Desulphurization of Model Oil using Immobilized [BMIM]$FeCl_4$ onto Polysulfone (PSF)

by

MOHAMAD IBRAHIM BIN MOHD ZOLKEPLI

Dissertation submitted in partial fulfillment of
the requirements for the
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(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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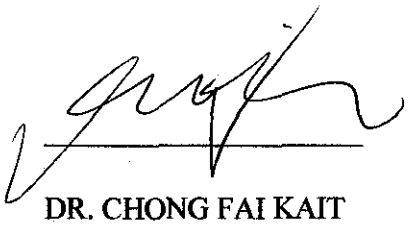
Approved by,



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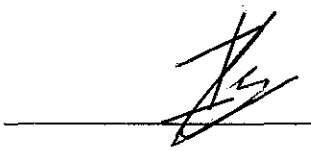
June 2010

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.



MOHAMAD IBRAHIM BIN MOHD ZOLKEPLI

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ABSTRACT

Final Dissertation of the experiment "Desulphurization of Model Oil using Immobilized [BMIM]$FeCl_4$ onto Polysulfone (PSF)" is the requirement of complementation of Final Year Project 2. Desulphurization has become one the important criteria that need to be concentrated especially in oil industries. Other than the conventional Hydrodesulphurization, many methods and alternatives have been discovered and yet to be discovered on order to cater the advance technology of Chemical Engineering, as well as the quality of the existing crude oil throughout the world. One of the major methods is desulphurization using ionic liquids. Ionic liquid is a new technology that can help to improve the quality of desulphurization due to its nature and function. [BMIM]$FeCl_4$ has been found out that it is the most suitable ionic liquid to desulphurize model oil. However, a limitation occurs as the ionic liquid exists in liquid form which later will cause a problem in doing the Liquid-Liquid Extraction. Thus, a new method is required to overcome this problem, which is the immobilization technique, Spraying Suspension Dispersion (SSD). SSD can immobilize any ionic liquid onto a solid structure, such as [BMIM]$FeCl_4$ onto Polysulfone (PSF). It works by dissolving the [BMIM]$FeCl_4$ together with PSF using dichloromethane and later they are sprayed into water solution. The water will wash away dichloromethane and as a result, droplets of PSF with [BMIM]$FeCl_4$ onto it are produced. These droplets will solidify and become a solid compound. The results from characterization has proven that [BMIM]$FeCl_4$ has been successfully hooked onto PSF. The desulphurization results also have shown that the immobilized [BMIM]$FeCl_4$ can still remove sulphur from model oil. Thus, this is a new method of desulphurization that engineers can go into and study into details.

CHAPTER 1: INTRODUCTION

1.1 Background Study

In the oil industry, crude oil is one of the major feed besides condensates. In the past years, oil refineries have been processing sweet crude and sour crude. However, the process design may have to be changed due to certain problem regarding the contents of the crude. One of the major concerns is the high amount of sulphur in the crude.

Although there are very few instances of naturally occurring low-sulphur crude oil (<0.5% sulphur), such as sweet crude, the limited availability makes these crude oil very expensive. The usage of high sulphur crude oil, on the other hand, will produce low quality oil and also excessive sulphur gases emission which in return will increase the operation cost for the industries. Moreover, the numbers of well that can supply sweet crude are decreasing and in the future, the sweet crude may be depleted. Thus, oil industries may have to process sour crude oil with very high sulphur contents.

In order to reduce the sulphur content of crude, a removal process is required, termed as desulphurization. There are several methods to remove sulphur from crude oil that is applied in the industries such as hydrodesulphurization (HDS). HDS is a process of using Hydrogen (H_2) as the medium to remove sulphur contents from a crude oil. HDS is done at a temperature around 300 – 400 °C with a temperature around 30 – 130 atm.

1.2 Problem Statement

HDS is a H_2 intensive process conducted at high temperature and pressure. Therefore, an alternative desulphurization technique has been identified. Although ionic liquid has been proven to extract sulphur species, separation of the ionic liquid from the oil phase seems to be an issue. In order to overcome the separation problem in Liquid-Liquid Extraction (LLE), immobilization of the ionic liquid onto a solid support is an interesting option.

1.3 Objectives

The objectives of the project involve:

1. To immobilize [BMIM]$FeCl_4$ onto Polysulfone (as solid structure).
2. To determine the sulphur removal efficiency of the immobilized [BMIM]$FeCl_4$ from model oil.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

Ionic liquids have become one of the choices in the daily activities as its unique properties such as negligible vapour pressure, low toxicity, high chemical and thermal stabilities, and ability to dissolve in the many types of organic and non-organic compounds. Due to the special properties, Ionic Liquids can be used in many applications such as synthesis, catalysis and separation.

2.2 Understanding Ionic Liquid

Ionic liquid (also known as liquid electrolytes, ionic fluids, liquid salts) is a salt that form stable liquid. Ionic liquid is good due to its extremely low vapor pressure. Which means it will not easily evaporate like other liquid at certain temperature. This can be a good impact for commercial purposes.

Ionic liquids are poor conductors, non-polar, high viscous and exhibit low vapor pressure. However, ionic liquid can still perform other chemical reactions, such as Diels-Alder reactions and Friedel-Crafts reactions.

Due to these characteristics, ionic liquid can have multiple applications, since it can be customized to possess desirable properties. For instance, nowadays, there are many companies that employ ionic liquids in their production process or conduct research to extend the application of ionic liquid in the industries. For example, BASF from Germany has commercialized BASIL (Biphasic Acid Scavenging utilizing Ionic Liquids), which use 1-alkylimidazole to scavenge the acid from existing processes.

2.3 Desulphurization Using Ionic Liquid

Conventionally, desulphurization of crude oil or other oil products such as gasoline and diesel are conducted using hydrodesulphurization (HDS). During the process, sulphur compound will react with hydrogen (H_2) to produce Hydrogen Sulfide (H_2S), a dangerous chemical that can be harmful to our health. Although paraffinic sulphur-containing compounds such as thiols, thioethers, and disulphides, are readily desulphurized using HDS, aromatic sulphur contents such as benzothiophenes (BTs) and dibenzothiophenes (DBTs) are hardly removed.

Thus, many studies have been carried out in order to improve the desulphurization process. Among the process developed, ionic liquid has shown good enhancement for desulphurization. Ionic liquid amazingly has high affinity towards sulphur-containing compound.

In the article by Eun Soo Huh (Huh, 2008), it is stated that Lewis Acid ionic liquids containing halide anions, such as $AlCl_4^-$ and $CuCl_2^-$ showed promising results on the selective removal of aromatic sulphur compounds even though the extraction is done at high temperatures around 70^{O}C. From the research on deep desulphurization (DDS) the author, he have found out that Lewis Acid Ionic Liquid from 3-butyl-1-methyllimidazolium chloride ([BMIM]Cl) and $FeCl_3$ are highly effective for the extraction process of sulphur compounds present in the hydrocarbon mixtures (model oil).

The extraction ability of [BMIM]$FeCl_4$ is evaluated from the removal of DBT from the model oil. As depicted in Table 1, the amount of DBT extracted increases with the molar ratio of $FeCl_3$/[BMIM]Cl.

Table 2-1 Desulphurization of DBT in various molar ratio of FeCl3/[BMIM]Cl

molar ratio ($FeCl_3$/[BMIm]Cl)	degree of desulfurization (%)
[BMIm]Cl[b]	17.2
0.5	34.1
0.7	38.9
1	42.2
1.5	77.4
2	100
2.5	100
3	100
5	100
$FeCl_3$[c]	33.9

[a] The extraction of DBT was conducted at room temperature with the model oil containing 5000 ppm of DBT and 20 000 ppm of *n*-octane as an internal standard in *n*-heptane. The weight ratio of model oil/IL was set at 5. [b] [BMIm]Cl only. [c] $FeCl_3$ only.

(source: Huh, E. S. (2008). Extractive Desulfurization Using Fe-Containing Ionic Liquid. *Energy & Fuel*, 22.)

This result may be related to by the increase Lewis Acidity of the IL at higher molar ratios. In advance, at the molar ratio of 2 and higher, DBT is completely extracted from the model oil. Although $FeCl_3$ alone may not be able to extract DBT as much as the IL, this shows that how important [BMIM]Cl in the ILs.

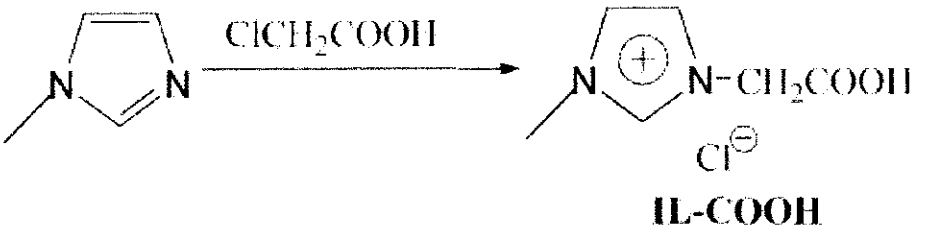
Focusing on separation, ionic liquid is an interesting option to desulphurize crude oil. When the ionic liquid is mixed with crude oil, it can extract sulphur. However, problem arises due to difficulty in separating the ionic liquid from the crude oil. Thus, this will result in restriction of its application in industry.

However, ionic liquid can be immobilized onto a solid to overcome the separation issue between the ionic liquid and the crude oil.

2.4 Immobilization of Ionic Liquid

The aim for immobilizing ionic liquids is to transfer the desired properties of Ionic Liquids to a solid supports. It is found that Ionic Liquids can be bound onto the surface either in covalent bond or non-covalent bond. There are several methods of immobilization of Ionic Liquid such as electro-phoresis or layer-by-layer (LbL) assembly. In this context (Ivaska, 2005), a polyelectrolyte-functionalized Ionic Liquid (PFIL) was prepared by covalent bonding of Ionic Liquid onto a polyelectrolyte.

To anchor an Ionic Liquids to a polyelectrolyte, a carboxyl terminated Ionic Liquid (IL-COOH) is synthesized. Then, IL-COOH is grafted covalently onto a polyelectrolyte with amine terminal groups, polyethylenimine (PEI) via an amidation reaction.



IL-COOH

Figure 2-1 Preparation of carboxyl-functionalized Ionic Liquid (IL-COOH)

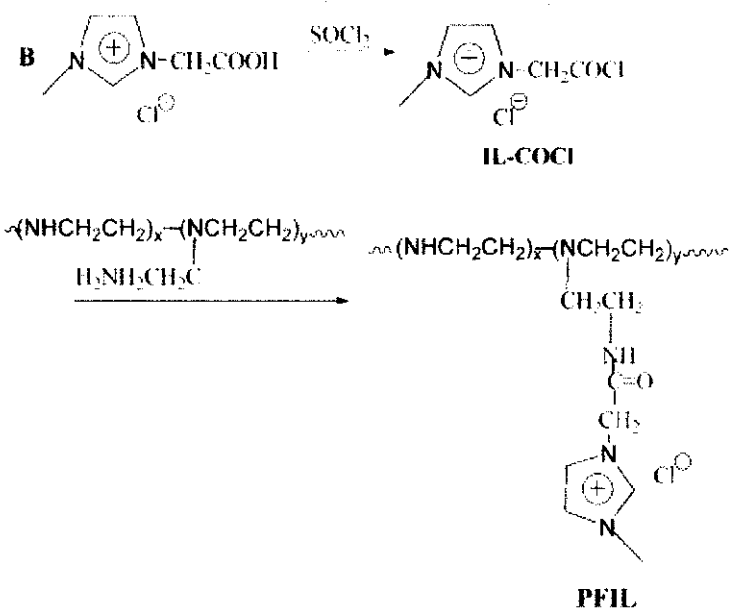


Figure 2-2 Preparation of polyelectrolyte-functionalized Ionic Liquid (PFIL) through amidation reaction

In the article entitled "Immobilization Chloroferrate Ionic Liquid: An Efficient and Reusable Catalyst" suggest that IL can be grafted onto mesoporous silica (MCM-41). It is done in two steps, which is synthesis of 1-trimethoxysilylpropyl-3-methylimidazolium chloride-$FeCl_3$ and then graft the IL by reacting the methyl terminal with Silicon on MCM-41.

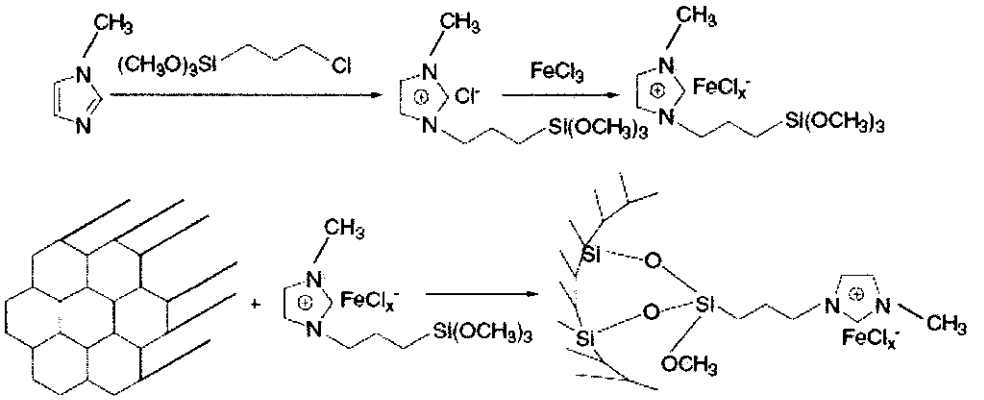


Figure 2-3 Procedure for synthesis of immobilized chloroferrate ionic liquid

Another method for immobilization is by using Spraying Suspension Dispersion (SSD) Method. SSD is a method where IL [BMIM][PF6] is immobilized onto polysulfone (PSF). In this article (Hongshuai, et al., 2008), a mixture of [BMIM][PF6], PSF and

dichloromethane is produced and stored in an oil phase storage tank. Another tank which is filled with 0.2wt% gelatine in deionized water is marked with aqueous tank. A spraying nozzle with bore size of 100μm is installed to spray the oil phase liquid to the aqueous tank. The distance between the bore and the aqueous surface is maintained at 20cm. After all the apparatus is set up, the [BMIM][PF6] mixture is sprayed to the aqueous tank at a pressure of 0.1MPA. It is stated in this article that any IL can be immobilized using this method.

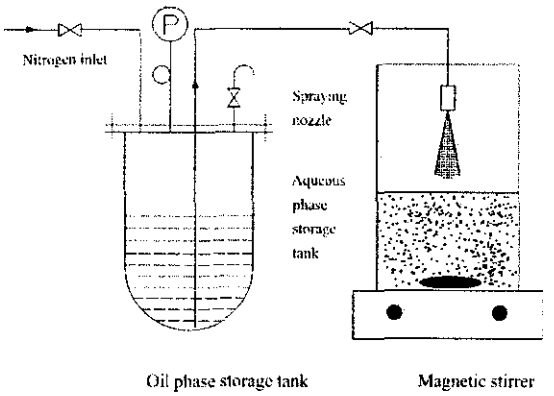


Figure 2-4 Spraying Suspension Dispersion (SSD) experiment set up

Another method of immobilization is by using Spraying Suspension Dispersion (SSD). Unlike the previous method, SSD can be carried out on any ILs and shells. After the IL is immobilized onto a shell, the product is observed under microscope.

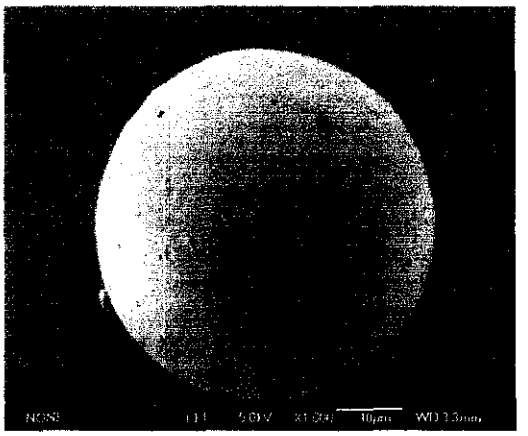


Figure 2-5 SEM micrographs of outer surface of microcapsule

(source: Hongshuai, et al. (2008). Immobilization of Ionic Liquid [BMIM][PF6] by Spraying Suspension Dispersion Method. *Ind. Eng. Chem. Res.* , 47.)

There are several points that need to be considered during the experiment. The distance between the nozzle and liquid surface must be fixed to a distance that the droplets are allowed to agglomerate and produce spherical shape. It has been proven that both polysulfone (PSF) and gelatine are suitable shell material and dispersant, respectively (Hongshuai, et al., 2008).

CHAPTER 3: METHODOLOGY

The purpose of this experiment is to immobilized the ionic liquid which is [BMIM]$FeCl_4$ onto PSF through the Spraying Suspension Dispersion.

3.1 Chemicals and Apparatus

The raw materials used for this experiments are 99% [BMIM]Cl (MERSK) with 99% $FeCl_3$ (MERSK). Polysulfone used is in powder form.

3.2 Synthesis of [BMIM]$FeCl_4$

First of all the experiment is started with the synthesizing of [BMIM]$FeCl_4$ by reacting [BMIM]Cl with $FeCl_3$. Since both exist in solid state, thus [BMIM]Cl is heated up first to liquefy it and then poured into the 3-neck flask to react it with $FeCl_3$ which is in powder form. The ratio of both chemicals is fixed to 1:1 by molar ratio. The mixture was thoroughly mixed in the flask for 24 hours. During this process, the exposure to the air must be reduced as much as possible since both chemicals are very sensitive to moisture. If both reactants and product are exposed to the moisture, the ionic liquid will react and produce other unwanted components. Thus, caution must be taken here. Later, the ionic liquid produced will be tested using SHIMADZU Fourier Transform Infra-Red (FTIR) Spectrometer and S-4800 HITACHI Field Emission Electron Microscope (FESEM) to characterize the component as [BMIM]$FeCl_4$.

3.3 Immobilization of [BMIM]$FeCl_4$ onto polysulfone (PSF)

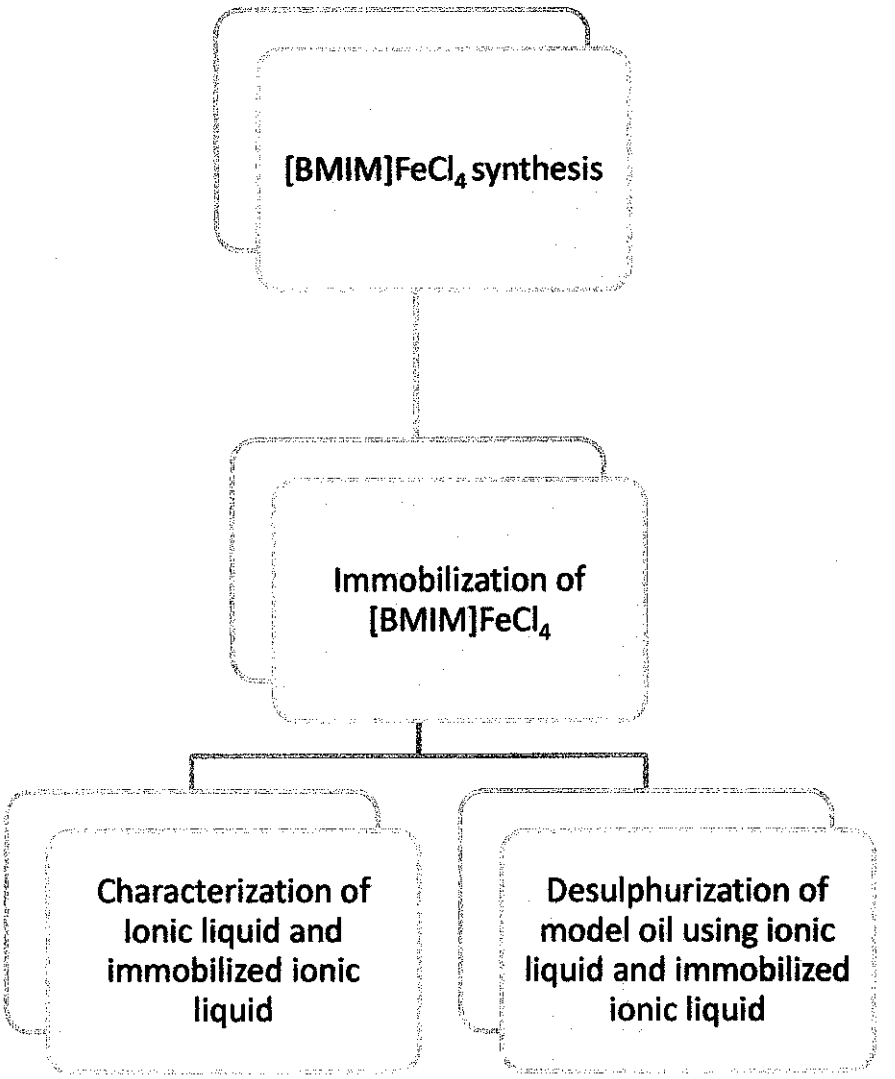
The [BMIM]$FeCl_4$ which is in liquid form is added to PSF for 12g each. Then, 80ml dichloromethane is added into the mixture the mixture was allowed to settle down. This is the oil phase preparation where it will be sprayed to the aqueous solution. The aqueous solution is prepared by adding 2wt% of gelatine into 100 mL water to increase the separation of the component. A spraying nozzle is prepared and the height of the sprayer is fixed to a certain level. When the oil phase is sprayed to the aqueous phase, the chemical will produce smaller particles. These particles will solidify before entering the aqueous phase. The water is used to wash the remaining dichloromethane to produce the immobilized ionic liquid. However, during the process, the sprayed ionic liquid does not fully solidify. There was still oily liquid remaining in the water and they tend to agglomerate. Still, the oil phase sooner will solidify and produced relatively bigger lump of immobilized ionic liquid. This may disrupt the

efficiency of the desulphurization of the ionic liquid. The immobilized [BMIM]FeCl4 is tested using SHIMADZU Fourier Transform Infra-Red (FTIR) Spectrometer and S-4800 HITACHI Field Emission Electron Microscope (FESEM) for Characterization.

3.4 Desulphurization of model oil using immobilized [BMIM]$FeCl_4$

After immobilized ionic liquid is produced, the ability to extract sulphur from the model oil is tested. As a comparison, the liquid [BMIM]FeCl4 is used to desulphurize 2wt% benzothiophene (BT), as the representative of sulphur content in dodecane (as the model oil). The separation is tested in 2 sets where the first experiment is done by adding liquid [BMIM]FeCl4 into model oil by 1:1 by weight ratio. After the addition, the test tube is closed properly and sealed to avoid any release of gas from the mixture. The test tube is rigorously mixed using Rotary Machine. Let them rigorously mixed for 1 hour. After the mixing, take some sample from the oil phase and test for the sulphur content after the desulphurization. To open the test tube, make sure to use face mask to avoid the inhalation of the released gas. The gas may be produced from the desulphurization which consists of H2S and SOx. The experiment is repeated by desulphurizing the model oil using 1:5 by weight ratio of [BMIM]FeCl4 to model oil. The experiment is continued by the desulphurization of model oil using immobilized ionic liquid. The sulphur content in the model oil are monitored using ARL 9900 X-Ray Fluorescence (XRF).

In summary; the processes are as follow;



CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 Ionic Liquid Synthesis

After the [BMIM]$FeCl_4$ is produced in batch, the component need to be tested first to check whether it is the ionic liquid that is required. Referring to Figure 4-1, the water is added to [BMIM]$FeCl_4$ and the result shows that the water and ionic liquid is not totally mix. When vigorously mixed the mixture, the water become brownish in colour and the reaction is exothermic, producing some amount of heat.

4.2 Desulphurization of model oil

[BMIM]$FeCl_4$ and model oil are added together in a ratio of 1:1 and 1:5. The reaction is done in a test tube and sealed to make sure no gas release during the reaction. After 30 minutes of mixing, the test tube is opened and a lot of gas is released which could be a mixture of H_2S and SO_x.

Figure 4-1 Figure showing different result from mixing ionic liquid with model oil

The sulphur contents of the extracted oil tested monitored using XRF. Comparison of the sulphur content prior to the extraction will provide the extraction efficiency of the immobilized [BMIM]$FeCl_4$.

4.3 Immobilizing ionic liquid using Spraying Suspension Dispersion (SSD)

[BMIM]$FeCl_4$ (12g) and polysulfone (PSF) (12g) were mixed together and stirred. Then, dichloromethane (80ml) was added to the mixture to dissolve the PSF. After conduction the SSD, the mixture was slimy and not totally solid as seen in Figure 4-2. Suspected that dichloromethane is not the perfect solvent for PSF and [BMIM]$FeCl_4$.

Figure 4-2 Insoluble component that is not dissolved in the mixture

An experiment is conducted to test the solubility of [BMIM]$FeCl_4$, PSF and DCM among each other:

- [BMIM]$FeCl_4$ + PSF: PSF does not dissolved
- [BMIM]$FeCl_4$ + DCM: both liquid mix together
- PSF + DCM: PSF dissolved in DCM

This prove that all the liquid can dissolved among each other except for [BMIM]$FeCl_4$ and PSF. Figure 4-3 explains the result visually.

Figure 4-3 Experiment to check the solubility of each component

The experiment is repeated but using different amount of [BMIM]$FeCl_4$ (6g), PSF (6g) and DCM (80ml). The results show that there is still some remaining but this time only small amount. This may prove that dichloromethane has certain degree of solubility for PSF. The experiment is continued by spraying the oil phase solution to the water phase solution. The water phase mixture is prepared with 0.2 wt% of gelatin mixed into deionized water.

Figure 4-4 Immobilized ionic liquid sprayed into water phase

Small spherical shape droplets (Figure 4-4) are observed in the water phase. The droplets tend to aggregate and form bigger lump. However, when the ionic liquid is exposed to the air, the round shape break and become a layer of polymer instead. The water also becomes a little yellowish in color. It is suspected that there are some ionic liquids leached out into the water.

Another possible substance that may have ionic liquid in the oil phase storage is the slimy substance that does not dissolve in dichloromethane. The substance is produced due to the solubility limit of the dichloromethane towards PSF. Pieces of the substance is taken out bit by bit and put into the water. A layer of dichloromethane is observed on the water surface as in Figure 4-5.

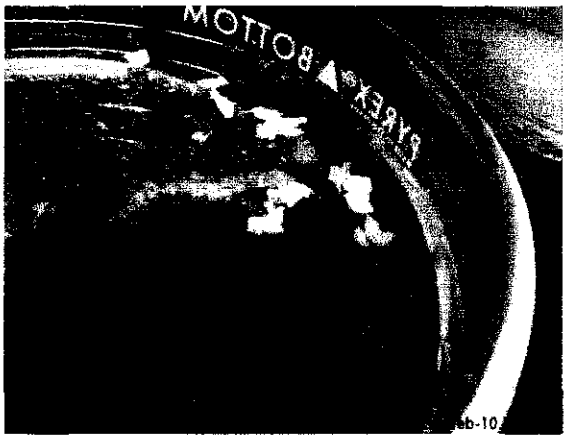


Figure 4-5 Small pieces of the substance in the water

The pieces are left for around 1 hour. The pieces become harden and became easy to handle. The substance is then used to desulphurize model oil, 2wt% BT in dodecane. Sulphur contents before and after the extraction were monitored using XRF.

Figure 4-6 The solid substance in model oil

As seen in Figure 4-6, the immobilized [BMIM]$FeCl_4$ does not mix with model oil. Thus, it can be easily separated through solid liquid separation.

4.4 XRF desulphurization results

Table 4-1 XRF results on sulphur contents for BT in dodecane

Sample	Description	Sulphur contents (wt ratio)	Oil contents (wt ratio)	% of desulphurization
IL_4	2 wt% BT in dodecane (sample 3)	2.0360	98.0	-
IL_5	IL : model oil (sample 3) 1 : 1	0.04654	100.0	97.71
IL_6	IL : model oil (sample 3) 1 : 5	0.05364	100.0	97.32

Table 4-2 XRF results on sulphur contents for BT in dodecane using immobilized ionic liquid

Sample	Description	Sulphur contents (wt ratio)	Oil contents (wt ratio)	% of desulphurization
IL_7	2 wt% BT in dodecane (sample 4)	2.0430	98.0	-
IL_8	Immobilized [BMIM]$FeCl_4$: model oil (sample 4) 1:1	0.8192	99.2	59.90
IL_9	Immobilized [BMIM]$FeCl_4$: model oil (sample 4) 1:1	0.7689	99.2	62.24

The experiments is started by desulphurization using liquid form of [BMIM]$FeCl_4$. In sample IL_4 and IL_5, the desulphurizations give positive results where the ionic liquid can desulphurize the model oil. The desulphurization degree/efficiency is calculated using this equation:

$$\text{Efficiency} = \frac{Initial\ Sulphur\ content - Final\ Sulphur\ Content}{Initial\ Sulphur\ content}\ X\ 100\%$$

Since 1:1 ratio gives better desulphurization, the ratio is fixed and test for 2wt% BT in dodecane. The results give out better desulphurization which is 97.71%. This shows that more sulphur contents can give better desulphurization results. After immobilizing IL onto PSF through SSD, the IL in solid form is the tested using 2wt% BT in dodecane. The mass ratio is fixed to 1:1. The results show lower desulphurization compared to liquid form of ionic liquid. This may be due to the addition of PSF in the mixture, making the ratio of model oil to ionic liquid differs much. In regards of the results difference between IL_8 and IL_9, it is due to the different shape of the immobilized ionic liquid. However, as stated above, the ratio of 1:1 by weight of model oil to immobilized IL, is actually considering the combination of IL and PSF. Thus, by back calculation, the actual ratio of ionic liquid to model oil is 1:2. Although ionic liquid is reduced to half, the desulphurization degree is greater than half from the initial efficiency, which is around 60%. Thus, this shows that immobilization of IL can also increase the efficiency of the separation of ionic liquid.

4.5 FTIR characterization results

Immobilized [BMIM]$FeCl_4$ are produced by hooking the ionic liquid on to PSF. The chemical bonding between the chemical does not change since no chemical bonding is produced during the synthesis.

Figure 4-7 displays the FTIR spectroscopy of [BMIM]$FeCl_4$. [BMIM]$FeCl_4$ has an ionic bonding between the carbon compound in [BMIM] and chlorine compound in $FeCl_4$. The interaction of aromatic C-H bonding with Cl can be seen in wavelength of 3100 – 3000 cm^{-1}. There is also the alkyl group represented within 2900 – 2800 cm^{-1} wavelength and amine alkyl group within within 1200 – 1025 cm^{-1} (Huh, 2008).

The ionic liquid will be hooked onto PSF. The FTIR spectra for PSF (Figure 4-8) shows the functional group of sulfone (1050 – 1300 cm^{-1}) and O-H bend (1440 – 1400 cm^{-1}).

From the result shown in Figure 4-9, it shows that there are bondings that exist in the synthesised immobilized [BMIM]$FeCl_4$ onto PSF. The spectrum displays Represented by certain wavelength that is same as the reference. Thus, this shows that [BMIM]$FeCl_4$ does produced from the synthesis. In Figure 4-9, the results shows that there are wavelength from [BMIM]$FeCl_4$ and also PSF. However, there is a high peak at the range of 4500 – 2500 cm^{-1}. The peak covers the C-H with Cl bonds. This peak may be in the results of excessive water,

H_2O, that cause the peak to rise within that range. The water comes during the solidification process of the liquid mixture of [BMIM]$FeCl_4$, PSF and dichloromethane. The liquid state mixture is sprayed into the water, and the water will wash away the dichloromethane and make the mixture to solidify. However, during the process, there may be a possibility of the water being trapped in the solid compound resulting in the strong O-H stretching band out 3500 cm^{-1}.

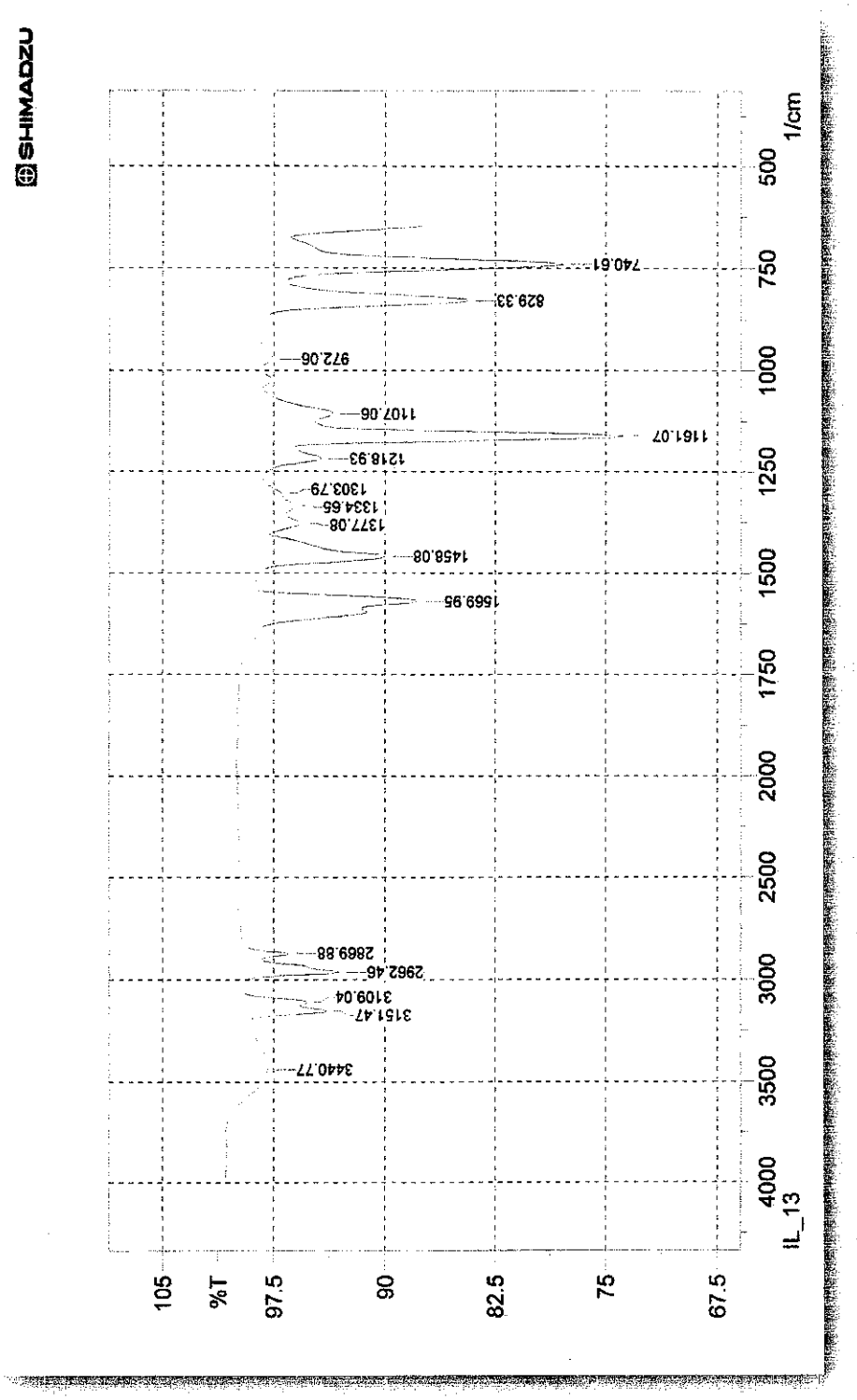


Figure 4-7 FTIR result for [BMIM]$FeCl_4$

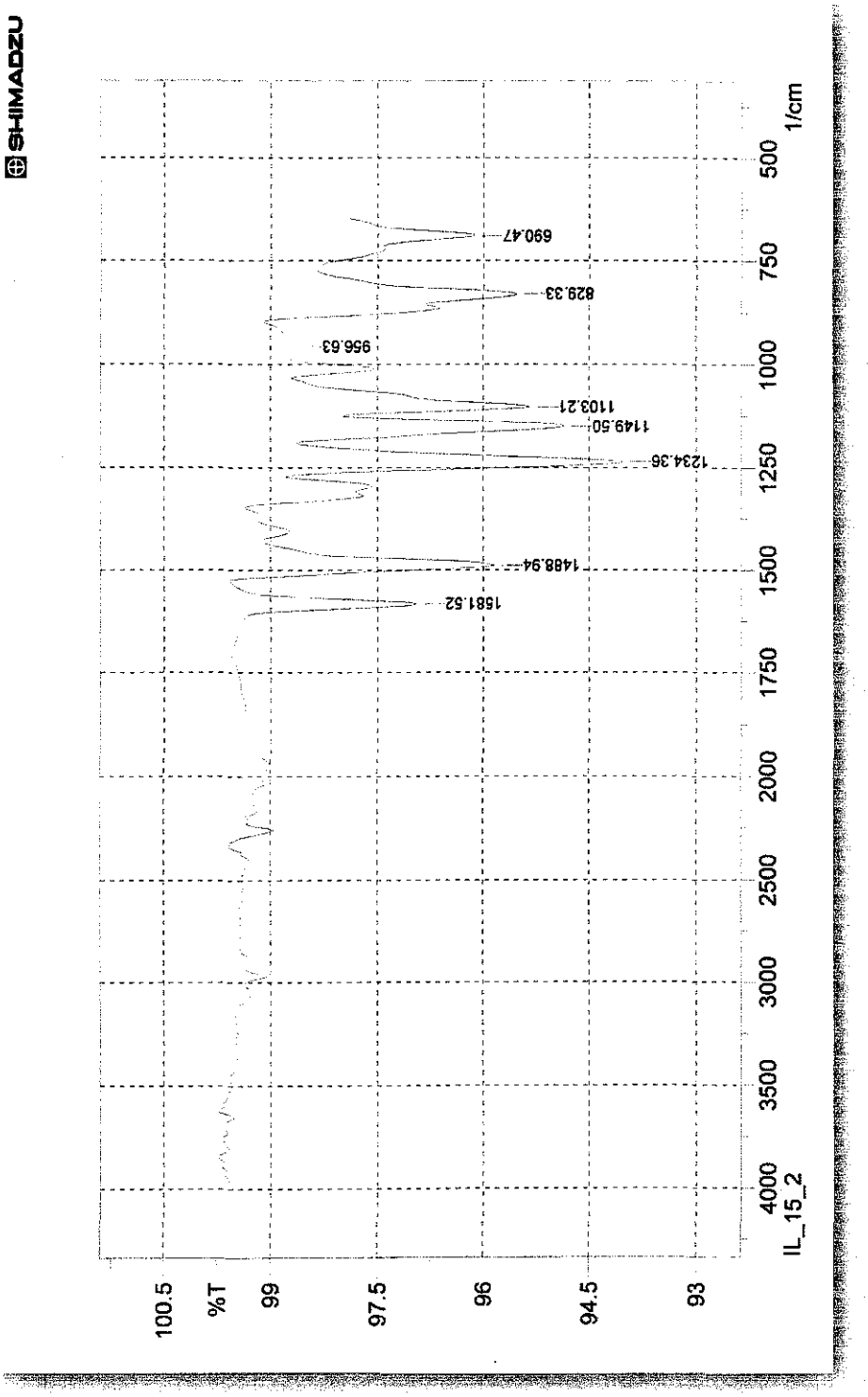


Figure 4-8 FTIR results for PSF

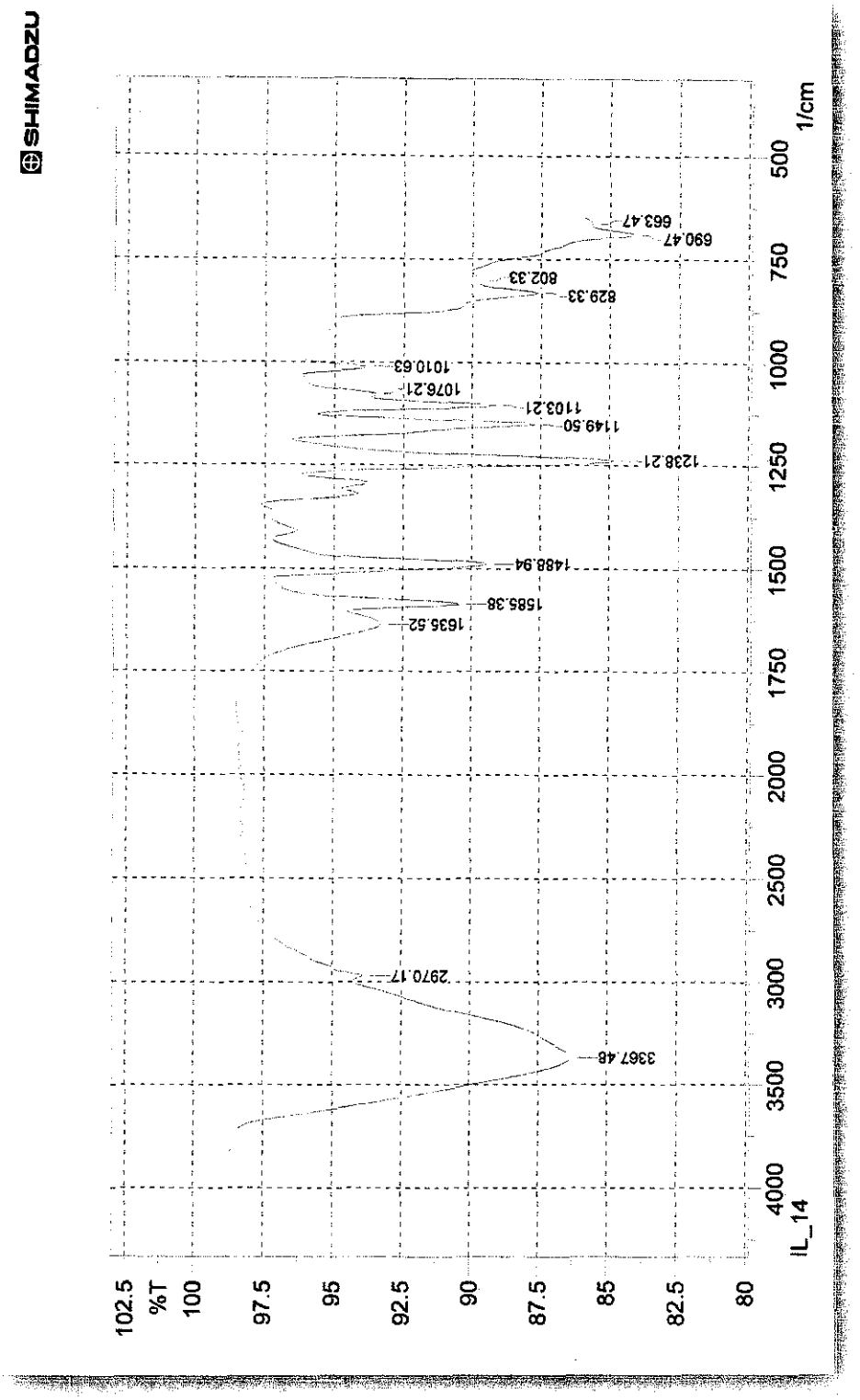


Figure 4-9 FTIR of immobilized [BMIM]$FeCl_4$ onto PSF

4.6 FESEM characterization results

Field Emission Scanning Electron Microscope (FESEM) is used to analyse microscopic composition of the immobilized ionic liquid. The FESEM images can determine the bounding of the ionic liquid onto PSF.

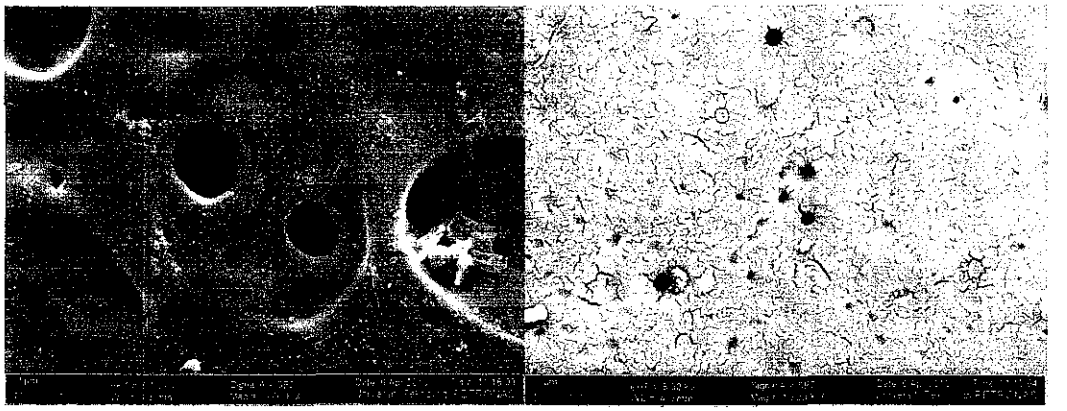


Figure 4-10 FESEM image of immobilized [BMIM]$FeCl_4$ onto PSF

The image above shows how the ionic liquid is scattered throughout the PSF. Since the mixture is not exactly solidified after the purging from the sprayer, it tends to form irregular shape as above. However, the ionic liquid is still evenly distributed around the PSF surface.

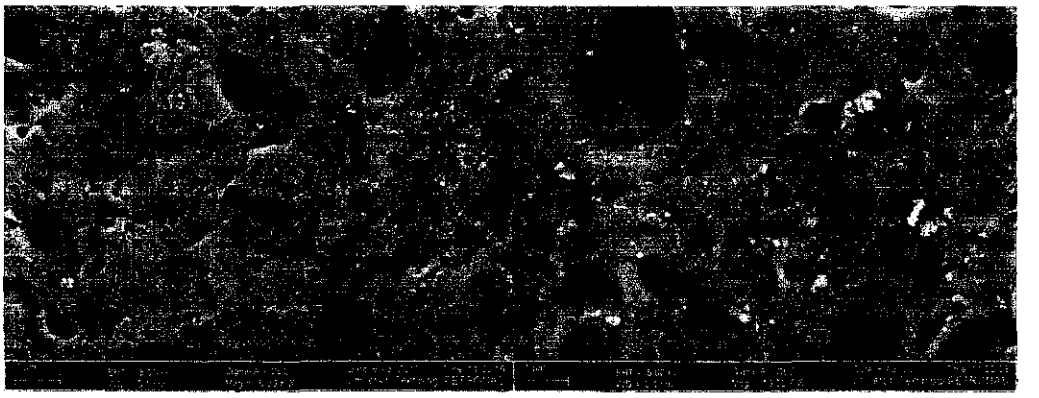


Figure 4-11 FESEM image of immobilized [BMIM]$FeCl_4$ onto PSF after desulphurization

Figure 4-11 shows the results of the immobilized ionic liquid after desulphurization of model oil. As depicte, there is still remaining ionic liquid after desulphurization. This shows that PSF is able to fix the ionic liquid onto it and does not let it mixed with the model oil after a rigorous mixing. This may indicate that the immobilized product can be recycled to a certain extent.

CHAPTER 5: CONCLUSION

[BMIM]$FeCl_4$ is a good IL option for desulphurization agent giving 97 % sulphur removal (1g IL : 1g model oil). The ratio $FeCl_3$/[BMIM]Cl of 1 gives the best extraction based on the model oil specs given before. Results from the immobilized IL showed ~60% sulphur removal (0.5g IL : 0.5g PSF : 1g model oil) considering the amount of IL used in the immobilized half the amount of IL used in the experiment employing [BMIM]$FeCl_4$ only (1g). It could indicate that the immobilization of IL displayed better performance compared to that utilizing ionic liquid alone.

Recommendation

Due to limited resources for the project, some experiments cannot be done at the perfect condition. For example, the sprayer currently used for the experiment has big pore size which is around 10mm. The experiment supposes to be done using smaller pore size nozzle, which is around 0.1mm pore size. In addition, more characterization is required to justify the immobilized ionic liquid. The experiment should be conducted with 2g immobilized IL (1g IL : 1g PSF : 1g model oil) for better performance comparison.

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APENDICES

A. Ionic Liquid Synthesis

Chemical Data:

Model oil (containing 5000 ppm of DBT and 20 000 ppm of *n*-octane), [BMIM]Cl, $FeCl_3$

Methodology:

1. Produce $FeCl_3$-[imidazolium]Cl ([BMIM]$FeCl_4$) by reacting $FeCl_3$ with 1-Butyl-3-Methylimidazolium chloride ([BMIM]Cl) in a molar ratio $FeCl_3$/[BMIM]Cl of 1.

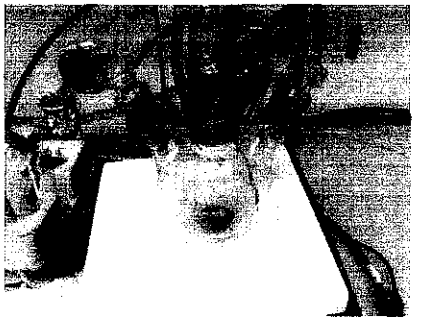

Figure 1 Reaction process of [BMIM]Cl and $FeCl_3$

2. Leave the reaction to occur for 24 hours.
3. Make sure no exposure to the air during the reaction because it may cause both ionic liquids to react with water vapour.
4. Take some sample of [BMIM]$FeCl_4$ and put into test tube. Add small amount of water and observe the difference.

Figure 2 [BMIM]$FeCl_4$ mix with water in test tube

5. Add the [BMIM]$FeCl_4$ to the model oil at room temperature (at a weight ratio oil/IL of 1) in a test tube.

6. Seal the test tube with sealer and parafilm so that no release of gas. (CAUTION: H_2S and SO_x may release during this process)
7. Stir the mixture for 30 minutes.
8. Leave the mixture to allow the liquid to separate
9. Test the upper layer with XRF and CHNS for sulphur contents.

B. Immobilization of Ionic Liquid

Chemical Data:

[BMIM]$FeCl_4$, Polysulfone (PSF)

Methodology:

Spraying Suspension Dispersion (SSD)

1. Weigh [BMIM]$FeCl_4$ for 6 g.
2. Weigh PSF for 6 g.
3. Add 80 ml of Dichloromethane to PSF and let the PSF dissolved.
4. Add [BMIM]$FeCl_4$ to the solution.
5. Store in a sealed beaker using parafilm and labelled as oil phase storage.

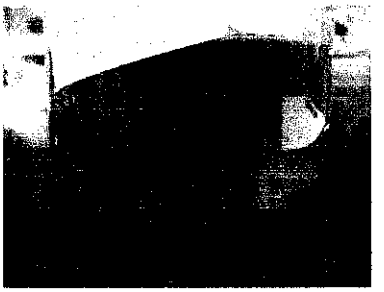

Figure 3 The Oil phase storage ([BMIM]$FeCl_4$, PSF and dichloromethane)

6. Prepare water phase storage by mixing 2g of gelatine in 100 ml of deionized water with constant stirring.
7. A spraying nozzle is installed to bring the liquid from oil phase storage to water phase storage.
8. The oil phase is purge into the water aqueous phase.

C: FTIR Correlation Table

(Source: 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^{o})	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