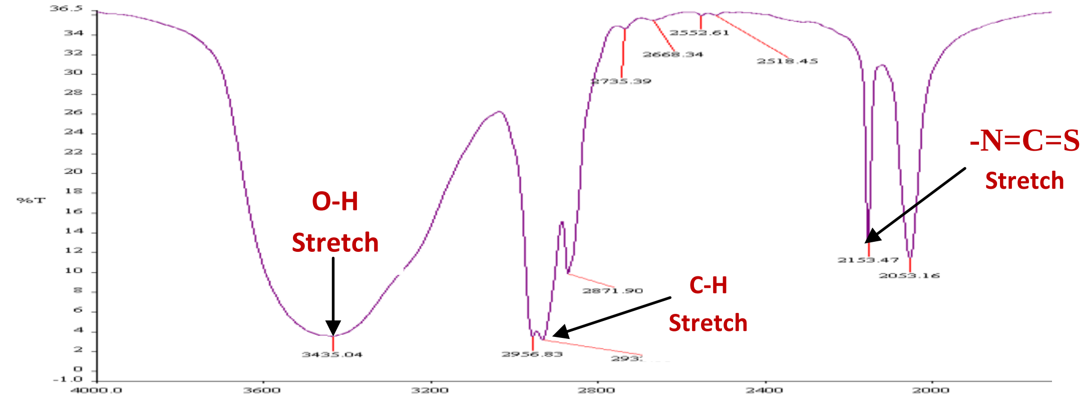


Figure 29: FTIR analysis of 1-Butyltetrahydrothiophenium thiocyanate

Based on the analysis of Figure 30, the 1-Butyl-tetrahydro-thiophenium thiocyanate ionic liquid contains of alkanes group (C-H bond) with wave number: 2800 – 2950 cm^{-1}; isothiocyanates group (-N=C=S) with wave number; 2250cm^{-1} which represent the presence of nitrile; and alcohol group (O-H) with wave number; ~3650cm^{-1} which represent the presence of some water. Therefore, the analysis illustrate that the 1-Butyltetrahydrohiophenium thiocyanate is verified.

4.2.3 Viscosity and Density Analysis

The physical properties of the ionic liquid such as density and viscosity are analyzed using the density meter and ciscosity meter. For this analysis 1-2 mL of ionic liquids were needed and only 1-Butyltetrahydrothiophenium thiocyanate had been characterized due to the enough amounts that have been prepared. For the other ionic liquids, there are only a small amount that have been prepared and not enough for this characterization. The result of the analysis of the density and viscosity is shown in Table 19, Figure 31 and Figure 32.

Table 19: Density and viscosity of 1-Butyltetrahydrothiophenium thiocyanate

Temperature (°C)	Density (g/cm³)	Viscosity (MPa.S)
20	1.1278	901.000
30	1.1262	451.020
40	1.1221	253.000
50	1.1193	149.190
60	1.1144	96.420
70	1.1095	64.447
80	1.1031	44.653
90	1.0957	30.388
100	1.0720	14.420

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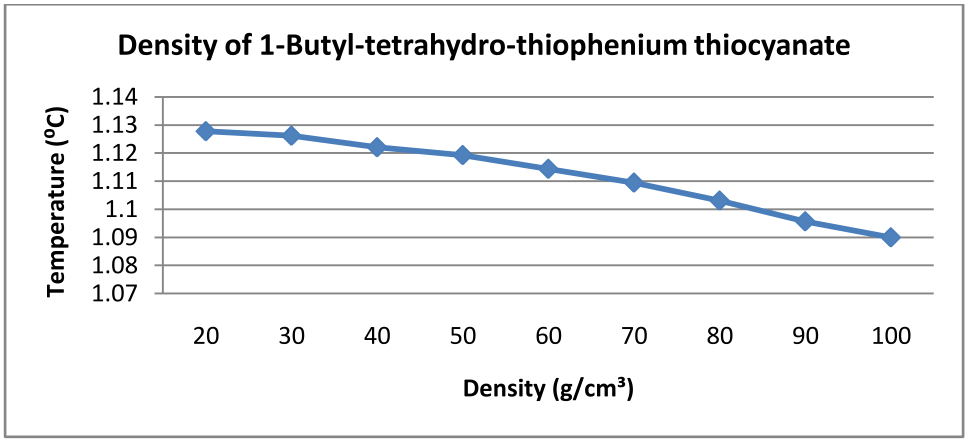

Figure 30: Density of 1-Butyltetrahydrothiophenium thiocyanate

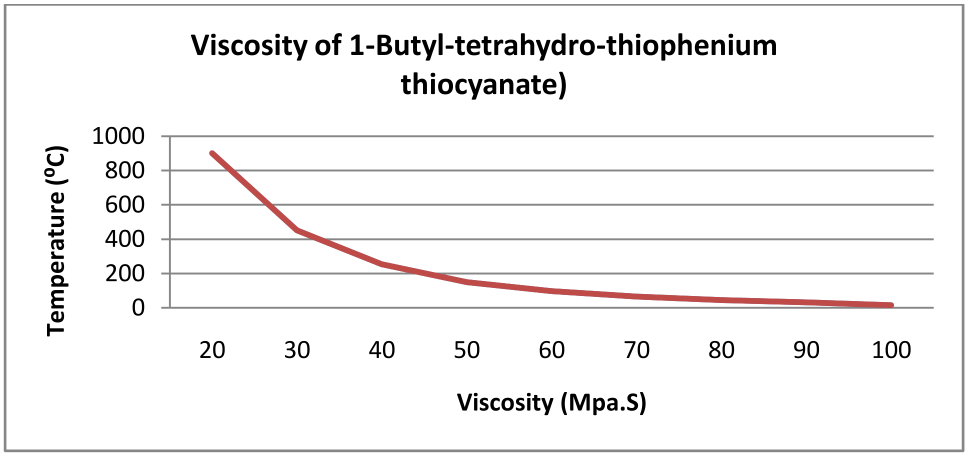

Figure 31: Viscosity of 1-Butyltetrahydrothiophenium thiocyanate

The density and viscosity of the 1-Butyltetrahydrothiophenium thiocyanate ionic liquid was analyzed as a function of temperature. The analysis was performed within a temperature range of 20 ºC to 100 ºC. As can be seen in the Figure 31 and Figure 32, the influence of temperature on density and viscosity is significant.

4.3 Extractive Desulfurization Process

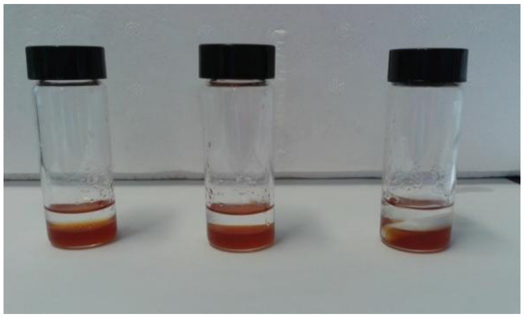

Figure 32: 2 layers formed during process of extraction desulfurization

In the liquid-liquid extraction process, the model oil and ionic liquids were mixed by 1:1 ratio. A higher amount of ionic liquids needed which is around 4.5 g and nly 1-Butyltetrahydrothiophenium thiocyanate ionic liquid is used for the extraction due to the enough amount. The mixture was mixed using the sample bottles so that the mixture can be heated and stirred during the extraction process. As the model oil was added and into ionic liquids, two layers were formed as shown in Figure 33. The upper layer was model oil phase while the bottom layer was ionic liquid phase. For this extraction, the mixture was heated at 30^0C and stirred at 500 rpm for 30 minutes. The removal of dibenzothiophene (DBT) from model oil is believed to happen during this extraction stage. After the heating process, the mixture was cooled at room temperature before analyzed by using Gas Chromatography. Generally the extraction process will be repeated by three times for the accurate results.

4.3.1 Gas Chromatography Analysis

Gas chromatography analysis was carried out in order to determine the percentage of dibenzothiophene, DBT presents in the model oil before and after extraction. The sample of model oil contains DBT before extraction was first to be analyzed to find out the initial amount of DBT content in the model oil followed by the sample of model oil after extraction process. The spectrum result of the Gas Chromatography can be referred to the Appendix C. All the data were summarized in the Table 20.

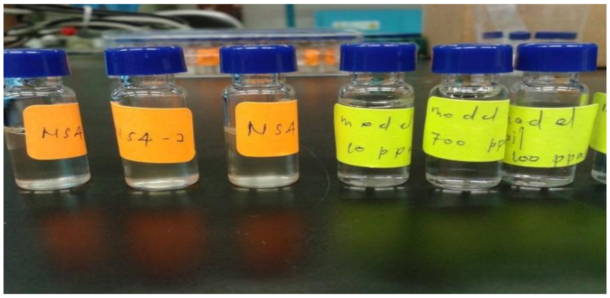

Figure 33: Sample prepared for Gas Chromatography Characterization (GC)

Efficiency of the ionic liquid is defined by the percentage of dibenzothiophene (DBT) removal in model oil. It has been determined as follows:

$$Extraction\ Performance = \frac{Initial\ DBT\ content - Final\ DBT\ content}{Initial\ DBT\ content} \times 100\%$$

Table 20: Extraction performance of 1-Butyltetrahydrothiophenium thiocyanate

No.	Solution	Amount of Dibenzothiophene contains in Model Oil (ppm)		Extraction Performance (%)
		Before Extraction	After Extraction	
1	Model Oil (Dodecane + 0.2873 wt% DBT)	524.11230	285.88012	45.45
2	Model Oil (Dodecane + 0.2873 wt% DBT)	524.11230	301.74433	42.43
3	Model Oil (Dodecane + 0.2873 wt% DBT)	524.11230	290.96393	44.48

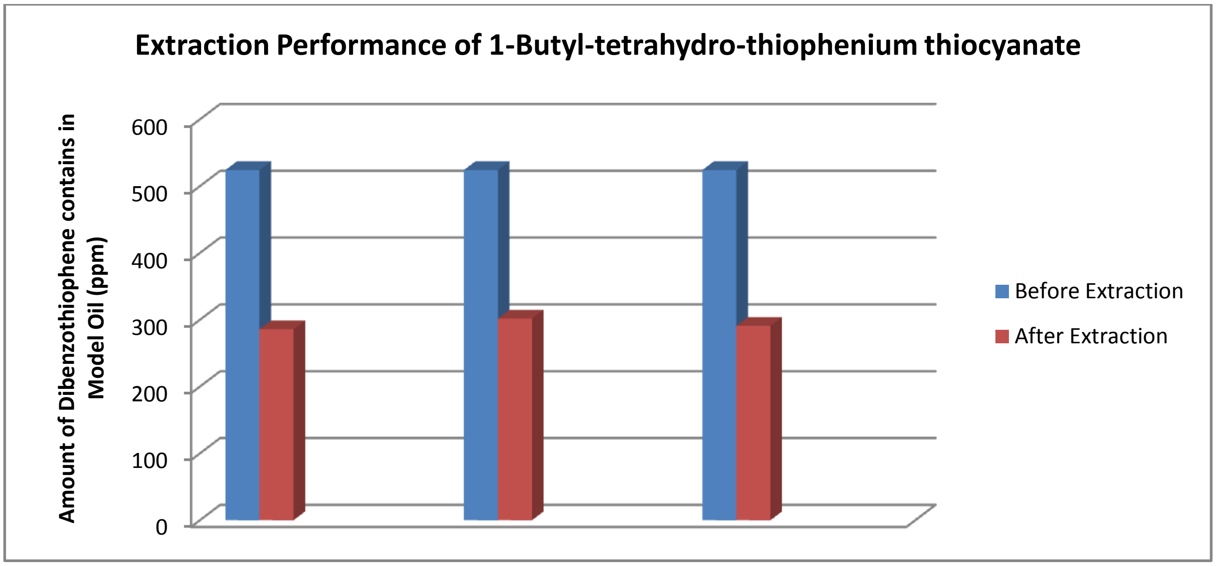

Figure 34: Bar chart of extraction performance for 1-Butyltetrahydrothiophenium thiocyanate

Based on the results in Table 20 and Figure 35, it shows that the extraction performance for 1-Butyltetrahydrothiophenium thiocyanate with the amount of DBT content in dodecane before and after extraction. The average efficiency performance of the extraction DBT from the model oil by using this ionic liquid is 44.12%. From this result, it can be proved that the 1-Butyltetrahydrothiophenium thiocyanate ionic liquid has the ability to extract DBT sulfur from the model oil. Factor for low performance may be due to water content in the synthesized ionic liquid (Gao, et al., 2008). Future work should include the determination of water content in the synthesized ionic liquid. Although the performance of 1-Butyl-tetrahydrothiophenium thiocyanate ionic liquid is not impressive, other contributing factor should be looked into (water content, equilibrium time, purity of the product, etc.) for the improvement in efficiency of extraction process.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Based on the result obtained from previous part, it can be proved that 1-Ethyltetrahydrothiophenium thiocyanate, 1-Ethyltetrahydrothiophenium dicyanamide, 1-Butyltetrahydrothiophenium dicyanamide and 1-Butyltetrahydrothiophenium thiocyanate ionic liquids have been synthesized in this project. Nevertheless only Ethyltetrahydrothiophenium thiocyanate, 1-Ethyltetrahydrothiophenium dicyanamide have been successfully characterized by using proton NMR and FTIR whereas 1-Butyltetrahydrothiophenium thiocyanate has been characterized by FTIR only. The characterization result from the proton NMR and FTIR shows that this ionic liquids had produce the correct structures and functional group even though there is still some other functional group have been detected in the ionic liquids which is alcohol group (O-H) that represent the water. But further characterization by using Karl Fischer titration need to be conducted in order to determine the amount of water content in the ionic liquids.

For the desulfurization process, it is also proved that 1-Butyltetrahydrothiophenium thiocyanate ionic liquid have an ability to extract sulfur from model oil. As stated, the objective of this project also is to determine the effectiveness of ionic liquid in extracting sulfur. The average of sulfur removal for this type of ionic liquid is 44.12%. Hence, the ionic liquid can be further improved during the preparation and synthesized to enhance the extractive desulfurization process.

5.2 Recommendations and Future Work

5.2.1 Synthesis and Characterization of Ionic Liquids

- The ionic liquids need to be prepared in a high amount in order to conduct the characterization and also desulfurization process
- The characterization by Proton NMR need to be conducted for each of ionic liquids synthesized in determination of structures and purity of ionic liquids. For this project, future work is to conduct the Proton NMR for 1-Butyltetrahydrothiophenium dicyanamide and 1-Butyltetrahydrothiophenium thiocyanate ionic liquids.
- The characterization with FTIR need to be conducted for each of ionic liquids synthesized in determination of functional group that contains in the ionic liquids. For this project, future work is to conduct the FTIR for 1-Ethyltetrahydrothiophenium dicyanamide, 1-Butyltetrahydrothiophenium dicyanamide and 1-Butyltetrahydrothiophenium thiocyanate ionic liquids.
- The characterization with Karl Fischer need to be conducted for each of ionic liquids synthesized in order to determine the water content in ionic liquids. The high water content in ionic liquid will reduce the performance of ionic liquids in extracting the sulfur compound. For this project, future work is to determine the water content of 1-Ethyltetrahydrothiophenium thiocyanate, 1-Ethyltetrahydrothiophenium dicyanamide, 1-Butyltetrahydrothiophenium dicyanamide and 1-Butyltetrahydrothiophenium thiocyanate ionic liquids.
- Determine all the physical and chemical properties for the synthesized ionic liquids such as density, viscosity, thermal decomposition temperature and melting point.
- All the equipments must be functioning well to ensure the smoothness of the project.

5.2.2 Extractive Desulfurization Process

- All the synthesized ionic liquids need to be tested for the desulfurization process in order to do a comparison of extraction performance between difference ionic liquids
- The optimization for the desulfurization process need to be conducted such as to vary the temperature used during extraction, to increase the ratio of ionic liquids to the model oil and etc
- The real crude oil can be used for the application part in order to determine the successful of this project

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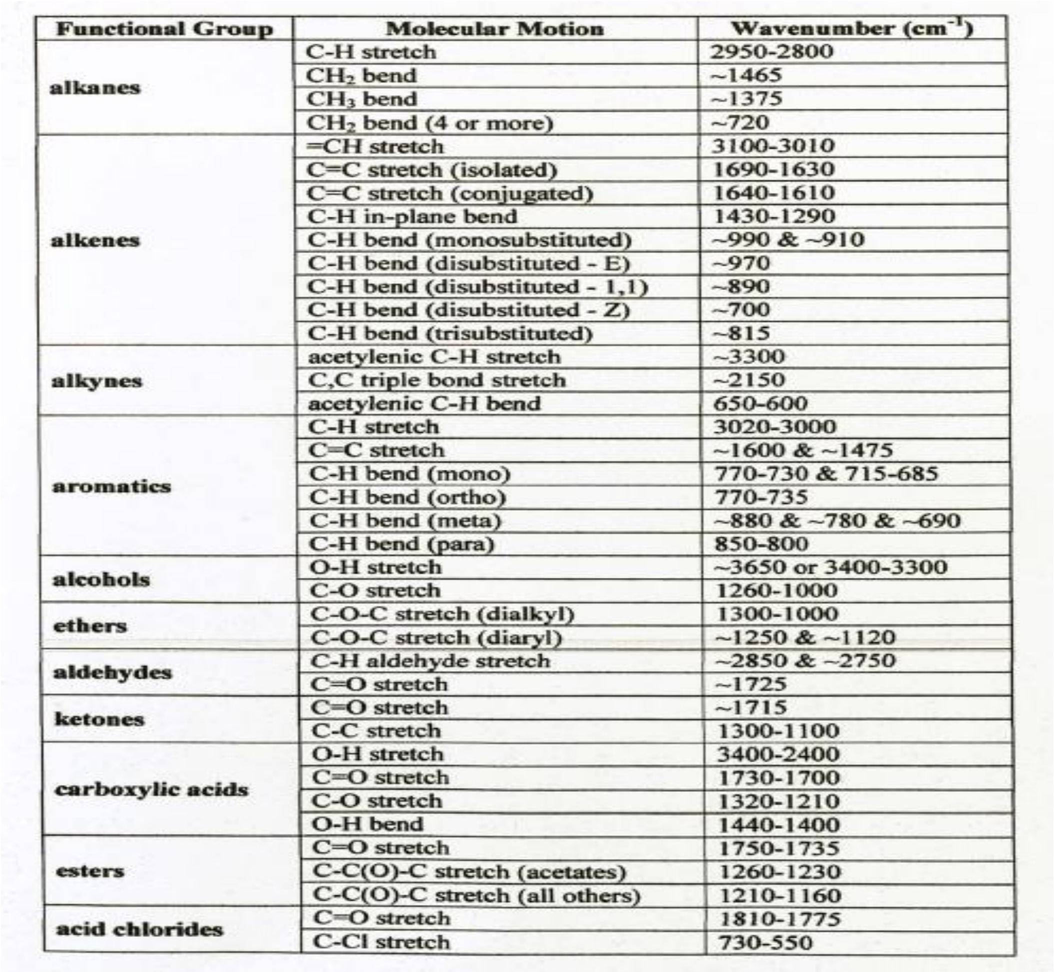
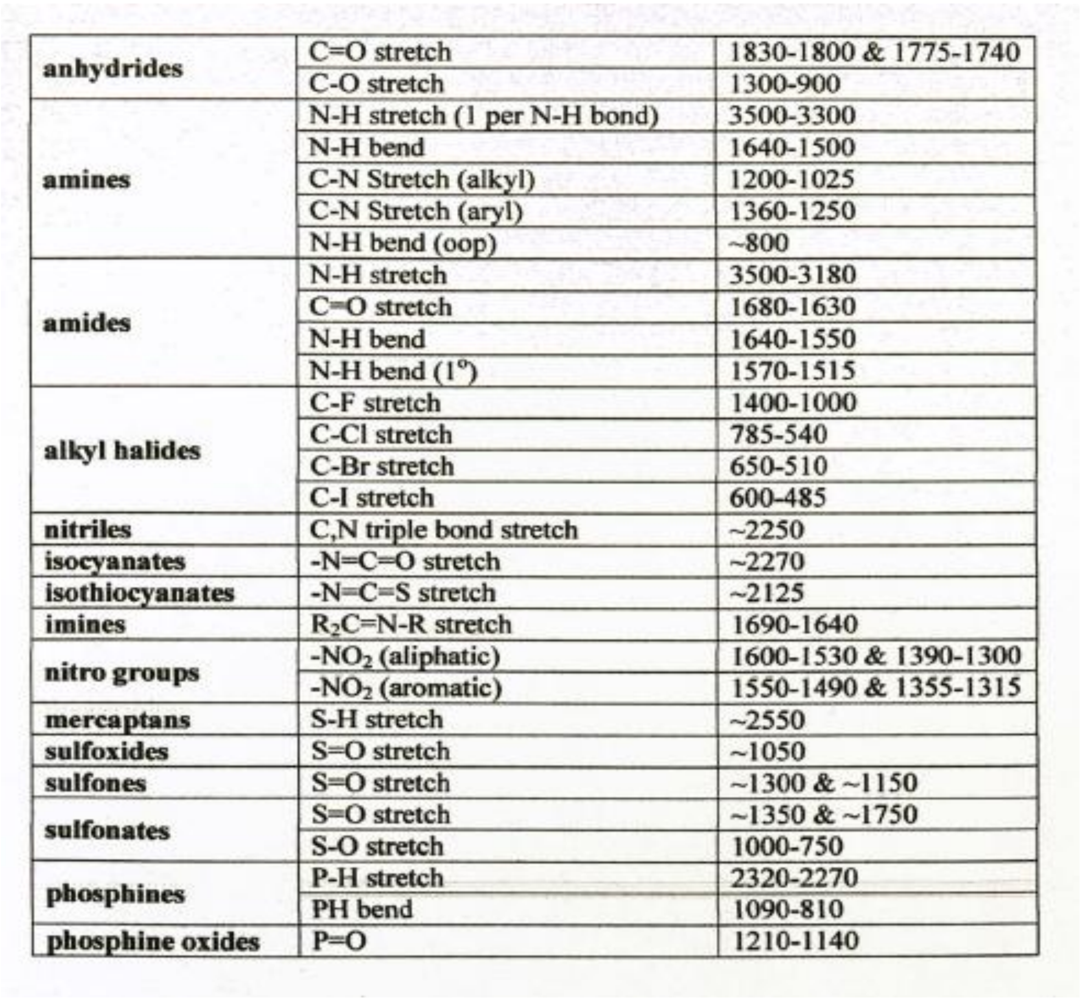
APPENDICES

Appendix A: FTIR Correlation Table

Table below shows the Infrared Spectroscopy – IR absorption for representative functional groups retrieved from http://www.chemistry.ccsu.edu/glagovich/teaching/316/ir/table.html



Functional Group	Molecular Motion	Wavenumber (cm^{-1})
alkanes	C-H stretch	2950-2800
	CH_2 bend	~1465
	CH_3 bend	~1375
	CH_2 bend (4 or more)	~720
alkenes	=CH stretch	3100-3010
	C=C stretch (isolated)	1690-1630
	C=C stretch (conjugated)	1640-1610
	C-H in-plane bend	1430-1290
	C-H bend (monosubstituted)	~990 & ~910
	C-H bend (disubstituted - E)	~970
	C-H bend (disubstituted - 1,1)	~890
	C-H bend (disubstituted - Z)	~700
	C-H bend (trisubstituted)	~815
alkynes	acetylenic C-H stretch	~3300
	C,C triple bond stretch	~2150
	acetylenic C-H bend	650-600
aromatics	C-H stretch	3020-3000
	C=C stretch	~1600 & ~1475
	C-H bend (mono)	770-730 & 715-685
	C-H bend (ortho)	770-735
	C-H bend (meta)	~880 & ~780 & ~690
	C-H bend (para)	850-800
alcohols	O-H stretch	~3650 or 3400-3300
	C-O stretch	1260-1000
ethers	C-O-C stretch (dialkyl)	1300-1000
	C-O-C stretch (diaryl)	~1250 & ~1120
aldehydes	C-H aldehyde stretch	~2850 & ~2750
	C=O stretch	~1725
ketones	C=O stretch	~1715
	C-C stretch	1300-1100
carboxylic acids	O-H stretch	3400-2400
	C=O stretch	1730-1700
	C-O stretch	1320-1210
	O-H bend	1440-1400
esters	C=O stretch	1750-1735
	C-C(O)-C stretch (acetates)	1260-1230
	C-C(O)-C stretch (all others)	1210-1160
acid chlorides	C=O stretch	1810-1775
	C-Cl stretch	730-550



anhydrides	C=O stretch	1830-1800 & 1775-1740
	C-O stretch	1300-900
amines	N-H stretch (1 per N-H bond)	3500-3300
	N-H bend	1640-1500
	C-N Stretch (alkyl)	1200-1025
	C-N Stretch (aryl)	1360-1250
	N-H bend (oop)	~800
amides	N-H stretch	3500-3180
	C=O stretch	1680-1630
	N-H bend	1640-1550
	N-H bend (1°)	1570-1515
alkyl halides	C-F stretch	1400-1000
	C-Cl stretch	785-540
	C-Br stretch	650-510
	C-I stretch	600-485
nitriles	C,N triple bond stretch	~2250
isocyanates	-N=C=O stretch	~2270
isothiocyanates	-N=C=S stretch	~2125
imines	R_2C=N-R stretch	1690-1640
nitro groups	$-NO_2$ (aliphatic)	1600-1530 & 1390-1300
	$-NO_2$ (aromatic)	1550-1490 & 1355-1315
mercaptans	S-H stretch	~2550
sulfoxides	S=O stretch	~1050
sulfones	S=O stretch	~1300 & ~1150
sulfonates	S=O stretch	~1350 & ~1750
	S-O stretch	1000-750
phosphines	P-H stretch	2320-2270
	PH bend	1090-810
phosphine oxides	P=O	1210-1140

Figure A 1: FTIR correlation table

Appendix B: ^{1}H NMR Results and Spectrum Generated from Software

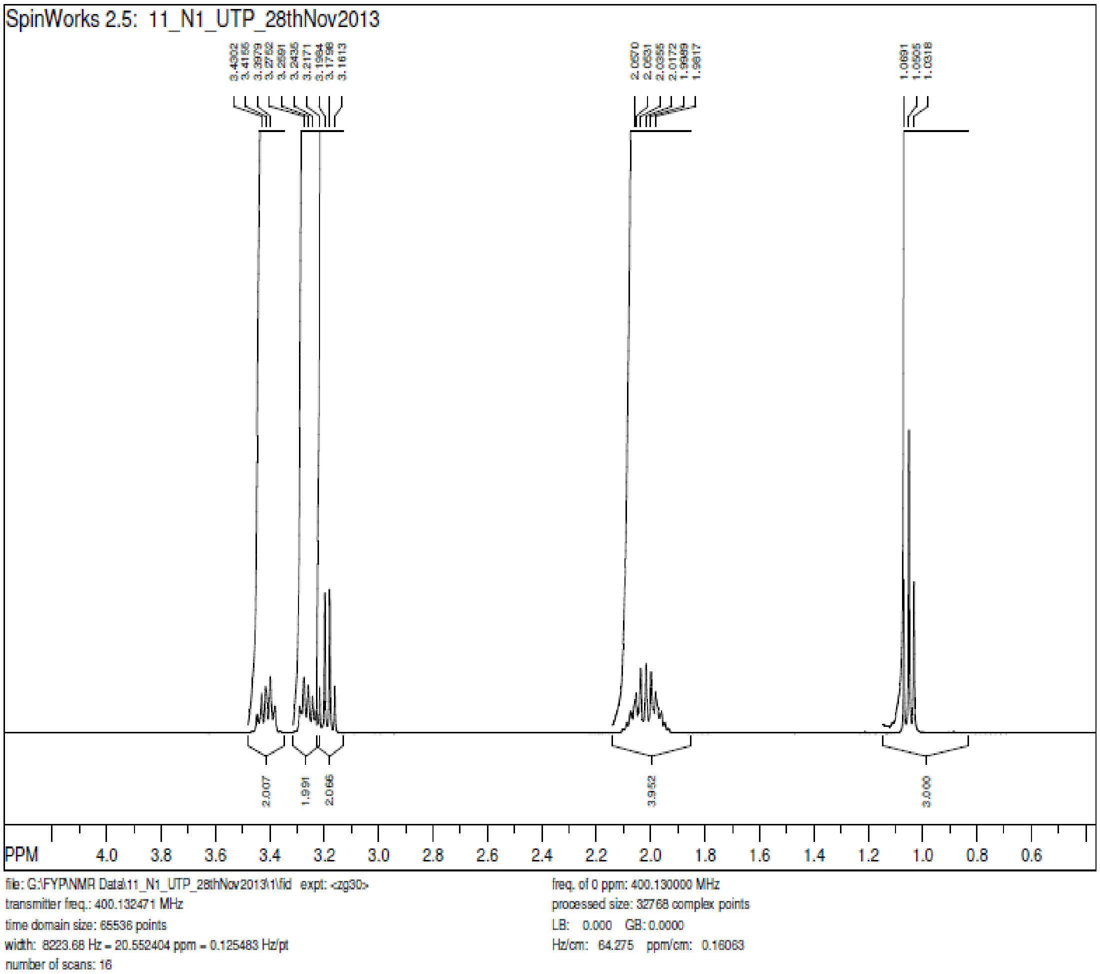


Figure B 1: Proton NMR of 1-Ethyltetrahydrothiophenium bromide

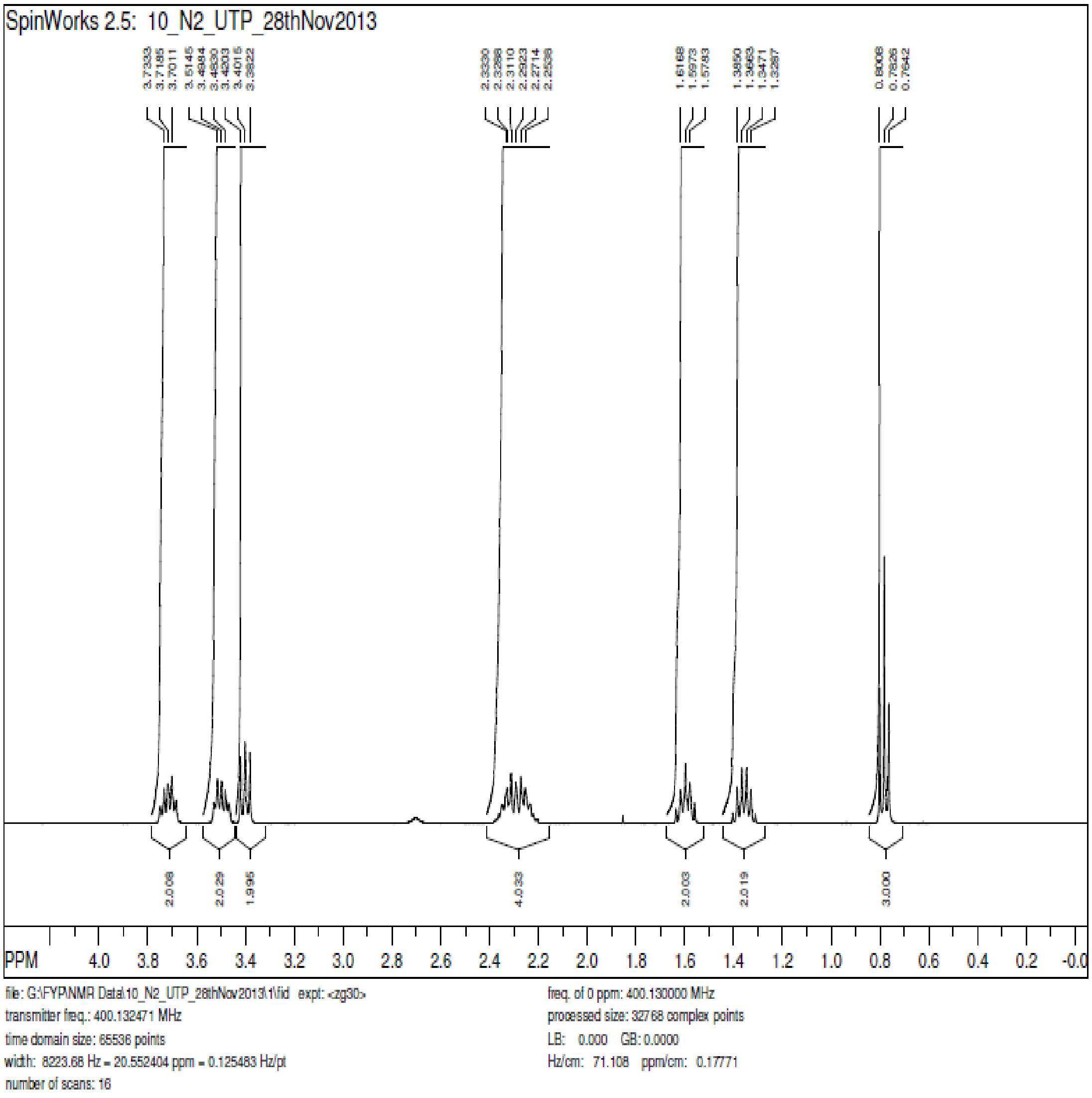


Figure B 2: Proton NMR of 1-Butyltetrahydrothiophenium bromide

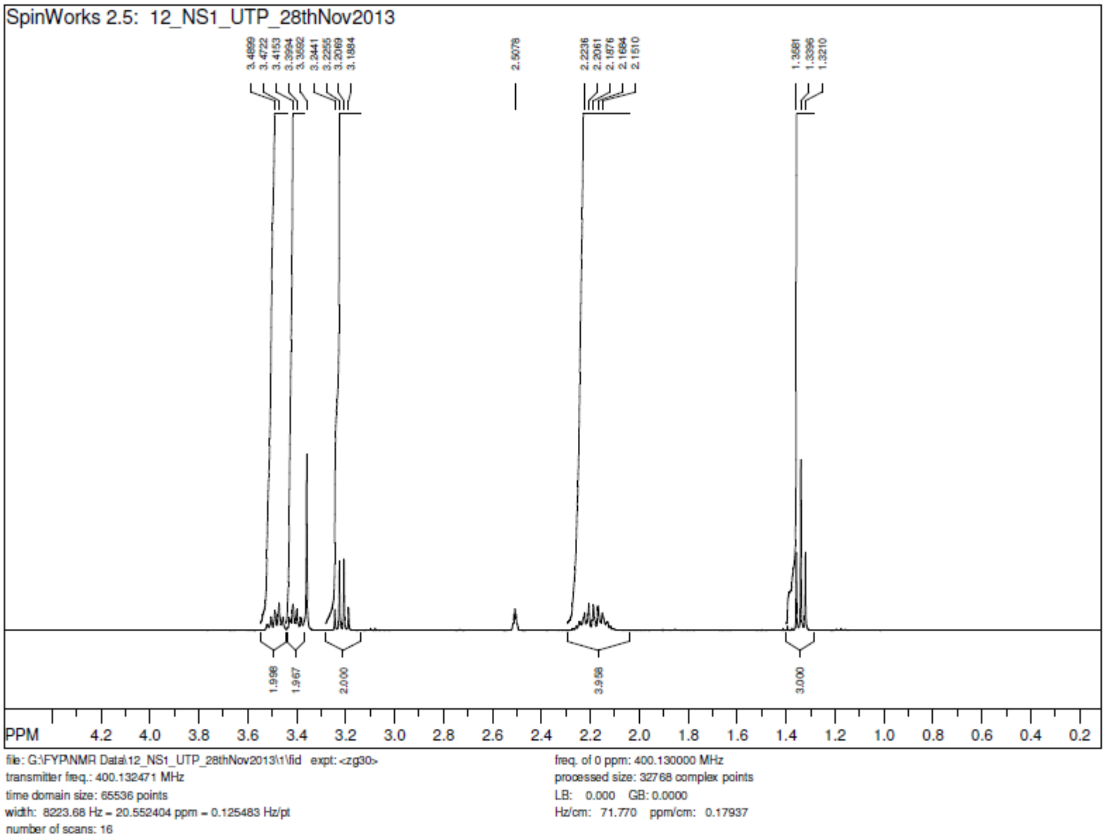


Figure B 3: Proton NMR of 1-Ethyltetrahydrothiophenium thiocyanate

Appendix C: FTIR Results and Spectrum Generated from Software

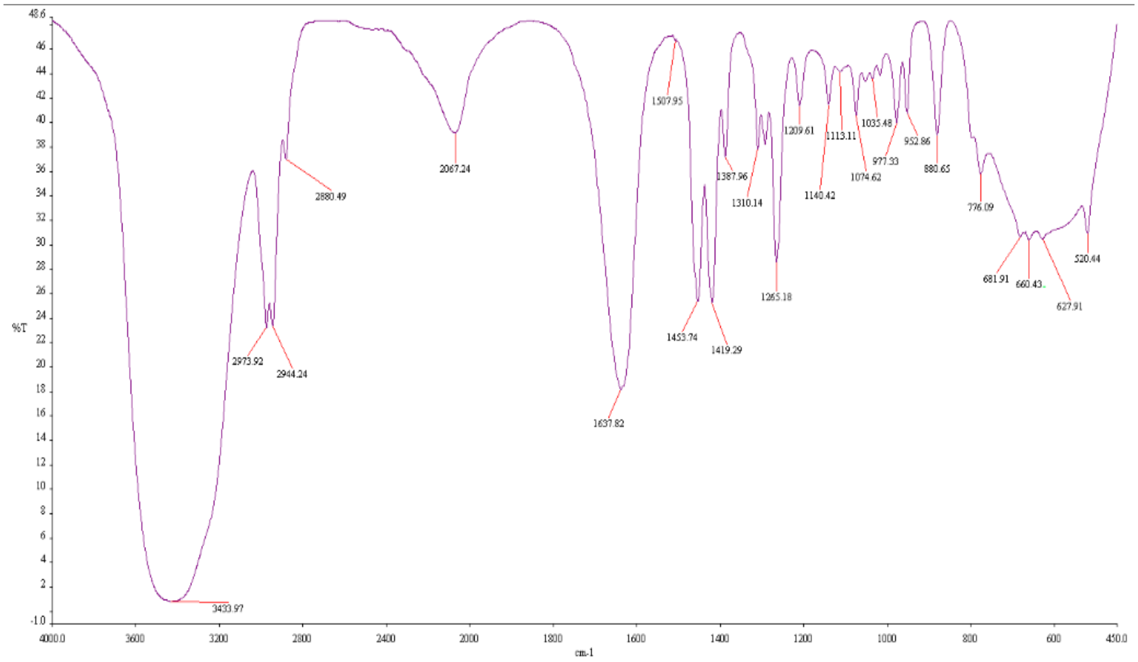


Figure C 1: 1-Ethyltetrahydrothiophenium bromide

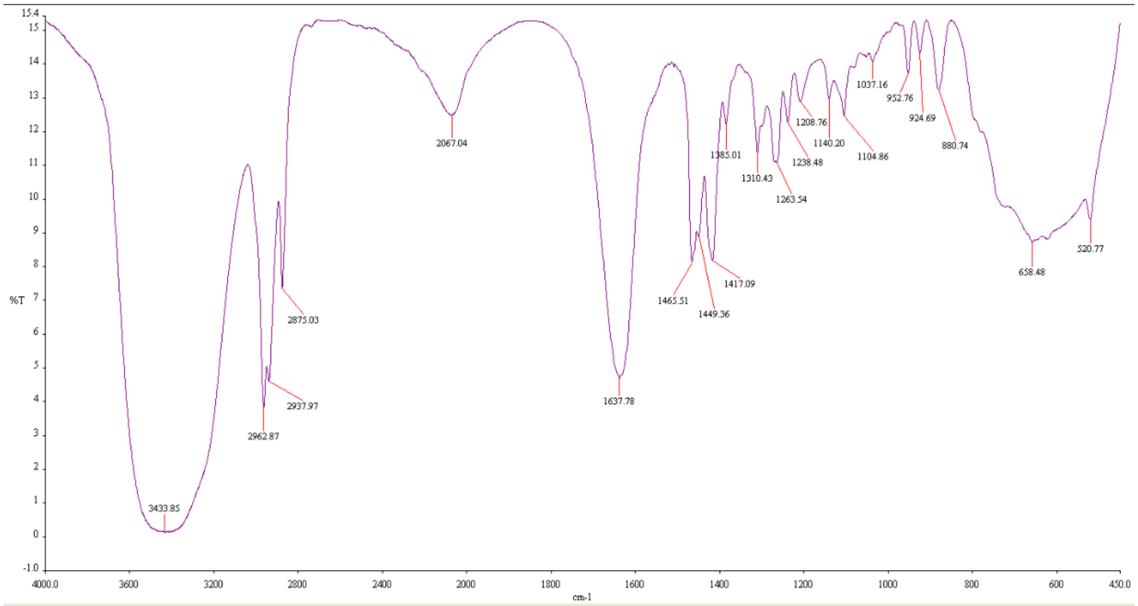


Figure C 2: 1-Butyltetrahydrothiophenium Bromide

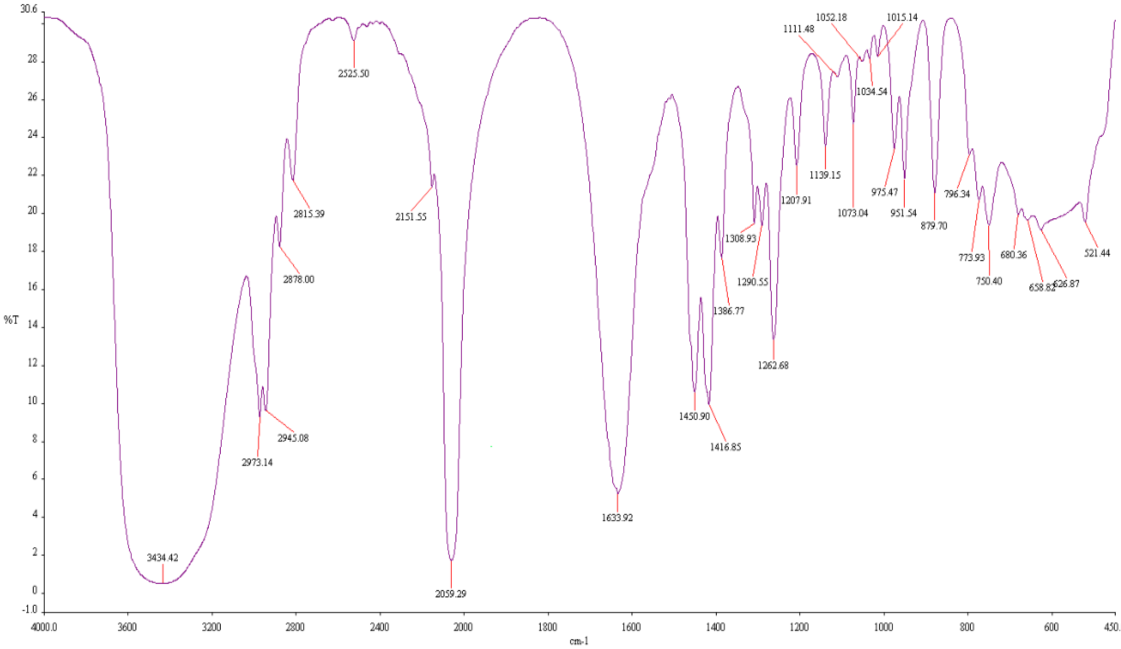


Figure C 3: 1-Ethyltetrahydrothiophenium Thiocyanate

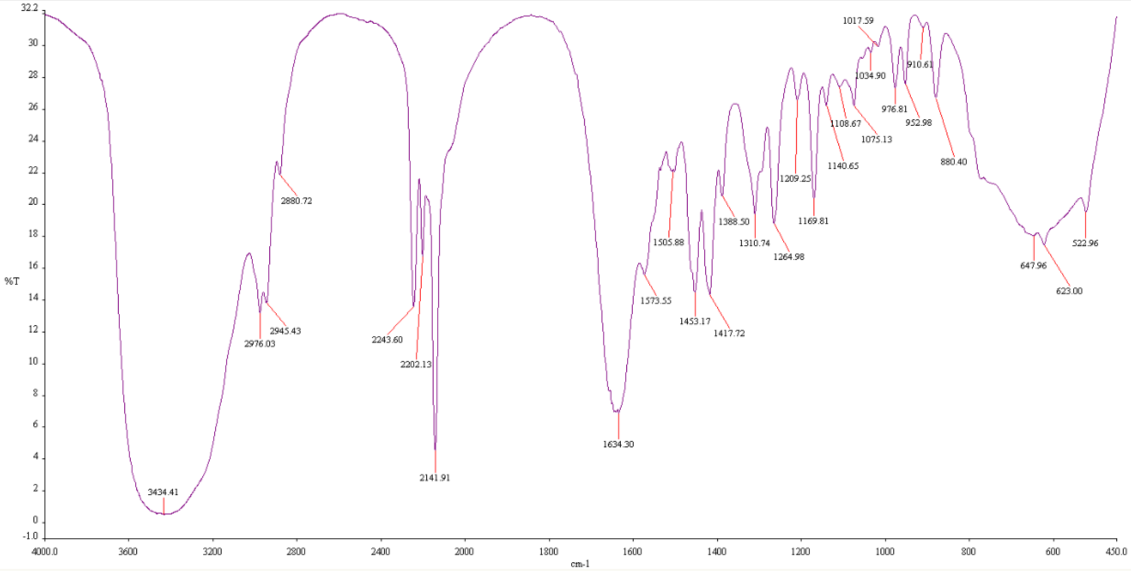


Figure C 4: 1-Ethyltetrahydrothiophenium Dicyanamide

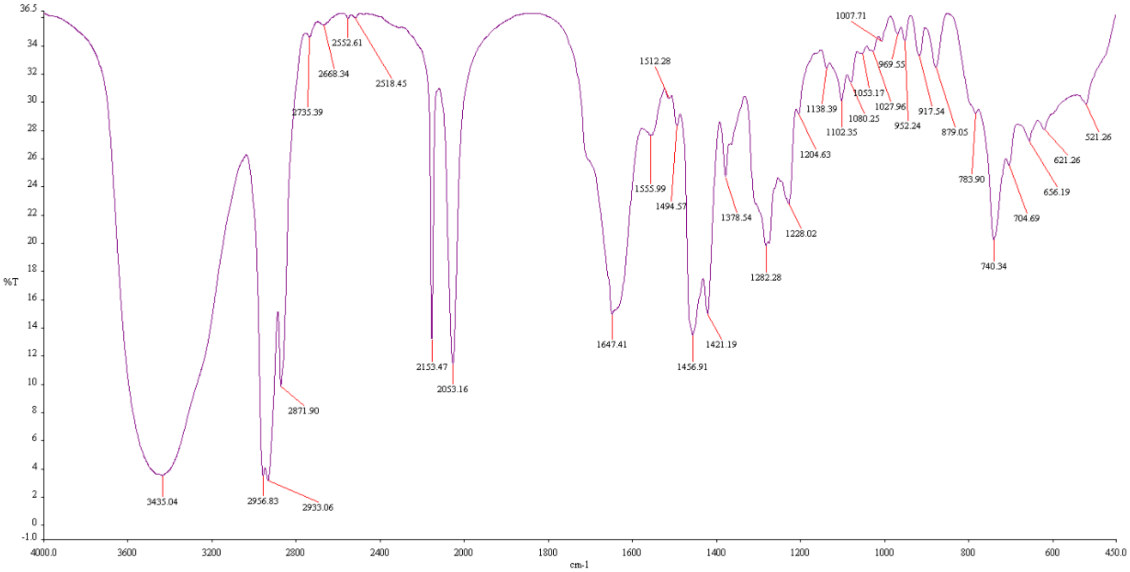
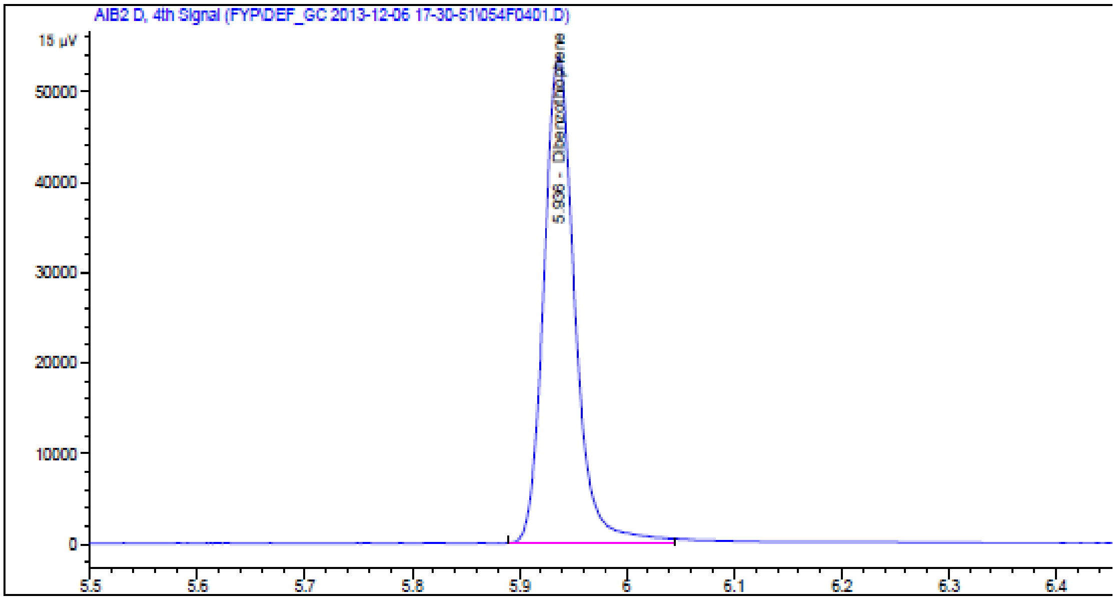
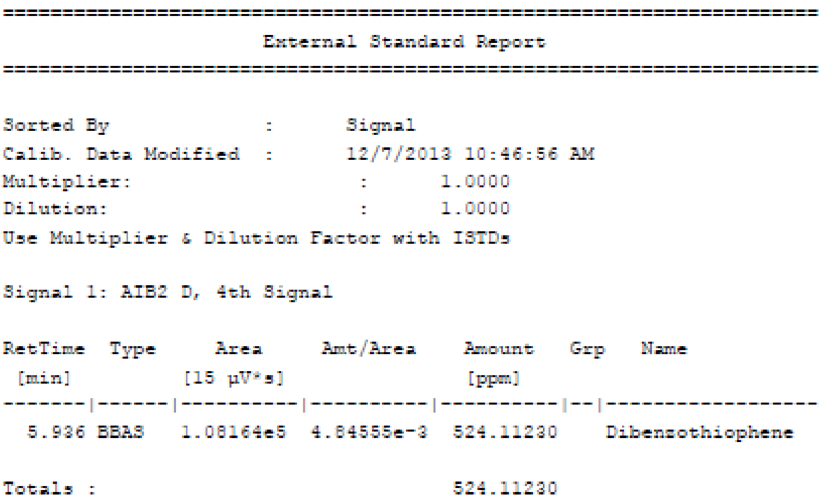


Figure C 5: 1-Butyltetrahydrothiophenium Thiocyanate

Appendix D: Gas Chromatography Results and Trend Generated from Software





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Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

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 [min]         [15 µV*s]               [ppm]
-------|------|----------|----------|----------|--|------------------
  5.936 BBAS   1.08164e5  4.84555e-3  524.11230    Dibenzothiophene

Totals :                              524.11230
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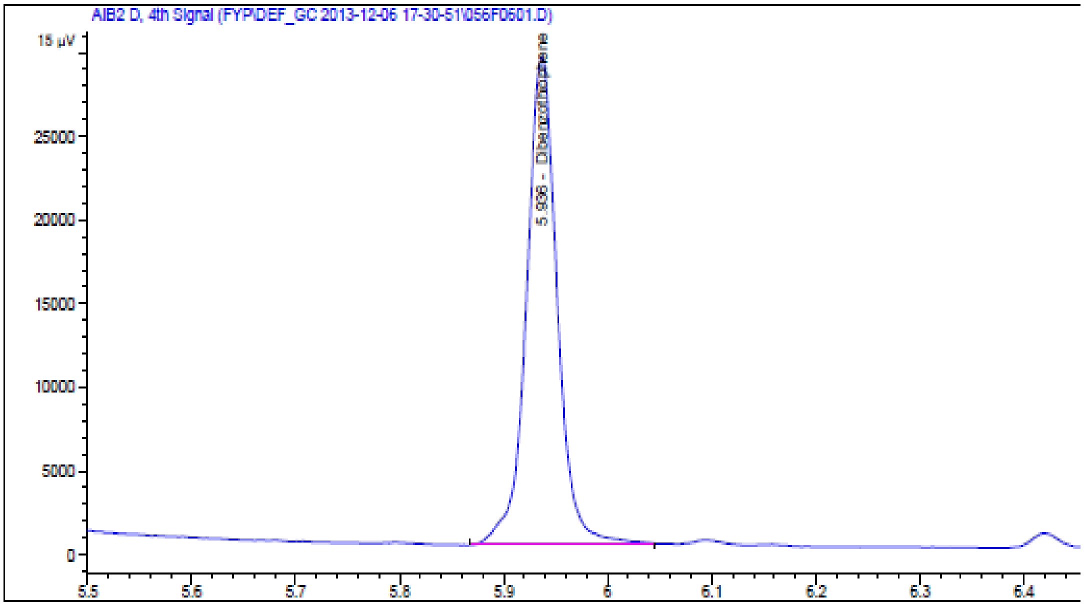
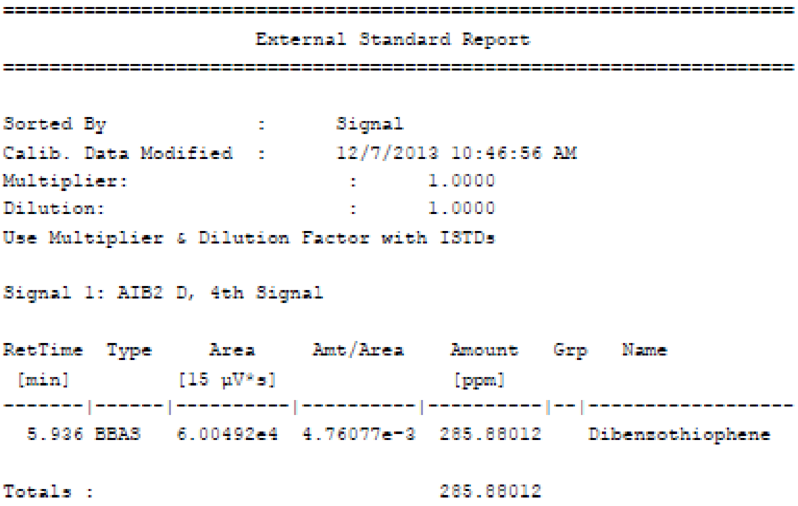
Figure D 1: Gas Chromatography for model oil before extractive desulfurization





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Use Multiplier & Dilution Factor with ISTDs

Signal 1: AIB2 D, 4th Signal

RetTime  Type     Area      Amt/Area     Amount   Grp   Name
 [min]          [15 µV*s]                [ppm]
-------|------|----------|----------|----------|--|------------------
  5.936 BBAS   6.00492e4  4.76077e-3  285.88012     Dibenzothiophene

Totals :                              285.88012
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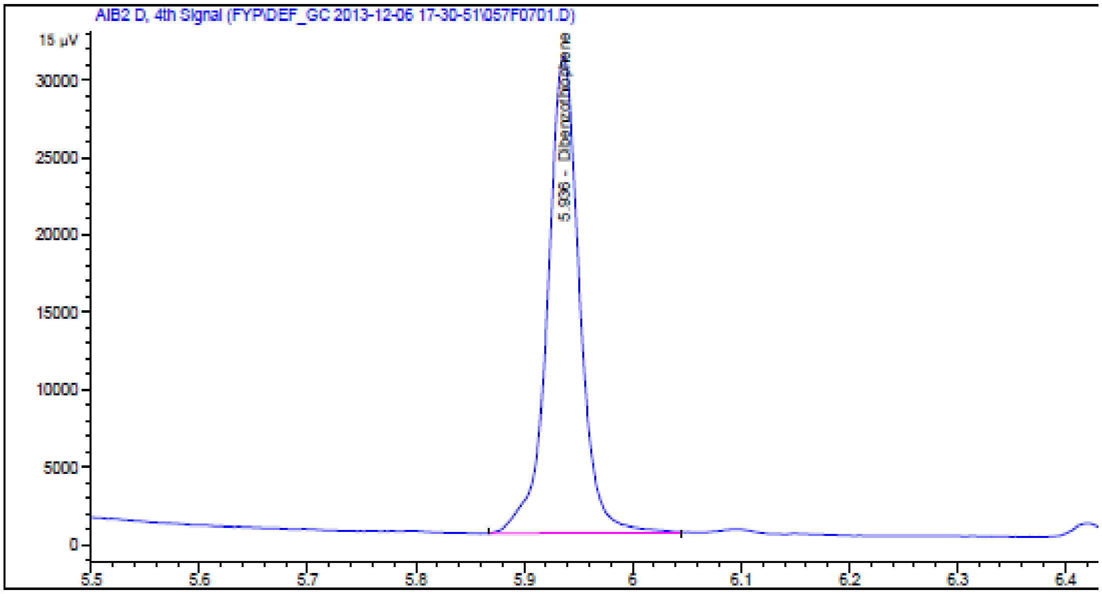
Figure D 2: Gas Chromatography for model oil after first extractive desulfurization



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Use Multiplier & Dilution Factor with ISTDs

Signal 1: AIB2 D, 4th Signal

RetTime  Type     Area     Amt/Area    Amount   Grp   Name
 [min]          [15 µV*s]              [ppm]
-------|------|----------|----------|----------|--|------------------
  5.936 BBAS   6.32532e4  4.77042e-3  301.74443    Dibenzothiophene

Totals :                              301.74443
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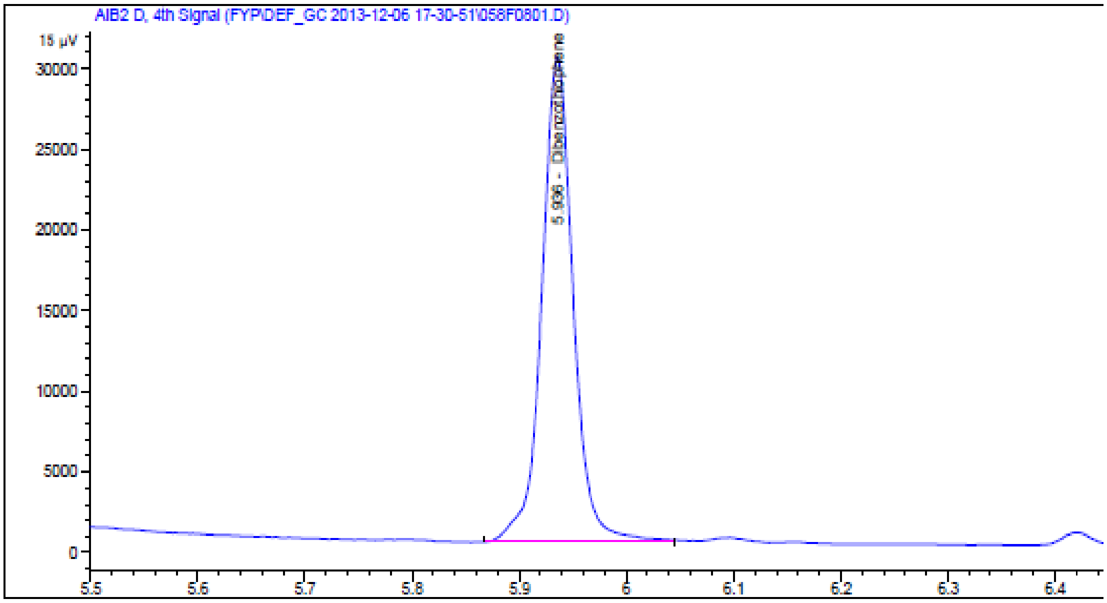
Figure D 3: Gas Chromatography for model oil after second extractive desulfurization



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Dilution:                      :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: AIB2 D, 4th Signal

RetTime  Type     Area      Amt/Area     Amount    Grp   Name
 [min]          [15 µV*s]               [ppm]
-------|------|----------|----------|----------|--|------------------
  5.936 BBAS   6.10759e4  4.76397e-3  290.96393     Dibenzothiophene

Totals :                              290.96393
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Figure D 4: Gas Chromatography for model oil after third extractive desulfurization