

**Removal of Sulfur-containing Compounds from Crude Oil Model Using
Phosphate Based Ionic Liquids**

by

Syed Mubashir bin Syed Mohammad

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

JANUARY 2009

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CERTIFICATION OF APPROVAL

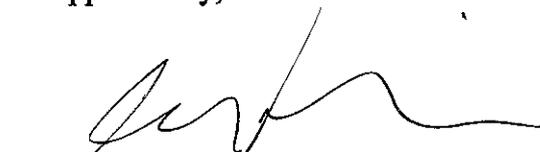
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A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

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CERTIFICATION OF ORIGINALITY

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



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ABSTRACT

The objective of the project is to determine the sulphur-compounds (thiophene and benzothiophene) removal efficiency of selected ionic liquids ([EMIM] [DEP]) from crude oil model (dodecane). [EMIM] [DEP] can be synthesis via one-pot method with high yield, easy for purification and low cost. [EMIM] [DEP] also proved to be effectively removing the sulfur compounds compared to conventional method, hydrodesulfurization (HDS).

The preparation of [EMIM] [DEP] was carried out in the laboratory starting from the purification of 1-methylimidazole till drying the ionic liquid. The experiment went well and the ionic liquid seems to be successfully made based on the color that produced (light red). Then, [EMIM] [DEP] has been washed with diethyl ether as solvent for 2-3 times before proceeding with the drying process using rotary evaporator. After that, [EMIM] [DEP] was ready to be tested its efficiency to extract sulfur compound (thiophene and benzothiophene) from model oil.

Two categories of model oil was prepared: 1) Model oil containing some amount of thiophene (2%, 4% and 6%) and 2) Model oil containing some amount of benzothiophene (2%, 4% and 6%). The extraction results seem promising to be commercialized since K_N values for each sample ranging from 0.4000 to 0.4400 which are quite high.

ACKNOWLEDGEMENT

First of all, I would like to take the opportunity to express my utmost gratitude to the individual that have taken the time and effort to assist me in completing the project. Without the cooperation of these individuals, no doubt I would have finished the project without faced even minor difficulties throughout the course.

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Secondly, I would like to take this opportunity to thank Kak Hawa for her willingness to sacrifice her precious time and sharing her great knowledge with me in order to make this project complete.

To the Final Year Research Project Coordinator, Mr Tazli Azizan for provide me with all the initial information required to begin the project.

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CHAPTER 1

INTRODUCTION

1.1 Background Study

Sulfur removal from transportation fuels has become an increasing technical challenge as oil refineries face growing environmental pressures and strict regulatory requirements. Refinery industry utilizes catalytic processes for desulfurization of transportation fuels through hydroprocessing. While the performance of conventional hydroprocessing catalysts have been highly effective for the reduction of sulfur levels, further removal of residual sulfur from the processed fuels seemed to largely increase the cost of hydroprocessing. The processes are highly energy intensive and consume large amount of hydrogen. Alternative technologies are of particular interest for ultra low sulfur clean fuels. One attractive approach is the removal of sulfur containing compounds from fuel by absorption.

1.2 Problem Statement

Ionic liquids have gained increasing interest over the past years due to its unique properties both as extractant and also as catalyst. The classical desulfurization process involves catalytic hydrogenation of sulphur compounds (hydrodesulfurization, HDS) into hydrogen sulfide. Typical reaction conditions are 350°C and 30-100 bar hydrogen pressure. The hydrogen sulfide which is separated from the desulfurized oil is oxidised catalytically with air into elemental sulphur. However, some S-compounds such as dibenzothiophene, methyl dibenzothiophene, and 4, 6-di methyl dibenzothiophene are less reactive to HDS. Therefore, extraction or reactive extraction of S-compounds from crude oil could be an alternative to HDS.

1.3 Objective and Scope of Study

The main objective of this research is to determine the sulphur-compounds removal efficiency of Ethylmethylimidazolium Diethylphosphate, (EMIM[DEP]) from crude oil models.

The scope of the project deals mainly with desulfurization process using selected ionic liquids. The variables that will be studied:

- Crude models (using dodecane)
- Different sulfur-containing compounds (thiophene, benzothiophene)
- Ionic liquids (EMIM[DEP])

Extraction or reactive extraction using selected ionic liquids will be conducted on the crude oil models and the efficiency of the process will be determined using total sulphur analyzer and XRF. Other relevant analytical equipments may be proposed for the purpose. Comparison studies will also be conducted on dead crude.

CHAPTER 2

LITERATURE REVIEW

Many oil refinery processes plants needs to comply with the current regulatory requirements which to achieve very low sulfur content, for less than 50 ppm. That is quite challenging and difficult to obtain if the conventional method of desulfurization still take into practice. The conventional method is called hydro desulfurization (HDS). The method is converting sulfur within the crude oil to hydrogen sulfide in the presence of hydrogen gas as catalyst. This method required extreme temperature and pressure condition for the process to take place. The removal of sulfur compound is less effective for thiophene, benzothiophene, and dibenzothiophene which are found mainly in the crude oil. Thus, in conclusion the conventional method is expensive and not really effective in removing sulfur compound.

So nowadays, people seek for new alternative methods to remove the sulfur compound in crude oil effectively with lower cost and safe compared to HDS. The alternatives are adsorption, oxidation and extraction. Since the alternatives are new, only extractive desulfurization (EDS) is well established process. The process is carried out at ambient temperature and pressure and required no catalyst to enhance the reaction. The process also does not change the chemical structure of the crude oil. The ionic liquid use for EDS is shows greater sulfur removal from crude oil for thiophene, benzothiophene and dibenzothiophene compared to the conventional method. The ionic liquid itself is easy to handle and having some advantages which it is insoluble with crude oil.

When the ionic liquid mixes together with crude oil, it will form two phase system. Then the ionic liquid can easily be separated from the crude oil by gravity or centrifugal separation. This can eliminate the possibilities of cross contamination in the crude oil. The characteristic of ionic liquid which is non flammable, nonvolatile and thermally stable over various ranges of temperature and pressure makes it easy to handle. The size of ions is really important for ionic liquid to study on the performance of extracting sulfur compound from crude oil. Thus, the size increase due to the alkyl group in the ionic

liquid (imidazolium) , is the more likely for the increase of sulfur removal. Below are the comparison of some ionic liquid on its preparation and performance.

Table 2.1: Ionic Liquids Comparison

No	Articles	Preparation	Characterization	Performance	Remark
BMI.BF ₄	"On the Extraction of Aromatic Compounds from Hydrocarbons by Imidazolium Ionic Liquids", Claudia C. Cassol, Alexandre P. Umpierre, Gunter Ebeling, Bauer Ferrera, Sandra S. X. Chiaro and Jairton Dupont, Int. J. Mol. Sci. 2007, 8, 593-605.	Mixing 1-butyl-3-methylimidazolium chloride and LiBF ₄ in acetonitrile followed by filtration to remove a LiCl precipitate and distillation to remove acetonitrile.	Van Der Waals Volume: ca. 39 Å ³	n-octane : IL : benzene 1 : 1 : 0.11	
BMI.PF ₆	"On the Extraction of Aromatic Compounds from Hydrocarbons by Imidazolium Ionic Liquids", Claudia C. Cassol, Alexandre P. Umpierre, Gunter Ebeling, Bauer Ferrera, Sandra S. X. Chiaro and	Mixing 1-butyl-3-methylimidazolium chloride and LiPF ₆ in acetonitrile followed by filtration to remove a LiCl precipitate and distillation to remove acetonitrile.	Van Der Waals Volume: ca. 52 Å ³	n-octane : IL : benzene 1 : 1 : 0.17	

1-butyl-4-cyanopyridinium bis(triflyl)amide	Jairton Dupont, Int. J. Mol. Sci. 2007, 8, 593-605.	<p>“Ionic liquids and their use in extraction processes”, Holbrey, John David, Mullan, Claire Lisa, European Patent Application, Bulletin 2007/46.</p>	<p>4-Cyanopyridine (20.8 g, 0.2 mol) and 1-bromobutane (42 g, 1.5 eq) were combined and heated with stirring at 135°C in a round-bottomed flask sealed with a Safe-Lab® pressure seal. After heating for 18 h, the resultant yellow solid mass was taken, filtered rapidly to remove excess 1-bromobutane, washed with ethanoate which removed the yellow colouration, and then dried under reduced pressure to yield a pale cream coloured microcrystalline powder. This powder was mixed with water and with Li[NTf₂] as described above. The lower ionic liquid phase was separated, extracted into CH₂Cl₂ and dried with heating under reduced pressure to give a clear, pale yellow liquid which was immiscible with CHCl₃ and soluble in dmso.</p>	<p>H NMR (dmso-d₆) 9.35 (2H, d), 8.69 (2H, d), 4.65 (2H, t), 1.90 (3H, tt), 1.292 (2H, t), 0.90 (3H, t).</p>	<table border="1"> <tr> <td data-bbox="238 521 345 689">Initial DBT content /ppm</td> <td data-bbox="238 232 345 521">521</td> </tr> <tr> <td data-bbox="353 521 457 689">After treatment/ppm (percent extraction)</td> <td data-bbox="353 232 457 521">428(18)</td> </tr> <tr> <td data-bbox="464 521 494 689">Temperature</td> <td data-bbox="464 232 494 521">40°C</td> </tr> <tr> <td data-bbox="501 521 531 689"></td> <td data-bbox="501 232 531 521">70°C</td> </tr> <tr> <td data-bbox="538 521 568 689"></td> <td data-bbox="538 232 568 521">359(31)</td> </tr> <tr> <td data-bbox="575 521 605 689"></td> <td data-bbox="575 232 605 521">68(35)</td> </tr> <tr> <td data-bbox="612 521 642 689"></td> <td data-bbox="612 232 642 521">80(23)</td> </tr> </table>	Initial DBT content /ppm	521	After treatment/ppm (percent extraction)	428(18)	Temperature	40°C		70°C		359(31)		68(35)		80(23)
Initial DBT content /ppm	521																		
After treatment/ppm (percent extraction)	428(18)																		
Temperature	40°C																		
	70°C																		
	359(31)																		
	68(35)																		
	80(23)																		

<p>1-hexyl-4-cyanopyridinium bis(triflyl)amide</p>	<p>“Ionic liquids and their use in extraction processes”, Holbrey, John David, Mullan, Claire Lisa, European Patent Application, Bulletin 2007/46.</p>	<p>4-Cyanopyridine and 1-bromohexane were heated in toluene at 16-0 °C in a sealed vessel for 24 h. with stirring. On cooling, colourless crystals of 1-hexyl-4-cyanopyridinium bromide were formed and were collected by filtration, washing with diethylether. Water and Li[N(Tf)₂] were added and the product formed as a dense yellow phase liquid which was collected, extracted into dichloromethane dried over anhydrous Na₂SO₄, filtered and dried in vacuo.</p>	<p>Melting point <25°C</p>	<p>Initial DBT content /ppm</p> <p>521</p>	<p>After treatment/ppm (percent extraction)</p> <p>Temperature</p> <p>40°C</p> <p>328(37)</p> <p>70°C</p> <p>366(30)</p>	
<p>106</p>	<p>63(39)</p>	<p>69(33)</p>				

CHAPTER 3

METHODOLOGY

3.1 Preparation of ionic liquid, [EMIM] [DEP]

3.1.1 Distillation of 1-Methylimidazole

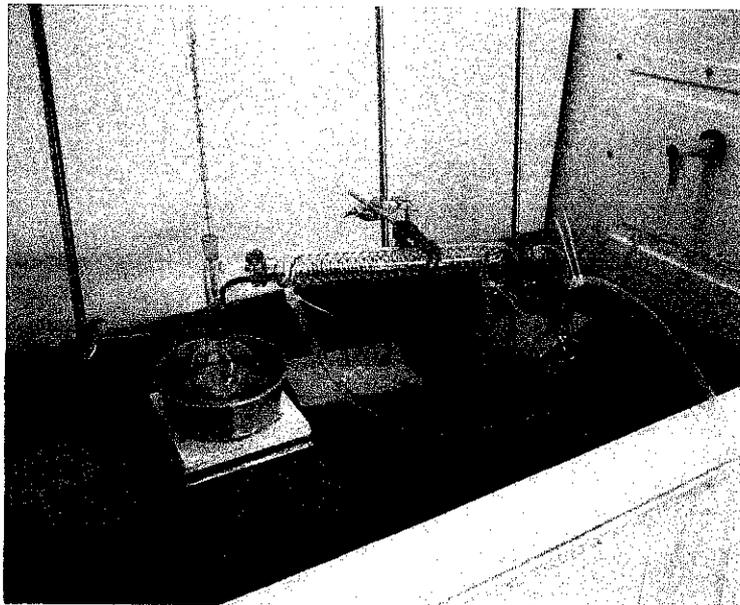


Figure 3.1: Distillation equipments

- 1) 100ml of 1-methylimidazole and some potassium hydroxide (KOH) was put in a round bottom flask.
- 2) The solution was heated until it reaches the boiling point (approximately 170°C)
- 3) The product (purified 1-methylimidazole) was retrieved in the receiver flask.
- 4) The residue (impure 1-methylimidazole and KOH) is removed.

3.1.2 Preparation of Ethylmethylimidazolium Diethylphosphate, [EMIM] [DEP]

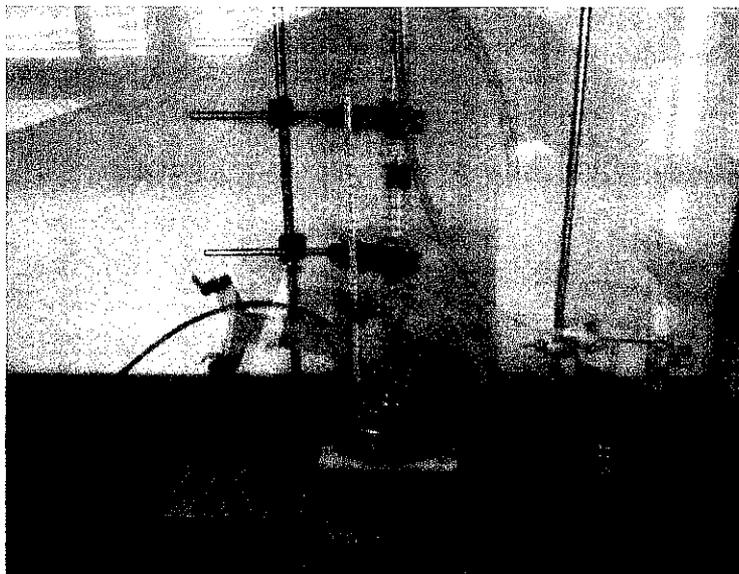


Figure 3.2: Reflux equipments

- 1) 0.02mol (1.6ml) of 1-methylimidazole was poured into three necked round bottom flask and stirred at room temperature in a nitrogen gas flows.
- 2) 0.021mol (3.6ml) of triethyl phosphate was added slowly into the flask to mix with 1-methylimidazole.
- 3) The solution was heated to 60°C and left refluxing to produce [EMIM] [DEP] for 2 days.

After washing the ionic liquid several times with diethyl ether, the ionic liquid was dried using a rotary evaporator. The temperature was set to 80°C and the drying was conducted about 3 hours.

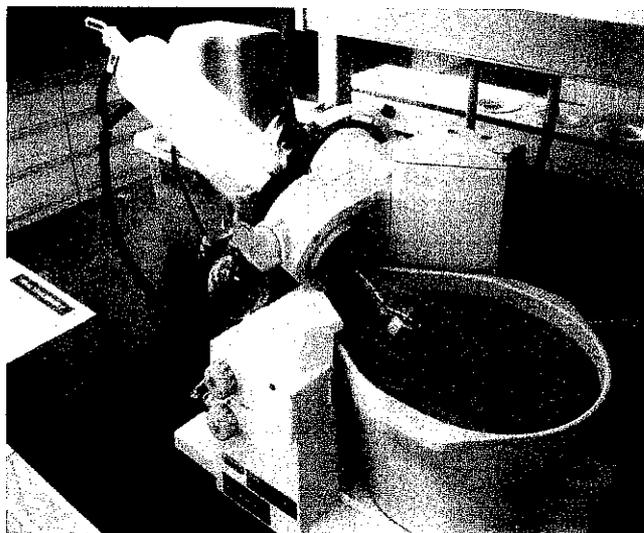


Figure 3.3: Rotary evaporator of ionic liquid

3.2 Ionic Liquid Characterization

3.2.1 Water Content using Karl Fischer Titration

The ionic liquid was characterized using Karl Fischer Titration to determine the water content in it. The amount of ionic liquid being tested was about 2.1213g and the water content could be identified is 4019.64 ppm. The water content in the ionic liquid is quite high approximately 4% of the solution.

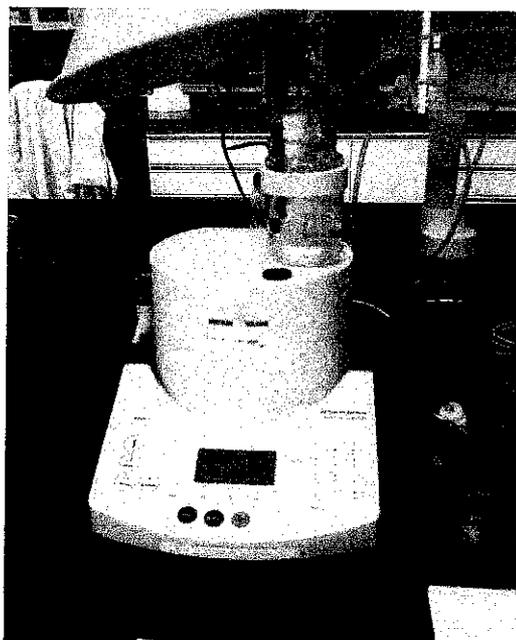


Figure 3.4: Water content measurement

3.2.2 Density Meter at 25°C, 35°C and 45°C.

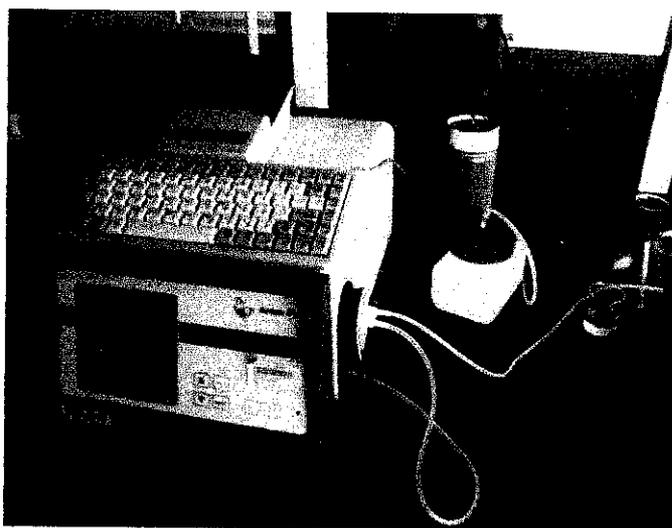


Figure 3.5: Density measurement

3.3 Liquid-liquid Extraction

3.3.1 Extraction of Thiophene from Dodecane Model Oil

- 1) Put 2 ml of [EMIM] [DEP] (ionic liquid) in a syringe which the bottom is being closed.

- 2) Then, add 2 ml of 2%, 4% or 6% of thiophene in dodecane in the same syringe.
- 3) Mix the solution using vortex mixer for about 1 minute for each sample.
- 4) Next, after mixing it properly, put the sample in centrifuge for 1 minute.
- 5) The mix solution formed two phases. The bottom phase is the ionic liquid while the upper phase is the model oil. Then, fill in the ionic liquid n the model oil in a veil separately. The transition phase will be filled in to the waste container.
- 6) Step 5) is being done the same for 4% and 6% of thiophene in dodecane.

3.3.2 Extraction of Benzothiophene from Dodecane Model Oil

- 1) Put 2 ml of [EMIM] [DEP] (ionic liquid) in a syringe which the bottom is being closed.
- 2) Then, add 2 ml of 2%, 4% or 6% of benzothiophene in dodecane in the same syringe.
- 3) Mix the solution using vortex mixer for about 1 minute for each sample.
- 4) Next, after mixing it properly, put the sample in centrifuge for 1 minute.
- 5) The mix solution is forming a two phase. The bottom phase is the ionic liquid while the upper phase is the model oil. Then, fill in the ionic liquid n the model oil in a veil separately. The transition phase will be filled in to the waste container.
- 6) Step 5) is being done the same for 4% and 6% of benzothiophene in dodecane.

Then, the entire sample is being labeled as below.

Table 3.1: Sample Labelling

EMIM DEP	U4001	After	
		Model oil	IL phase
	Before		
Dodecane + 2% T	U4002	U4003	U4004
Dodecane + 4% T	U4005	U4006	U4007
Dodecane + 6% T	U4008	U4009	U4010
Dodecane + 2% BT	U4011	U4012	U4013
Dodecane + 4% BT	U4014	U4015	U4016
Dodecane + 6% BT	U4017	U4018	U4019

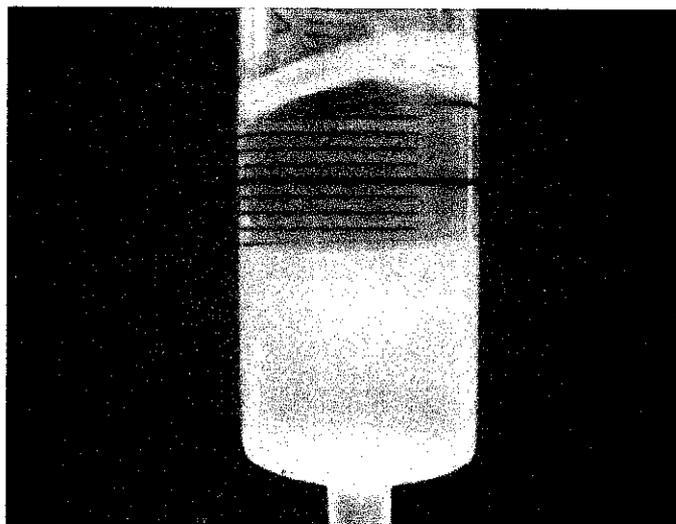


Figure 3.6: Mixing of ionic liquid and model oil

Picture above shows the mixture of model oil and ionic liquid which being separated by two layers. Above is the model oil while the bottom is the ionic liquid.

3.4 Equipments and chemicals required

Table 3.2: Equipments Used

Equipment	Quantity
1) Separating funnel (100ml)	3
2) Measuring cylinder (100ml)	3
3) Beaker	3
4) Pipette (10ml)	3
5) Distillation apparatus with tube	1 set
6) Reflux apparatus (round bottom flask and reflux condenser)	1 set
7) Stirrer	1
8) Rotavap with flask (50ml, 100ml, 200ml, 250ml)	1
9) Vacuum oven	1
10) Storage bottle	5
11) Liquid cup for XRF	1
12) XRF	1

Table 3.3: Chemical Used

Chemical	Amount
1) 1-methylimidazole	500g
2) Triethyl phosphate	1L
3) Diethyl ether	1L
5) Dodecane (crude model)	1L
6) Thiophene	25g
7) Dibenzothiophene	25g

CHAPTER 4

RESULT AND DISCUSSION

4.1 Preparation of ionic liquid, [EMIM] [DEP]

4.1.1 Distillation of 1-Methylimidazole

Hot plate magnetic stirrer is being replaced with heating mantle due to its function error. (the heating temperature is not constant). At about 140°C, the first distillate product droplet can be seen.

4.1.2 Preparation of Ethylmethylimidazolium Diethylphosphate, [EMIM] [DEP]

The nitrogen supply to the system is inconsistent. Sometimes, the bubbler indicates the presence of gas and vice versa. Then as a solution, regulator is being installed to control the flow of the nitrogen gas to the system.

4.1.3 Washing with Diethyl Ether

The mixture should have forming two layers. If there are no two layers, then the mixture must be continued to reflux until it become two layers during washing. During separation of the solvent (diethyl ether) from ionic liquid, make sure that the ionic liquid is not being disposed as well or otherwise the quantity of ionic liquid that already produced will decrease.

4.2 Ionic Liquid Characterization

4.2.1 Water Content using Karl Fischer Titration

The 4% of water content in the ionic liquid is considered as high compared to the theoretical value which should be less than 1%. The main reason that can be recognized is the Karl Fischer Titration solvent is having contaminant and need sufficient time to clean up before can be used.

4.2.2 Density Meter testing

Table 4.1: Density for Different Temperature

Temperature (°C)	Density (g/cm ³)
25	1.1401
35	1.1331
45	1.1261

4.3 Liquid-liquid Extraction

Table 4.2: Result from XRF

No	Solution	Sample Reference Number	S (wt %)	K_N
1	Ionic liquid, EMIM[DEP]	U 4001	0.0004	-
2	Model oil (2% thiophene)	U 4002	0.1460	-
3	Model oil after extraction	U 4003	0.0820	0.4024
4	Ionic liquid after extraction	U 4004	0.0330	
5	Model oil (4% thiophene)	U 4005	2.3080	-
6	Model oil after extraction	U 4006	1.6400	0.4116
7	Ionic liquid after extraction	U 4007	0.6750	
8	Model oil (6% thiophene)	U 4008	2.0700	-
9	Model oil after extraction	U 4009	1.5880	0.4068
10	Ionic liquid after extraction	U 4010	0.6460	
11	Model oil (2% benzothiophene)	U 4011	1.8030	-
12	Model oil after extraction	U 4012	0.7300	0.4329
13	Ionic liquid after extraction	U 4013	0.3160	
14	Model oil (4% benzothiophene)	U 4014	3.3500	-
15	Model oil after extraction	U 4015	1.3840	0.4314
16	Ionic liquid after extraction	U 4016	0.5970	
17	Model oil (6% benzothiophene)	U 4017	4.5030	-
18	Model oil after extraction	U 4018	2.1100	0.4190
19	Ionic liquid after extraction	U 4019	0.8840	

Based on the result above, the rate of extraction for [EMIM] [DEP] is decreasing as the model oil contain increasing amount of the sulfur compound. The rate decreasing in order of 2% > 4% > 6% of sulfur compound (thiophene or benzothiophene) in model oil.

CONCLUSION

For the preparation of ionic liquid, the distillation of 1-methylimidazole using heating mantle at 140°C gave the first droplet of product purification. Then, proceed with the reflux process of 1-methylimidazole and diethylphosphate under constant nitrogen gas supply. Next, the [EMIM] [DEP] was washed several times to remove the contaminant. Lastly, [EMIM] [DEP] was dried using rotary evaporator to completely remove the contaminant and solvent.

There are two types of characterization of ionic liquid. First was measuring the water content in [EMIM] [DEP] using Karl Fischer Titration and the result was 4% water of the solution. The other test was to determine the [EMIM] [DEP] density at 25°C, 35°C and 45°C.

As for liquid-liquid extraction, two different sulfur compounds in model were prepared. [EMIM] [DEP] shows impressive extracting result where the K_N values ranging from 0.4000 to 0.4400. However, based on the results, it can be concluded that as the percentage of sulfur compounds in model oil increase, the rate of extraction of [EMIM] [DEP] decrease.

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APPENDIX

Volume calculation for small amount of mixture,

Solvent	Mol	MW	Density	Volume
1-methylimidazole	0.020	82.11	1.03	1.6
Triethyl phosphate	0.021	182.16	1.06	3.6

1) $MW \times Mol = mass$

2) $Mass/density = volume$

E.g.

For 1-methylimidazole,

1) $0.020 \times 82.11 = 1.6422$

2) $1.6422/1.03 = 1.594 \approx 1.6 \text{ ml}$

For triethyl phosphate,

1) $0.021 \times 182.16 = 3.82536$

2) $3.82536/1.06 = 3.6 \text{ ml}$

Volume calculation for huge amount of mixture,

Solvent	Mol	MW	Density	Volume
1-methylimidazole	0.4	82.11	1.03	31.9
Triethyl phosphate	0.4	182.16	1.06	68.7

Calculation for K_N values,

$$K_N = \frac{S_{IL}}{S_{MO}}$$

Where K_N = ratio of sulfur concentration in IL to the sulfur concentration in model oil

S_{IL} = sulfur concentration in ionic liquid

S_{MO} = sulfur concentration in model oil

E.g.

For model oil with 2% of thiophene,

$$\begin{aligned} K_N &= \frac{0.0330}{0.0820} \\ &= 0.4024 \end{aligned}$$

For model oil with 2% of benzothiophene,

$$\begin{aligned} K_N &= \frac{0.3160}{0.7300} \\ &= 0.4329 \end{aligned}$$