Study on Equilibrium of Sulfur Species in Model Oil with Ionic Liquid

by

Abdul Hadi Azimi bin Abd. Wahab

Dissertation submitted in partial fulfilment of

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CERTIFICATION OF APPROVAL

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Approved by,

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(Assoc. Prof. Dr. Mohamed Ibrahim bin Abdul Mutalib)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

MAY 2011

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is m 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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ABDUL HADI AZIMI BIN ABD. WAHAB

ABSTRACT

Extraction of thianaphthene, one of the long sulfur chain existed in crude oil from model oil (which is dodecane in this study) is experimentally carried out by using an ionic liquid 1-butyl-3-methylimidazolium octyl sulfate. Result from the experiment is expressed as a ternary diagram. The objective of this study is to investigate the efficiency of the experimented ionic liquid as an extractor of long sulfur chain from model oil which can be used later to as a base comparison with another extractor.

This report will be divided into 4 parts which consist of introduction, which includes abstract, problem statement, and objective scope of study. Next part of this report will be covered on literature review which includes a brief introduction on equilibrium, and material used in the study. Methodology will be in the third chapter as all the methodology used to conduct the experiment is reported in this section. At the end of the report, details on result and discussion will be explained on last part of the report which is part 4.

ACKNOWLEDGEMENT

This report arose in part out of more than years of research that has been done for my Final Year Project course. By that time, I have worked with a great number of people whose contribution in assorted ways to the research. It is a pleasure to convey my gratitude to them all in my humble acknowledgment.

In the first place I would like to record my gratitude to my supervisor, Assoc. Prof. Dr. Mohamed Ibrahim bin Abdul Mutalib for his supervision, advice, and guidance from the very early stage of this research as well as giving me extraordinary experiences throughout the work. Above all and the most needed, he provided me unflinching encouragement and support in various ways. His truly scientist intuition has made him as a constant oasis of ideas and passions in science, which exceptionally inspire and enrich my growth as a student, a researcher and a scientist want to be. I am indebted to him more than he knows.

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Lastly I want to thank my parents for their constant encouragement and support. Everyone mentioned has contributed to both the successful and pleasurable experience I have had while completing my Final Year Project at Universiti Teknologi PETRONAS.

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INTRODUCTION

1.1   Project Background

Due to awareness of impact from sulfur to environment, new regulations have been imposed requiring low sulfur content in fuel such as diesel etc. The shift to reduce maximum concentration allowable for sulfur content in fuel is expected to drive new technologies and applications of more advance emissions control technologies that as the result should significantly decrease the emissions of sulfur compound.

Currently, Hydrodesulfurization (HDS) is used to remove sulfur compound from fuel oils. This method however requires extreme process conditions (temperatures ranging from 300 to 400 °C and elevated pressures ranging from 30 to 130 atmospheres of absolute pressure) and hence is expensive. By using this process, some of aromatic sulfur is difficult to be removed.

Due to mentioned reason, liquid – liquid extraction (LLE) using ionic liquid (IL) has been identified as the potential to perform deep desulfurization since the ability of LLE to be carried out under milder process condition. LLE separates compounds based on their relative solubility. Extraction of sulfur can be done from oil rich phase into IL phase without the need of extreme process condition as HDS. IL used also can be regenerated which will further reduce the cost of operation.

Ionic liquid is chosen due to its properties which is far superior to the conventional solvent such as benzene and toluene as IL has greener properties such as negligible vapor pressure and not carcinogenic. Ionic Liquid also is considered a tunable solvent as it could be designed to suit applications such as its physical properties, extraction selectivity etc.

1.2   Problem Statement

Recent study has confirmed that LLE using IL has shown promising results as an alternative to current conventional HDS for removal of sulfur from fuel (will be detailed later in literature review). In order to proceed for the process design for LLE using IL, an equilibrium data of the selected IL is needed. Since the LLE using IL study is new, reliable LLE data needed for the process design is currently rare and lack.

1.3   Objective

To perform experimental work for measuring LLE data for constructing the ternary diagram for Benzothiophine (BT) in Dodecane system with ionic liquid 1-Butyl-3-methylimidazolium octyl sulfate (Bmim $OcSO_4$).

1.4   Scope of study

This study will only focused on producing equilibrium data needed for the use of LLE. Other study such as the LLE using IL simulation, costing comparison between LLE & HDS or between different IL can be derived later by referring to this study but is not covered.

LITERATURE REVIEW

2.1   Ionic liquid

2.1.1   Definition

In general, ionic liquid is defined as a salt that has a melting point below the boiling point of water even though in reality most of the ionic liquid is in the form of liquid in room temperature. The ionic liquid differs from the ordinary molten salt in the sense that where the liquidus range in the scale of temperature.

2.1.2   Properties of Ionic Liquid

In order to fully understand the usage and benefit of ionic liquid compared to the other solvent, the properties of the ionic liquid need to be known:

Low Melting Point

Melting point can be described as a point in temperature where a compound change it phase from solid to liquid. Ionic compound is said to have low melting point if it has melting point below room temperature. Low melting point is a result of chemical composition of the ionic liquid, which contains larger asymmetric organic cations compared to their inorganic counterparts of molten salts. This large asymmetry lowers the lattice energy, and hence in the same time also affects the melting point of the ionic medium. In several cases, even the anions are comparatively large and play a role in decreasing the melting point.

Stability

As stated in diydoctor.org.uk chemical stability is defined as *the tendency of a substance to remain unchanged over a wide range of physical, environmental, and chemical conditions*. In most applications, the stability of ionic liquids, at least in a certain degree, is crucial for optimum individual and overall process performance. There are studies stated that, even though not achieving 100% inert criteria, certain ionic liquids containing 1,3-dialkyl imidazolium cations are proven that it is more resistant than conventional solvents in some bizarre process conditions, such as those taking place in oxidation, photolysis and radiation processes[1].

Hygroscopicity

Hygroscopy is defined as *the ability of a substance to attract water molecules from the surrounding environment through either absorption or adsorption* (wikipedia.org). The viscosity of the ionic liquids can be influence by water content in it. A previous study in viscosity measurement indicates proves that ionic liquids became less viscous with increasing water content.

Hydrophopicity

Hydrophobicity can be defined as *the property of being water-repellent; tending to repel and not absorb water* (princeton.edu).The degree of polarity can be varied by adjusting the length of the 1-alkyl chain (in 1,3-substituted imidazolium cations), and the counter ion. Due to their liquid-crystalline characteristic long-chain ionic liquid salts have attracted some interest to researcher[2].

The properties of ionic liquid are highly influenced by the anion chemistry. Although little dissimilarity in properties might be expected among same-cation salts of these species, the actual variation can be dramatic: for example, $[bmim]PF_6^-$ is immiscible with water, whereas $[bmim]BF_4^-$ is water-soluble[3].

Zero Vapour Pressure

As mentioned before, ionic liquid is in a liquid form in a room temperature. It is consist of ions. Unlike another hydrocarbon solvent like benzene, ionic liquid is practically having a zero vapour pressure due to its nature of ionic bond.

Beside properties mentioned before, several other notable characteristic of ionic liquid are:

- high thermal stability,
- high electrical conductivity,
- large electrochemical,
- low nucleophilicity and capability of providing weekly coordinating or non-coordinating environment,
- very good solvents properties for a wide variety of organic and inorganic compounds

With all these properties, it is believed that it can act as "green solvents" and the ionic liquid in future will replace conventional carcinogenic volatile organic solvents such as benzene and toluene in several chemical reactions.
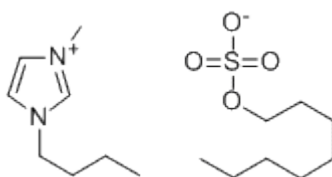

Figure 2.1: Molecular Structure of 1-Butyl-3-methylimidazolium octyl sulfate

2.1.3   Usage and Application

In term of usability, this ionic liquid can be design as per need. By just altering the anion, cation and other properties, one can obtained different properties of the ionic liquid such as hidrophobicity and viscosity. This is why ionic liquid steadily gain popularity in the area of research and development. Around 1995, an estimate of 2 articles regarding ionic liquid is made per year. It dramatically increase more than thousands articles per year in 2009, after people has aware of the usage and flexibility of the compound especially the main properties of it that can be tailored to meet our need, just like plastic.

Several example of the usage and application of the ionic liquid are state below:

Chemical industry

BASF processes first major industrial ionic liquid application, Biphasic Acid Scavenging utilizing Ionic Liquids (BASIL). This increased the space/time yield of the reaction by a factor of 80,000. (BASF, 2004)

Ionic based plan is operated by Eastman for the synthesis of 2,5-dihydrofuran from 1996 to 2004.

Petrochina claims that they are the biggest company that applied ionic liquid in industrial application to date by producing 65,000 tonne per year product of ionikylation process.

Gas handling

Ionic liquid is used by company Air Products instead of pressurized cylinders as a transport medium for reactive gases such as trifluoroborane, phosphine and arsine. The gases are dissolved in the liquids at or below atmospheric pressure and are easily withdrawn from the containers by applying a vacuum.

<u>Nuclear fuel reprocessing</u>

It has been explored that 1-butyl-3-methylimidazolium chloridea is a non-aqueous electrolyte media for the recovery of uranium and other metals from spent nuclear fuel and other sources[4].

<u>Batteries</u>

It has been found out that water in metal-air batteries that acts as an electrolyte can be replaced with ionic liquid. The low rates of evaporation makes the battery last longer because the electrolyte used does not evaporate and cause the batteries dry.

<u>High Purity Organometallics</u>

Ionic liquid is also used with micro reactors to produce and refine extremely reactive Organometallic Compounds for ALD and CVD applications, with enhanced operational safety and higher purity[5].

2.2   Sulfur in crude oil

2.2.1   Introduction

Study has found that crude oil contains sulfur[6]. The crude oil is classified as sweet or sour crude based on the sulfur content. The sweet crude oil contains less than 0.5% sulfur hence are less expensive to recover and refine. On the other hand, sour crude oil contains more sulfur and therefore is harder to recover and refine causing the price of the crude oil lesser than the sweet crude.

2.2.2 Impact on organism and environment

The existence of sulfur in crude oil has turn out to be a problem since sulfur is dangerous to both organism and environment. Laboratory tests with test animals have indicated that sulfur can results on serious vascular damage in veins of the brains, the heart and the kidneys. As for the environment, sulfur emitted can easily dilute in rain water to form acid rain.

2.2.3 New regulations

For this reason, European Union (EU) has started to commence "Euro IV" standard which stipulate a maximum of 50 ppm (0.005%) of sulfur in diesel fuel. This new stringent regulation has been applied since 2005 as general even in certain EU countries, a higher standards is introduced. For example beginning in January 2003, Germany introduce a tax incentive for each liter of "sulfur free" fuel (both gasoline and diesel) containing less than 10 ppm (0.001%). This results on further reduction of average sulfur content which was estimated in 2006 to be 3-5 ppm.

Environmental Protection Agency (EPA) in the United States has create policy require a reduction of the sulfur concentration in gasoline and diesel fuels. By December 1, 2010, all petroleum refining industry will produce an ultra low sulfur diesel (ULSD) fuel containing a maximum of 15 ppm sulfur[7].

As in Singapore, on June 16, 2005, the National Environment Agency (NEA) announced that the use of ULSD with maximum allowable sulfur species of 50 ppm would be mandatory beginning December 1, 2005. The regulation also offered tax incentives for Euro IV diesel taxis, buses and commercial vehicles between June 1, 2004 and September 3, 2006, pending a mandatory conversion to Euro IV-compliant vehicles in 2007.

2.3   Chronological Study of Ionic Liquid

2.3.1   Introduction of ionic liquid

Ethanolammonium nitrate (EAN) with melting point ranged between 52–55 °C was reported in late 1888 by S. Gabriel and J. Weiner.[8] However, due to high temperature range compared to room temperature (which is usually in the ranged of 25 – 35 °C), the claim is disputed by scientists.

Room temperature ionic liquids of ethylammonium nitrate $(C_2H_5)NH+3·NO−3$ which has a lower melting point at 12 °C, is synthesized in 1914 by Paul Walden.[9] In the late 20 centuries, ionic liquids based on alkyl-substituted imidazolium and pyridinium cations, with halide or trihalogenoaluminate anions, were synthesized for use as electrolytes in battery applications.

2.3.2   Ionic liquid in Liquid-Liquid Extraction

Recently, research on IL to be used in LLE has progressed progressively as academician and industry worldwide intensively doing numerous studies on the potential of this green solvent as alternative to conventional organic solvents. Most of the study is done in order to find the most feasible ionic liquid to be used in numerous process conditions and operations.

For example Luisa Alonso[10] has make a study on *(Liquid + liquid) equilibria of [C8mim][NTf 2] ionic liquid with a sulfur-component and hydrocarbons*. For the study they have used [C8mim][NTf 2] to extract thiophene with different type of model oil which is Dodecane and cyclohexane.

The extraction is done at room temperature for 2 hours and is leaved overnight to settle down. The sample is taken by using syringe and is analyzed by using Gas Chromatography (CG) test.

After the analysis, it has found out that the values of the solute distribution rations for both ternary systems studied are bigger than one at low and medium concentrations of solute, being higher for system with cyclohexane.

As for selectivity, in the journal it is reported that the values are higher for system with dodecane, which are bigger than one for both systems and all the concentrations except for high concentrations of solute in system with cyclohexane.

For the conclusion they have conclude that as extraction solvent must primarily exhibit high solute distribution ratio and high selectivity, which for the two systems studied, both of the parameters are higher than one at low thiophene concentrations. As the sulfur compound in the of fossil fuels the content of sulfur compounds is low, [C8min][NTf2] has become an appealing and potential solvent for the separation of thiophene from hydrocarbons as dodecane or cyclohexane.

Another study done by the same author[11] but by using a different ionic liquid 1-Butyl-3-methylimidazolium octyl sulfate, titled *Thiophene separation from aliphatic hydrocarbons using the 1-ethyl-3-methylimidazolium ethyl sulfate ionic liquid*, found out that both components thiophene and n-alkane are practically insoluble in the IL which means a practically total immiscibility for all the ternary mixtures.

It has been found out also that the tie-lines have negative slope with the n-dodecane and n-hexadecane in the low concentrations of the sulfur component. However the selectivity for all the systems is high, which is hypothesized by the author due to the very low concentrations of the hydrocarbons in the IL phase.

METHODOLOGY

3.1   Introduction

This study is done by using two approaches which are experimental work and simulation. Both results will be compared later to confirm its reliability.

3.2   Research Methodology

Problem Statement
- Identify issues that lead to the need of doing the research
- Significant of the project towards the issue

Literature Review
- Understand the concept of adsorption process
- Review the existing related research done by others
- Predict the hyphotesis of the project

Design the experiment
- Identify the equipment and chemicals needed to conduct the experiment

Conduct the experiment
- Conduct the experiment by manipulating the variables / condition of experiment (Semester 1 and 2)
- Record the result (Semester 1 and 2)

Result Analysis
- Analyze the result of experiment (Semester 1 and 2)
- Compare with the theory/hypothesis (Semester 1 and 2)

Conclusion
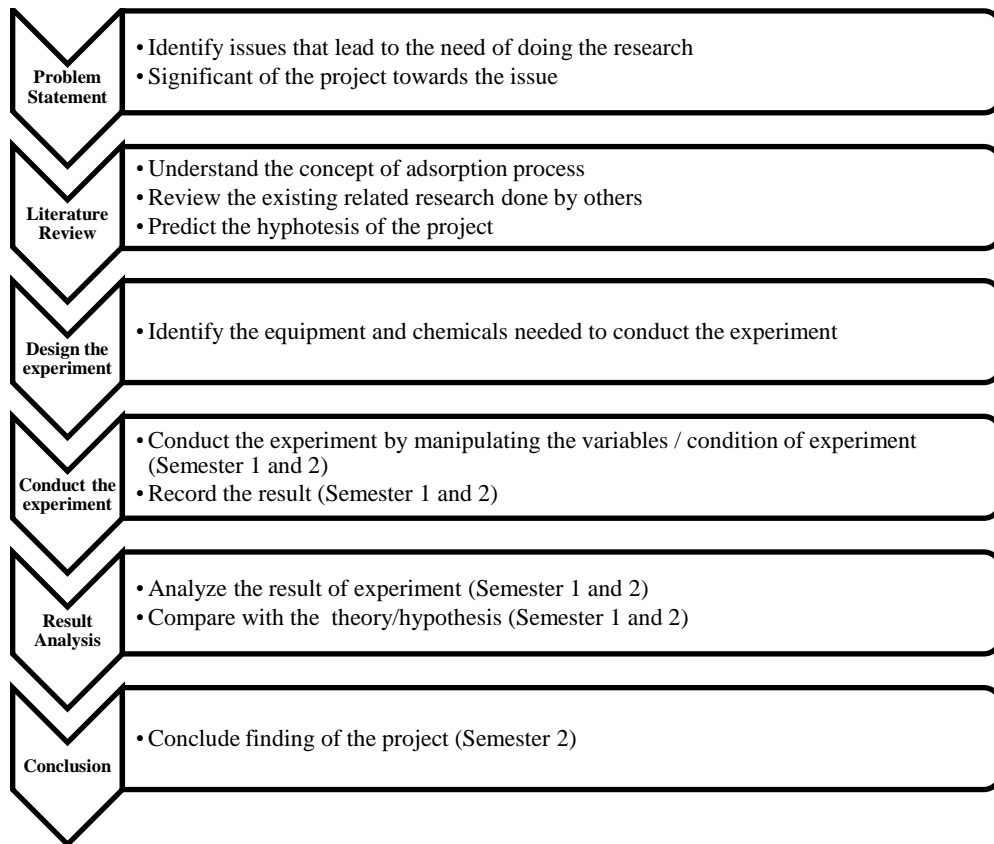- Conclude finding of the project (Semester 2)

Figure 3.2.1: Research Methodology

3.3   Equipments and Chemicals

The equipment and chemicals that will be used for the experiment procedure are tabulated in the table as shown below:

Equipments	Quantity(s)
Hot plate stirrer	1
High Precision Liquid Chromatography (HPLC)	1
Karl Fischer (for water content measurement)	1
Weight Scale	1
Shaking Water Bath	1
Gas Chromatography	1

Table 3.3.1: List of equipment used for the experiment

Chemicals	Amount
1-Butyl-3-methylimidazolium octyl sulfate	30g
Dodecane	75g
Thianaphthene	15g
Deionized Water	500 mL
Methanol	500 mL

Table 3.3.2: List of chemical used for the experiment

3.4   Test condition/standardization

In every experiment, it is assumed that it is done in room temperature (25˚C). All the reactant concentration is also assumed is at same concentration for each of the experiment. This is important due to properties of ionic liquid.

Before experiment is conducted, water content in the ionic liquid is checked. If the moisture content is exceeded certain amount, a certain process will be carried out to remove moisture content in the ionic liquid.

3.5   Experimental Procedure

3.5.1   Preparation of Extraction Sample

1. 0.0977 grams of thianaphthene is measured using Mettler Toledo weight measurer. The measurement is done in fume hood at room temperature. thianaphthene is put in a 16 ml capped test tube.
2. 1.9551 grams of dodecane is added as model oil. Both of the substance is mixed by shaking the test tube. The solution is considered as mix after thianaphthene dissolves in the dodecane.
3. 4g of 1-butyl-3-methylimidazolium octyl sulfate is added into the solution. Two separate immiscible liquid is observed. The cap is closed as soon as the ionic liquid is added to prevent sample contamination by water vapor.
4. Procedure 1, 2 & 3 are repeated by using 0.1955, 0.2933, 0.3910, 0.5865, 0.7820, and 0.9775 grams of thianaphthene and same amount of dodecane and 1-butyl-3-methylimidazolium octyl sulfate.

3.5.2 Extraction

1. The mixtures are stirred for 1 hour at 40°C and 400 rpm. Magnetic bar is used to increase the mixing efficiency.
2. The mixtures are left at the same temperature for another 1 hour.

3.5.3 HPLC sample preparation

1. The upper layer of the mixture is taken around 3ml by using syringe and is kept in 12 ml capped tube. The tube is sealed to avoid water contamination.
2. The same procedure is done for the lower layer of the mixture.

3.5.4 Preparation of standard

Thianaphthene – Dodecane

1. 0.25 gram of thianaphthene is measured. The thianaphthene then is mixed into 5 gram of dodecane. The mixture is left for 2 hours to make sure that all thianaphthene is dissolved into dodecane.
2. The same procedure is repeated by varying the amount of thianaphthene as the following table.

Sample no.	Mass Dodecane	Percentage	Mass Thianaphthene
1	5	5	0.2500
2	5	10	0.5000
3	5	15	0.7500
4	5	20	1.0000
5	5	30	1.5000
6	5	50	2.5000
7	5	80	4.0000

Thianaphthene – Ionic liquid

1. 0.1 gram of thianaphthene is measured. The thianaphthene then is mixed into 2 gram of ionic liquid. The mixture is left for 24 hours to make sure that all thianaphthene is dissolved into dodecane.

2. The same procedure is repeated by varying the amount of thianaphthene as the following table.

Sample no.	Mass IL	Percentage	Mass Thianaphthene
1	2	5	0.1
2	2	10	0.2
3	2	15	0.3
4	2	20	0.4
5	2	30	0.6
6	2	50	1
7	2	80	1.6

3.5.5 HPLC

1. Mobile phase for HLPC is prepared by using an equimolar mixture of deionized water and methanol.

2. The following condition is set:
   a. Flow rate   : 1mL/min
   b. Injection Volume   : 1μL
   c. Runtime   : 20 min
   d. Detector type
      i. RID   : C_6H_{12}
      ii. DAD   : C_4H_4S & Bmim

3.6   Simulation Using COSMOthermX

1. Experimental procedure is prepared and presented in a graph
2. All component used are inputted into global option in COSMOthermX
3. The data of molecular fraction is entered in into the software
4. Data obtained is then printed and saved for reference and comparison

REPORT ON FINDINGS OF THE STUDY

Due to some error and human mistake, the measured (actual) mass used for the experiment for example, is not same as the calculated mass needed as per calculation. In this first section, the value of the actual data measured is presented and compared with the calculated value.

For the extraction:

Ionic Liquid	Dodecane	Thianaphthene	Percentage Required	Percentage Obtained	Percentage Difference
3.9983	1.9552	0.0978	5	5.0020	-0.0020
3.9994	1.9553	0.1953	10	9.9882	0.0118
3.9991	1.9558	0.2930	15	14.9811	0.0189
4.0049	1.9547	0.3917	20	20.0389	-0.0389
4.0167	1.9556	0.5868	30	30.0061	-0.0061
4.0087	1.9556	0.7817	40	39.9724	0.0276
4.0117	1.9544	0.9815	50	50.2200	-0.2200

As for the standard:

For Dodecane-Thiaphthene

Dodecane	Thianaphthene	Percentage Required	Percentage Obtained	Percentage Difference
5.0027	0.2504	5	5.0053	-0.0053
5.0003	0.5003	10	10.0054	-0.0054
5.0000	0.7506	15	15.0120	-0.0120
5.0005	1.0004	20	20.0060	-0.0060
5.0004	1.5002	30	30.0016	-0.0016
5.0005	2.5002	50	49.9990	0.0010
2.0005	1.5998	80	79.9700	0.0300

For Ionic Liquid-Thiaphthene

| Ionic Liquid	Thianaphthene	Percentage Required	Percentage Obtained	Percentage Difference
0.9999	0.0495	5	4.9505	0.0495
0.9998	0.1000	10	10.0020	-0.0020
0.9990	0.1503	15	15.0450	-0.0450
1.0004	0.2005	20	20.0420	-0.0420
0.9997	0.3011	30	30.1190	-0.1190
1.0010	0.4992	50	49.8701	0.1299
1.0009	0.8009	80	80.0180	-0.0180

4.1   Result

Data from HPLC is obtained and analyzed. Wavelength of 310 is chosen due to clearer result on the sample. The analyzed data is shown in below table:
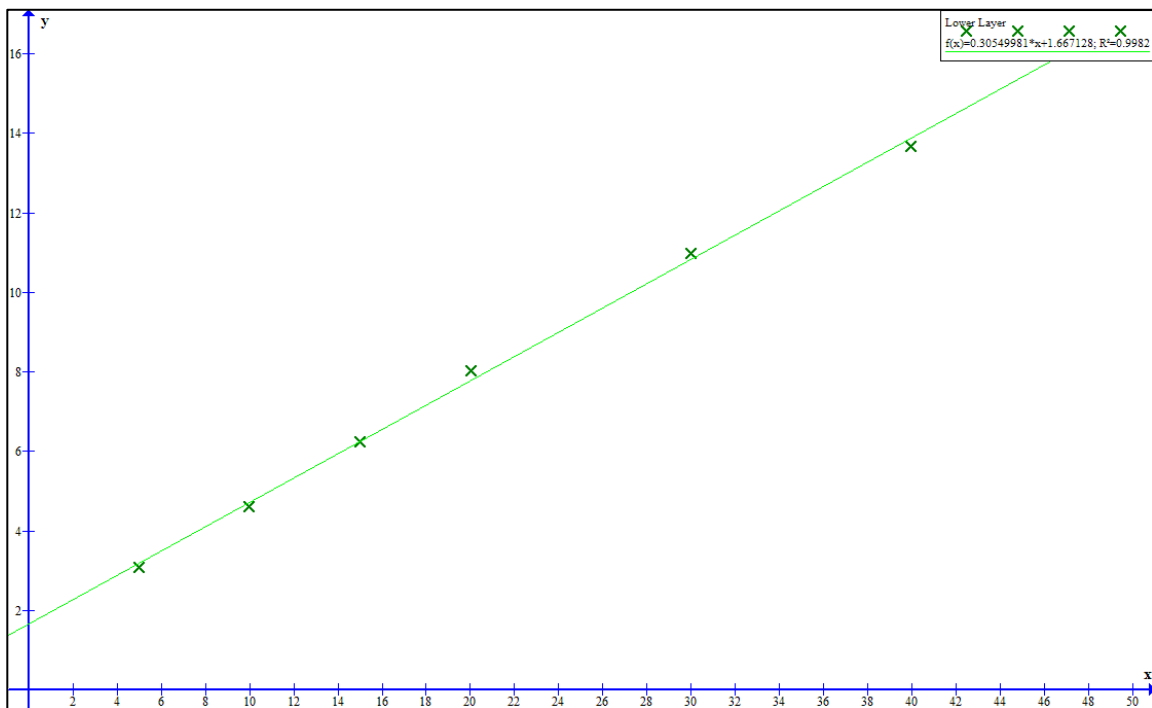
Percentage over BT	Dodecane	Ionic
5	151.43661	235.10785
10	298.0777	426.91199
15	421.6582	624.86676
20	520.98682	775.76019
30	731.43359	1051.203
50	1073.1841	1290.9454
80	1462.9769	1784.307

Data obtained from the HPLC is used to construct calibration curve.

For Dodecane-Thiaphthene:
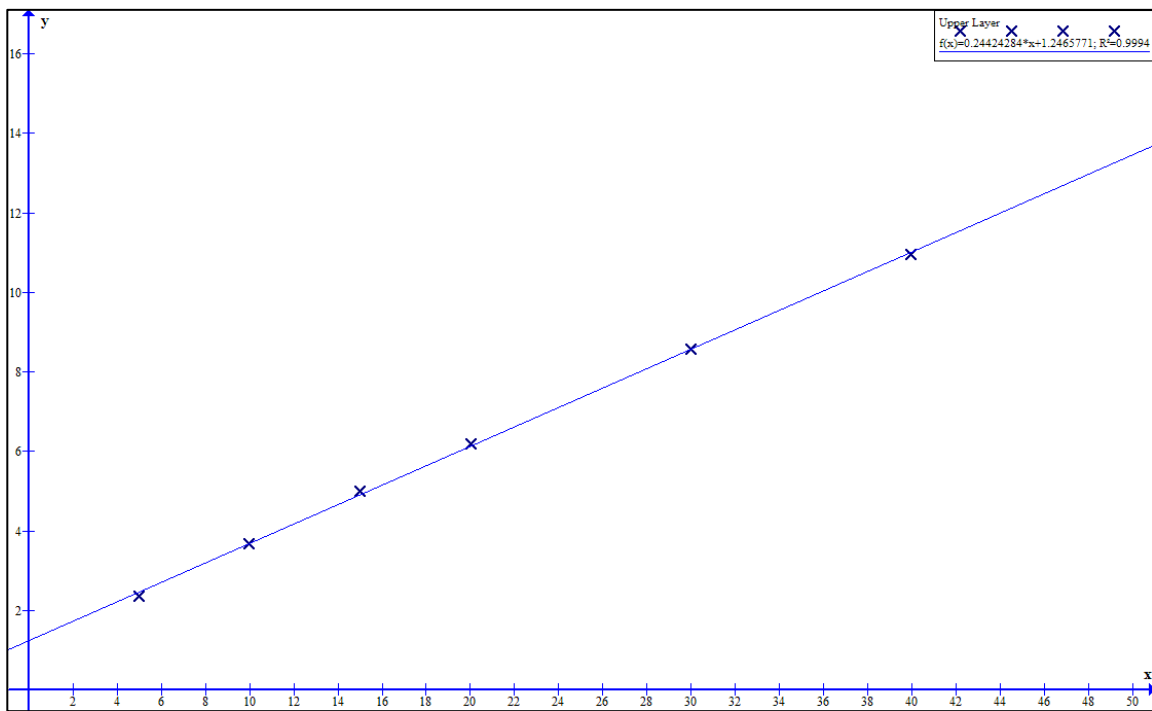
For Ionic Liquid-Thiaphthene:

4.2   Discussion

As can be expected, the value of area is increasing with an increase of thiaphthene. This is because of as more thiaphthene is present, HPLC will detect more hence giving a result of more area.
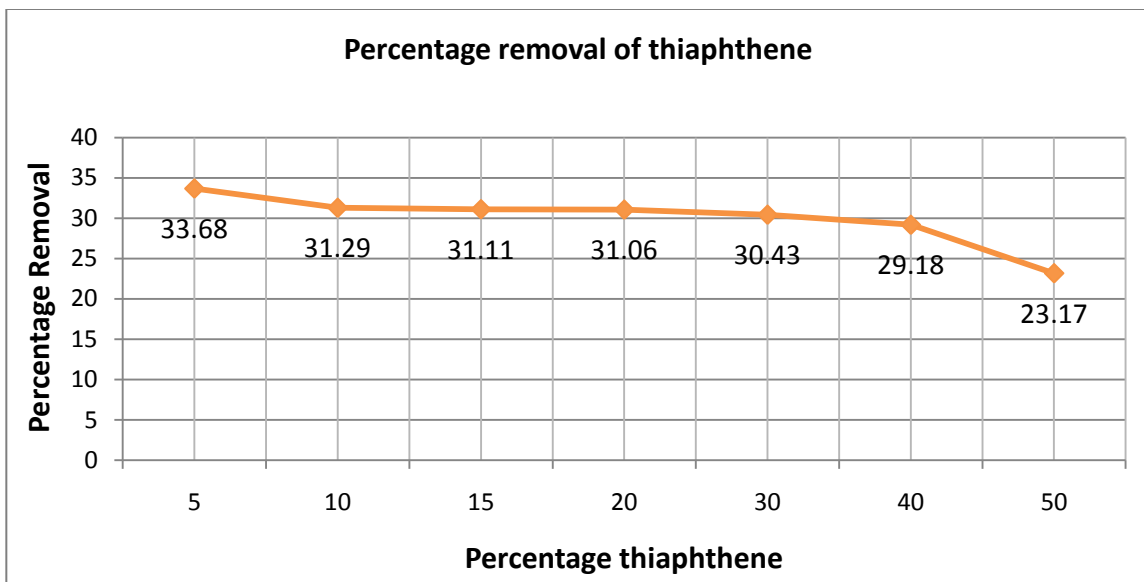
The trend of the calibration curve is linear with a function of $y = 0.24424284 x + 1.2465771$ for upper layer and $y = 0.30549981 x + 1.667128$ for the lower phase. For the upper layer R^2 obtained is 0.9994 while 0.9982 is obtained for the lower phase. Both of the value is show how perfect the line is (the line is at ideal case when the R^2 value obtained is 1).

This value later is used to measure amount of thiaphthene in upper layer and lower layer from extraction. From HPLC measurement this value is obtained:

Sample Percentage	Area for Upper Layer	Area for Lower Layer	Thiaphthene Percentage in Upper Layer	Thiaphthene Percentage in Lower Layer
5.0020458	43.36333	81.39405	1.3216259	1.6848847
9.9882371	79.61576	140.9399	2.6057016	3.12569294
14.981082	115.3584	204.4274	3.8717204	4.66187579
20.038881	147.41171	273.54419	5.0070616	6.33426843
30.006136	211.4081	389.20828	7.2738397	9.13294835
39.972387	272.0657	492.69415	9.4223565	11.6369565
50.220016	275.86057	493.8548	9.5567723	11.6650403

This result is also expected. As the concentration of thiaphthene increase, the value of thiaphthene extracted by IL is increasing. However at some point, the value is at constant. This is due to the thiaphthene is at saturated in IL.

The result can be used to calculate percentage removal of thiaphthene. This finding can be better expressed in graph form.

Percentage removal of thiaphthene

Chart: Percentage Removal (y-axis, 0 to 40) vs Percentage thiaphthene (x-axis)

Data points:
- 5: 33.68
- 10: 31.29
- 15: 31.11
- 20: 31.06
- 30: 30.43
- 40: 29.18
- 50: 23.17

From the chart above, the value of percentage removal of thiaphthene is decreasing with an increase thiaphthene in model oil. This can be explained by the constant amount of IL used throughout the experiment. As the value of thiaphthene increasing, the amount of thiaphthene that can be extracted by the IL is decreasing due to the ability of the IL to extract more thiaphthene is decrease.

From this graph it can conclude that the percentage of removal can be increase by two means. First, is by increasing the value amount of IL. By increasing amount of IL, it will give more space for IL to save more thiaphthene in it. We also can increase the percentage of removal by decreasing the amount of thiaphthene. This help a lot in application of IL in LLE since the value of sulfur in crude oil for example is generally low.

As for the data itself, the value of 33.68 percent removal is actually quite low. This value means that for model oil containing 5% of thiaphthene in it can only be extracted at the said amount of percentage by IL used in the study. This value however will change with the change of type of IL, type of sulfur, amount of both of the components and etc.

The value obtained from the HPLC calculation can later be used to calculate the composition data. After some calculation by using calibration curve formula obtained earlier, the composition data is obtained. The data is tabulated below:

Upper Phase (Oil Rich Phase)		Lower Phase (Ionic Liquid Rich Phase)	
Percentage Dodecane	Percentage Thiaphthene	Percentage IL	Percentage Thiaphthene
98.67	1.32	98.31	1.68
97.39	2.60	96.87	3.12
96.12	3.87	95.33	4.66
94.99	5.00	93.66	6.33
92.72	7.27	90.86	9.13
90.44	9.55	88.33	11.66
90.57	9.42	88.36	11.63

As mentioned in the table above, the percentage of dodecane in the upper phase is decreasing due to increase amount of thiaphthene. This also same for the lower liquid phase which show that the value of IL is decreasing as a result in increase in thiaphthene percentage.

There are slight amount about 0.01% left in both of the cases. This is due to present of cross contamination between ionic liquid and dodecane. The value however is too small that it can be neglected. Other contaminant like water is also present but can be safely ignored as the value is 0.024%, which is simply too small.

The value of the composition table can be express in ternary diagram. For this study, ternary diagram will be in an anti clockwise. The ternary diagram is shown below:
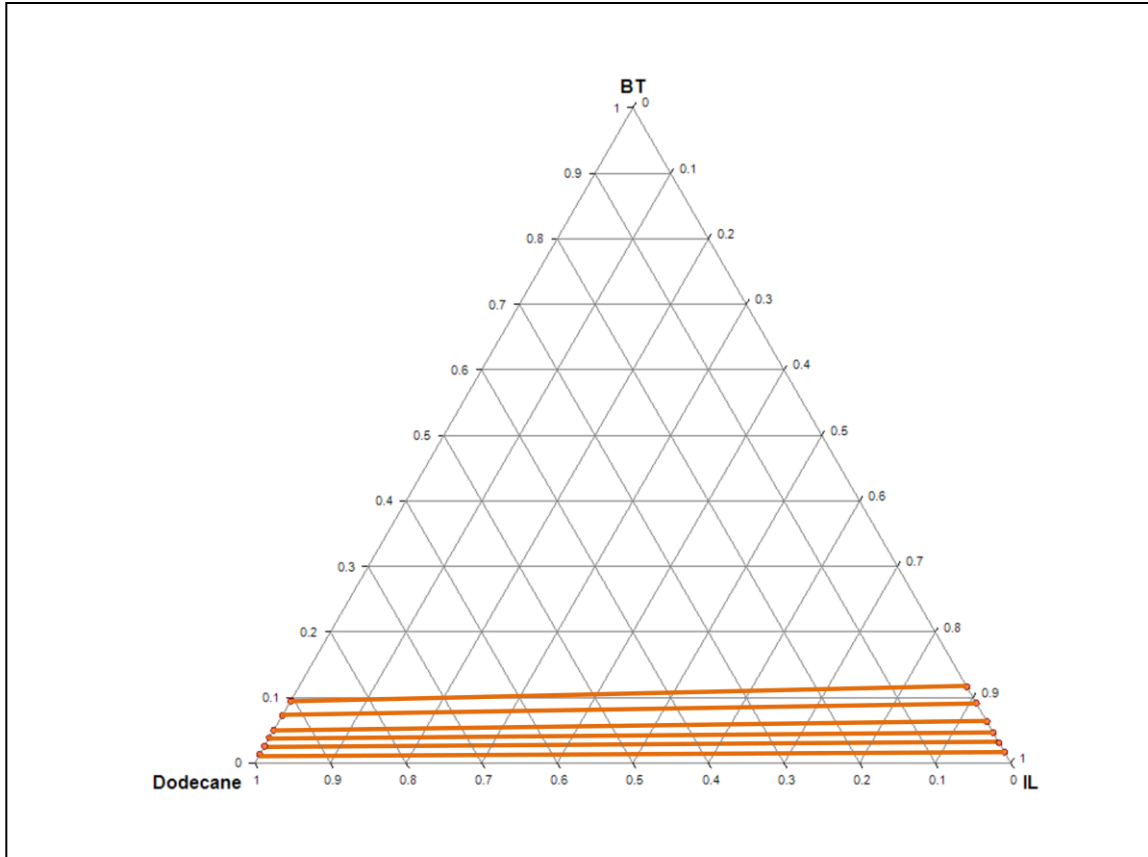
From the diagram, it can be observed that the amount of thiaphthene in dodecane is lesser than amount of thiaphthene in IL. In the other word, the amount of thiaphthene extracted in IL is higher compare to the amount of thiaphthene left in dodecane after extraction. This is good since the result shows that the extraction is properly done by IL.

However to quantitively express the result some mathematical calculation need to be done. In this case, by simply dividing the amount of thiaphthene found in the IL with the amount of thiaphthene found in the dodecane, we can obtain the value of k_d.

$$k_d = \frac{\text{thiaphthene found in the IL}}{\text{thiaphthene found in the dodecane}}$$

Percentage Thiaphthene	K_d value
5	1.2748576
10	1.199559
15	1.2040838
20	1.265067
30	1.2555883
40	1.2206046
50	1.2350368

As shown in the table above, the k_d value varies with an average value of 1.24. This value represent ratio of the thiaphthene found in the IL with the amount of thiaphthene found in the dodecane. So it means, if the value of k_d is bigger, the more amount of thiaphthene is extracted by IL.

Value of 1.24 is smaller compared to the other value found in previous study. This is mainly due to inefficient of the studied ionic liquid compared to other ionic liquid used in another study. However, the value still showing that the ability of the studied ionic liquid is acceptable for use for LLE.

CONCLUSION

Study on equilibrium of thiaphthene in model oil with 1-Butyl-3-methylimidazolium octyl sulfate has been done experimentally at 40˚C and 400 rpm for 1 hour. The value of thiaphthene found in the lower phase (ionic liquid phase) is higher that thiaphthene found in upper phase (oil rich phase) with an average ration value of 1.24. 1-Butyl-3-methylimidazolium octyl sulfate show satisfactory result in extracting Benzothiophine from Dodecane.

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