# SEPARATION OF AROMATIC FROM ALIPHATIC BY USING [EIM][EtSO$_4$] IONIC LIQUID

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# SEPARATION OF AROMATIC FROM ALIPHATIC BY USING [EIM][EtSO$_4$] IONIC LIQUID

**CHE AHMAD ARIF BIN CHE MUD**

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering (Gas Technology)

**Faculty of Chemical & Natural Resources Engineering**
**UNIVERSITI MALAYSIA PAHANG**

JULY 2013

# SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering (Gas Technology).

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# STUDENT'S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature :
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Date :

## ***Dedication***

*To my beloved parents for being supportive*

# ACKNOWLEDGEMENT

First of all, I would like to express my heartily gratitude to my research supervisor, Dr. Syamsul Bahari B. Abdullah for his guidance, advices, efforts, supervision and enthusiasm given throughout for the progress of this research. Although he always busy with his work, he still guided me in finishing my researched.

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I would like to express my sincere appreciation to my parents for their support to me in all this years. Without them, I would not achieved and completed this research and besides that, I would to thank all my course mates because their concern, support and encouragement.

# ABSTRACT

The separation of aromatic from the aliphatic hydrocarbon mixtures are very challenging since these hydrocarbons have boiling point in a close range and several combination form an azeotrope. Toluene and *n*-heptane are known to have a very close boiling point, thus difficult to separate by fractionation with distillation. The present studies focusing on separating toluene from *n*-heptane using 3-ethylimidazolium-ethylsulfate [EIM][$EtSO_4$]. From the analysis of data by using the FTIR and HPLC, the functional group of ionic liquid can be determined as amine group and for the analyzing the data for the extraction, the removal of the toluene from the mixture shows the positive results where the toluene was separated from the aromatic/aliphatic mixtures increases and it depends on the amount or percentages of the volume ratios of the toluene compound in the mixtures. From the results of stirring, it shows that the distribution coefficient of toluene was decreasing with the increasing of the removal of the toluene from the toluene/n-heptane and the selectivities at the temperature 30°C was increasing with decreasing toluene content in the feed.

**Keywords***: Separation, Toluene/n-Heptane mixture, Azeotrope, Ionic Liquids, 3-ethylimidazolium-ethylsulfate [EIM] [$EtSO_4$]*

# ABSTRAK

Pemisahan aromatik daripada campuran hidrokarbon alifatik sangat mencabar kerana hidrokarbon mempunyai takat didih dalam julat yang rapat dan beberapa bentuk gabungan azeotrope. Toluena dan n-heptana diketahui mempunyai takat didih yang sangat rapat, oleh itu sukar untuk memisahkan pemeringkatan dengan penyulingan. Kajian ini memberi tumpuan kepada memisahkan toluena daripada n-heptana menggunakan 3-ethylimidazolium etil-sulfat [EIM][EtSO4]. Daripada analisis data dengan menggunakan FTIR dan HPLC, kumpulan berfungsi bagi cecair ionik boleh ditentukan sebagai satu kumpulan amine dan untuk menganalisis data untuk pengekstrakan, penghapusan toluena daripada campuran menunjukkan hasil yang positif di mana toluene adalah dipisahkan daripada campuran aromatik / alifatik bertambah dan ia bergantung kepada jumlah atau peratusan nisbah jumlah kompaun toluena dalam campuran. Daripada keputusan mengacau campuran, ia menunjukkan bahawa pekali taburan toluena telah berkurangan dengan peningkatan penyingkiran toluene dari campuran toluena / n-heptana dan selectivities pada suhu 30 ° C telah meningkat dengan mengurangkan kandungan toluena dalam suapan.

**Keywords**: *Pemisahan, Campuran Toluene/n-Heptana, Azeotrope, Cecair Ionik, 3-ethylimidazolium-ethylsulfate [EIM][EtSO*$_4$*]*

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# LIST OF ABBREVIATIONS

| | |
|---|---|
| *n-heptane* | normal heptane |
| *°C* | Degree Celcius |
| *°F* | Degree Farenheit |
| *i-octane* | iso octane |
| *wt %* | weight percent |
| *v/v %* | volume ratio percent |
| *g* | gram |

# LIST OF ABBREVIATIONS

| | |
|---|---|
| VOC | Volatile Organic Compound |
| ILs | Ionic Liquids |
| FTIR | Fourier Transform Infra Red |
| HPLC | High Performance Liquid Chromatography |
| IFP | Institute Francies du Petrole |
| S | Selectivity |
| D | Distribution Coefficient |
| IR | Infra Red |
| RPM | Rotation per Minute |

# 1 INTRODUCTION

## *1.0 Motivation and statement of problem*

In the chemical industries, toluene and n-heptane are widely used in the processing and manufacturing. Toluene is a compound that occurs naturally in the crude oil in the very low level of the oil separation. This chemical also is a by product in the production in gasoline and coke fuel from the coal.

Compared with the other chemical, n- heptane is a chemical from the aliphatic group with the straight chain of alkanes. This chemical usually used and applied in the laboratories as a totally non- polar solvent and it also used as a fuel component in anti knock test engine. Because of the separation between two components are very challenging since these hydrocarbons have slightly different in the boiling point and several combinations form an azeotrope, common process like separation by fractionation with distillation become more difficult. To overcome this problem, the present studies found that the separation between this aliphatic and aromatic compound can be accomplished by separating by using ionic liquids (Meindersma *et al*., 2005).

### 1.0.1 Toluene

Toluene was used widely in processing and producing the product. With the characteristic of the aromatic hydrocarbon group, toluene is a chemical that are clear and colourless liquid with a strong sweet and pungent odour. According to Alelsto (2008), with the chemical formula $C_7H_8$, this compound occurs naturally in the crude oil though in very low levels and it also a by product in the production gasoline and coke fuel from the coal. Actually, this liquid is typically stable under the normal usage and storage condition but it will become danger when the container was heated or subjected to high temperature and mishandling because it may burst and cause explosions. Toluene is a chemically incompatible with strong oxidizing agents, sulfuric and nitric acids, and chlorine. When the toluene was heated and react with the nitro group, toluene can changed to di-nitro toluene and eventually into the volatile and explosive tri-nitro toluene. This thing can reacts strongly with the oxidizing agents and it may produce heat or can potentially ignite or explode when it not handled carefully and it was written by Canadian Centre for Occupational Health & Safety (2008).

This aromatic compound that are also known as volatile organic compound (VOC) which had the application in industries was proven with the achievement especially in production of benzene because this chemical was used to make plastics and synthetic fibers and also was used to boost the octane of gasoline. Other application of this compound are used as a solvent and to make aviation of gasoline, spray and wall paints, paints thinner, medicine, dyes, explosives, detergents and others. It is also used in some printing and leather tanning processes.

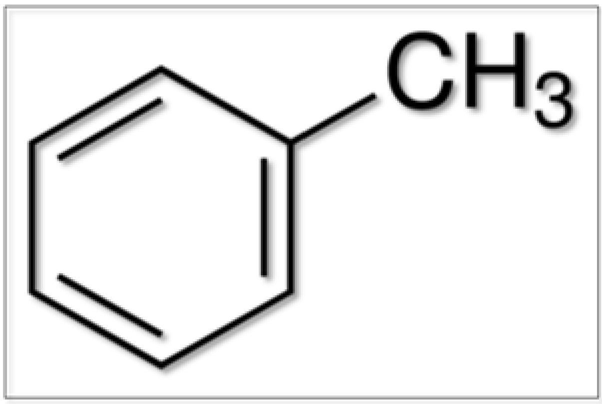


**Figure 1.1** Toluene structure

**Table 1.1** Physical properties and explosion data for the Toluene.
(Toluene MSDS, Science Lab.Com)

| | |
|---|---|
| **Chemical Name** | - Toluene, Methylbenzene<br>- Toluol<br>- Phenyl- methane<br>- Methyl- benzol |
| **Chemical Formula** | - C6-H5-CH3 or C7H8 |
| **Flammability of the products** | - Flammable |
| **Auto- Ignition Temperature** | - 480°C or 896 °F |
| **Flammable Limit** | - LOWER 1.1 % and UPPER 7.1% |
| **Physical state and appearance** | - Liquid state with sweet, pungent, benzene like odor. |
| **Molecular Weight** | - 92. 14 g/ mole |
| **Color** | - Colourless |
| **Boiling Point** | - 110.6 °C or 231.1 °F |
| **Melting Point** | - - 95 °C or -139 °F |
| **Specific Gravity** | - 0.8636 (water =1) |

### 1.0.2 Heptane (n- Heptane)

Heptane or n- Heptane is one of the aliphatic groups with the straight chain of alkane with the chemical formula $C_7H_{16}$. This hydrocarbon had nine isomers with different type of structure are widely used and applied in the laboratories as a totally non- polar solvent. When this hydrocarbon used as a test fuel component in anti knock test engine, a 100 percent of heptanes fuel is the zero point of octane rating scale where the 100 point is a 100 percent of i-octane. The numbers of octane in the ratios between octane and heptanes equates to anti-knock qualities which are expressed as the percentage of iso-octane in heptanes and listed on pumps for the gasoline where are dispensed in the US and internationally.

In state of liquid, this hydrocarbon it is really ideal for transport and storage. For the test like grease spot test, heptanes is used as a liquid to dissolve the oil spot to show the previous presence of the organic compounds on a stained of paper by shaking it in the heptanes solution for about half minute. In other uses, the liquids are commercially available as mixed isomers for use in paints and coating. For examples, n-haptane was use as the rubber cement solvent “Bestine”, the outdoor stove fuel, and for the pure n-Heptane was used for the research and development and also for the pharmaceutical manufacturing and as a minor component in gasoline.

In gasoline, heptanes one of primary reference fuels for the determination of the gasoline octane number. Consequently, the research community for the combustion has endeavoured to develop in detailed in chemical kinetics mechanism for the combustion of heptanes. For the mechanism combustion of heptanes, the oxidation of this hydrocarbon has been investigate in shock tubes, jet stirred reactor, premixed and diffusion flame (Zhuko *et al.*, 2004).

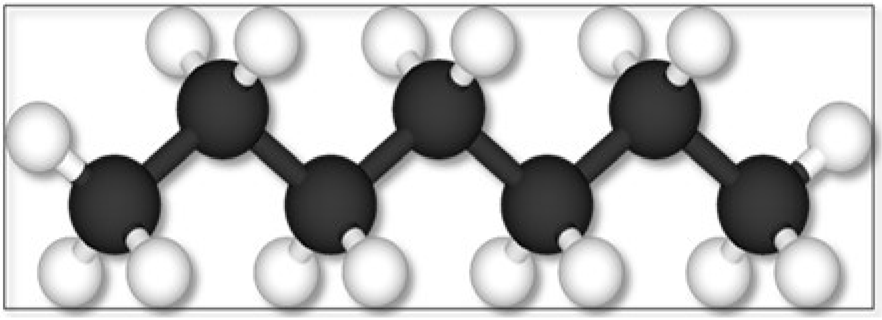


**Figure 1.2** Normal heptane (n- Heptane) structures.

**Table 1.2** Physical properties and explosion data for the n-Heptane.
(n- Heptane MSDS, Science Lab.Com)

| | |
|---|---|
| **Chemical Name** | - n- Heptane<br>- Dipropyl methane<br>- Heptyl hydride |
| **Chemical Formula** | - $C_7H_{16}$ |
| **Flammability of the products** | - Flammable |
| **Auto- Ignition Temperature** | - 203.89 °C or 399 °F |
| **Flammable Limit** | - LOWER 1.05 % and UPPER 6.7% |
| **Physical state and appearance** | - Liquid state with gasoline like odor |
| **Molecular Weight** | - 100. 21 g/ mole |
| **Color** | - Clear colorless |
| **Boiling Point** | - 98.4 °C or 209.1 °F |
| **Melting Point** | - - 90.7 °C or -131.3 °F |
| **Specific Gravity** | - 0.6838 (water =1) |

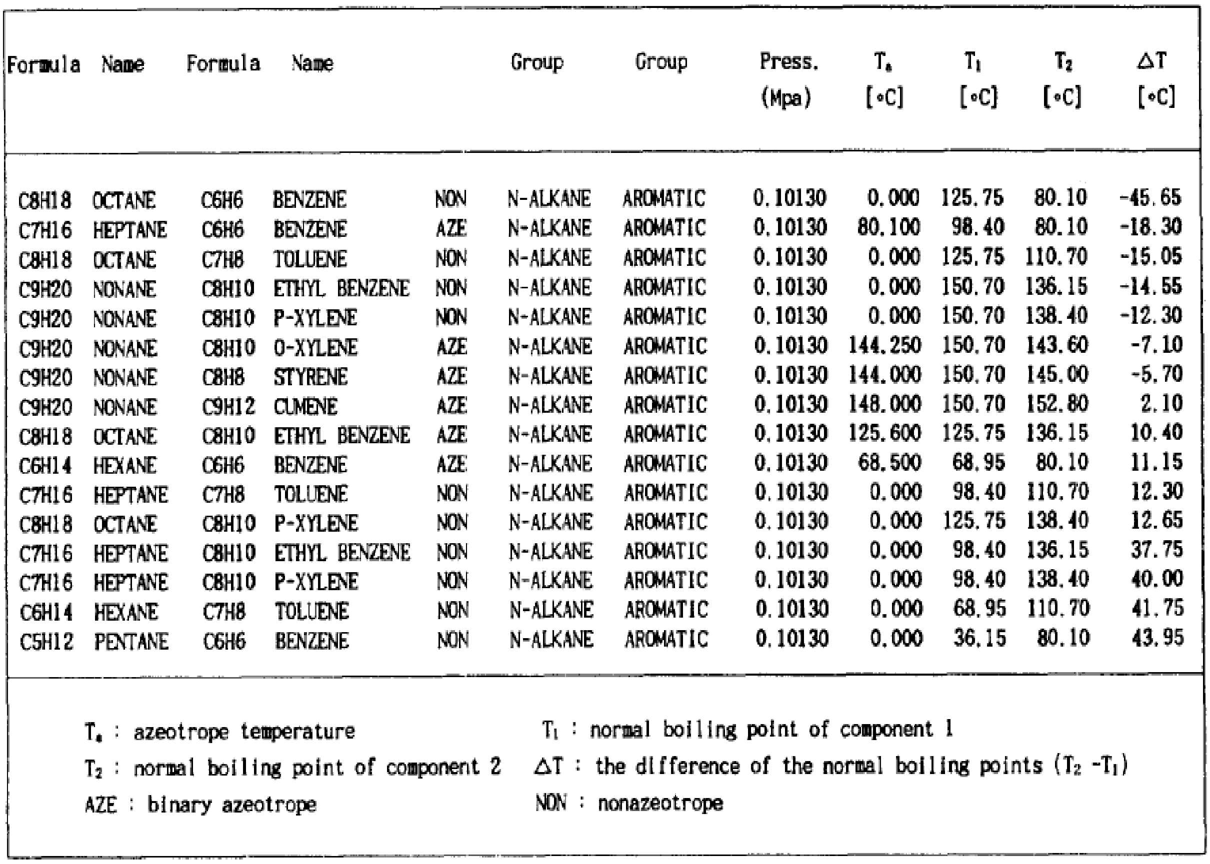
### 1.0.3 Separation of Azeotropic Combination.

An azeotrope is a mixture two or more liquids in such a way that its components cannot be altered by simple distillation (Moore &Walter., 1962). In the industries, the presents the azeotropes alter the product distribution and it also restricted the separation amount of the multi- component mixtures that can be achieved by distillation (Okasinski & Doherty., 1997). The azeotrope phenomenon can occur in reactive and in non- reactive mixture and they can be classify as homogeneous and heterogeneous depending on the number of liquids phases involved in the equilibrium condition. Like the non- reactive mixtures, the homogeneous azeotrope happen when the composition of the vapor liquid phases at equilibrium is identical and it also same for the reactive mixture but this system were using reaction invariant composition space (Moore & Walter., 1962).

In separation aromatic hydrocarbon (benzene, toluene, ethyl benzene and xylenes) and aliphatic hydrocarbon that are from $C_4$ to $C_{10}$ group, it will be more challenging since these two hydrocarbons have boiling point on close range and several combination form an azeotrope. There are some conventional processes that was practice in the industries for the liquid separation process such as liquid extraction where it suitable for the range 20- 65 percent of aromatic contents, extractive distillation for the range 65- 90 percent aromatic and azeotrope distillation for the high aromatic content which are more than 90 percent in the feeds. But according to Weissermel and Arpe (2003), there are no feasible processes that are available for the separation of aromatic and aliphatic hydrocarbon in the range below 20 percent aromatic in the feed mixture. From the preliminary calculation, the result shows that, extraction with conventional solvents are not an option since additional separation step are required to purified the raffinate, extract and solvent streams which may cause high investment and energy.

According to Meindersma (2005 & 2007), the other alternative to separate both group of hydrocarbons is extraction using ionic liquids. The application of ionic liquids in extraction process is promising because of their non- volatile in nature. For the separation unit, the solvent recovery facilities for this process are using techniques as simple as flash distillation or stripping where the extraction of aromatic from mixed aromatic and aliphatic streams with the ionic liquids are expected to require less process steps and less energy consumption compare to the extraction with conventional solvents because ionic liquids have a negligible vapor pressure, it can be recover back by evaporating the extracted hydrocarbon from the ionic liquid phase.

**Table 1.3** The structure of the data bank derived from the case study from system of aromatic/ n-alkane. (Korean, J. of ChemEng, 1995)



| Formula | Name | Formula | Name | | Group | Group | Press. (Mpa) | $T_a$ [°C] | $T_1$ [°C] | $T_2$ [°C] | ΔT [°C] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| C8H18 | OCTANE | C6H6 | BENZENE | NON | N-ALKANE | AROMATIC | 0.10130 | 0.000 | 125.75 | 80.10 | -45.65 |
| C7H16 | HEPTANE | C6H6 | BENZENE | AZE | N-ALKANE | AROMATIC | 0.10130 | 80.100 | 98.40 | 80.10 | -18.30 |
| C8H18 | OCTANE | C7H8 | TOLUENE | NON | N-ALKANE | AROMATIC | 0.10130 | 0.000 | 125.75 | 110.70 | -15.05 |
| C9H20 | NONANE | C8H10 | ETHYL BENZENE | NON | N-ALKANE | AROMATIC | 0.10130 | 0.000 | 150.70 | 136.15 | -14.55 |
| C9H20 | NONANE | C8H10 | P-XYLENE | NON | N-ALKANE | AROMATIC | 0.10130 | 0.000 | 150.70 | 138.40 | -12.30 |
| C9H20 | NONANE | C8H10 | O-XYLENE | AZE | N-ALKANE | AROMATIC | 0.10130 | 144.250 | 150.70 | 143.60 | -7.10 |
| C9H20 | NONANE | C8H8 | STYRENE | AZE | N-ALKANE | AROMATIC | 0.10130 | 144.000 | 150.70 | 145.00 | -5.70 |
| C9H20 | NONANE | C9H12 | CUMENE | AZE | N-ALKANE | AROMATIC | 0.10130 | 148.000 | 150.70 | 152.80 | 2.10 |
| C8H18 | OCTANE | C8H10 | ETHYL BENZENE | AZE | N-ALKANE | AROMATIC | 0.10130 | 125.600 | 125.75 | 136.15 | 10.40 |
| C6H14 | HEXANE | C6H6 | BENZENE | AZE | N-ALKANE | AROMATIC | 0.10130 | 68.500 | 68.95 | 80.10 | 11.15 |
| C7H16 | HEPTANE | C7H8 | TOLUENE | NON | N-ALKANE | AROMATIC | 0.10130 | 0.000 | 98.40 | 110.70 | 12.30 |
| C8H18 | OCTANE | C8H10 | P-XYLENE | NON | N-ALKANE | AROMATIC | 0.10130 | 0.000 | 125.75 | 138.40 | 12.65 |
| C7H16 | HEPTANE | C8H10 | ETHYL BENZENE | NON | N-ALKANE | AROMATIC | 0.10130 | 0.000 | 98.40 | 136.15 | 37.75 |
| C7H16 | HEPTANE | C8H10 | P-XYLENE | NON | N-ALKANE | AROMATIC | 0.10130 | 0.000 | 98.40 | 138.40 | 40.00 |
| C6H14 | HEXANE | C7H8 | TOLUENE | NON | N-ALKANE | AROMATIC | 0.10130 | 0.000 | 68.95 | 110.70 | 41.75 |
| C5H12 | PENTANE | C6H6 | BENZENE | NON | N-ALKANE | AROMATIC | 0.10130 | 0.000 | 36.15 | 80.10 | 43.95 |

$T_a$ : azeotrope temperature

$T_1$ : normal boiling point of component 1

$T_2$ : normal boiling point of component 2

ΔT : the difference of the normal boiling points ($T_2$ -$T_1$)

AZE : binary azeotrope

NON : nonazeotrope

## *1.1 Objectives*

In performing the extraction of the aromatic aliphatic hydrocarbon using imidazolium base ionic liquid 3-ethylimidazolium-ethylsulfate [EIM][EtSO$_4$], this research has highlighted two objectives which are:

- To study and characterized the ionic liquid.
- To analyze the content of aromatic from aliphatic hydrocarbon after the extraction.

## *1.2 Scope of this research*

This research focus on the main scope to experimentally investigate the effectiveness of the imidazolium based ionic liquid in extraction of the aromatic hydrocarbon group from aliphatic hydrocarbon group.

## *1.3 Main contribution of this work*

It is very efficient to separate or extract the aromatic hydrocarbon from aliphatic hydrocarbon by using ammonia base ionic liquid because of the step that needs to achieve the separation is less and the recovery facilities for this process are using technique ad simple as flash distillation or stripping compare to the other conventional separation that need more equipment and steps. Other than that, because of ionic liquids have a negligible vapour pressure, it can recovered back by evaporating the extracted hydrocarbon from the ionic liquid phase and this process promising less investment cost and also energy consumptions.

## *1.4 Organisation of this thesis*

The structure of the reminder of the thesis is outlined as follow:

Chapter 1 is the introduction of the researched. This chapter provide provides the motivation and problem statement of this research. In order to define the problem of the mixture of aromatic and aliphatic mixture, the properties and application of the toluene and n-heptane was being study and analyzed. The separation of azeotropic combination between the mixtures is the one of the major problem in this research that was highlighted and need to studies.

Chapter 2 provides a description of the applications and general knowledge for the extraction of aromatic/aliphatic mixture. This chapter also provide the several types of ionic liquids that used in the industries which are about the anion and cation for the effectiveness for separation of aromatic from aliphatic compound. In the chapter 2 also provide the some knowledge about the ionic liquid that used in this experiment and also the equipment to analyze the functional group in the ILs.

Chapter 3 gives a review of the FTIR and HPLC approach applied for analyzing the ionic liquids and also the sample. In analyzing the samples and also developing the calibration curve, the HPLC equipment needs to be setup to fulfil the standard for detected the samples to analyze the results that was developed.

Chapter 4 is the results and discussion part where the data was analyzed to achieved the objectives of this experiment and also to discuss the results that collected from the analysis of samples. In this chapter, the result was compared to the prediction from the common method for solving the problems. The details explanation of the results that was used to analyze the sequences that happen to the results is also outlines.

Chapter 5 draws together a summary of the thesis and outlines the future work which might be derived from the model developed in this work.

# 2 LITERATURE REVIEW

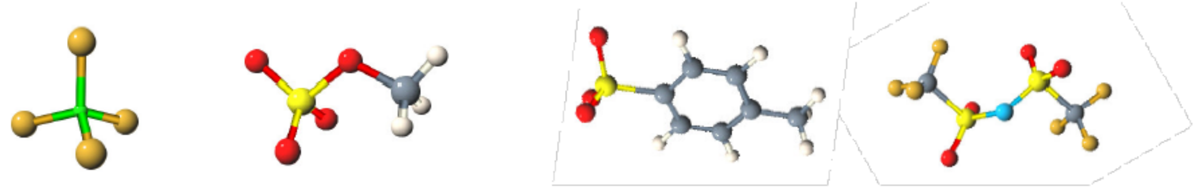
## *2.0 Overview*

This paper presents the experimental studies of the separation of the aromatic hydrocarbon from aliphatic hydrocarbon mixtures that are very challenging since this hydrocarbon had boiling points in a closed range and several of the combination of hydrocarbon form azeotropes. There are several conventional processes in industries for the separation aromatic/aliphatic hydrocarbon mixtures. Different process will separate different range of weight percent (wt %) like liquids extraction suitable for the range of 20-65 wt % aromatic content, extractive distillation for the range of 65-90 wt % aromatics and azeotropic distillation for the high content which are for more than 90 wt %. According to Weissermal and Arpe (2003), there is no feasible processes are available for the separation aromatic/aliphatic mixture in the range below 20 percent aromatics and because of the selectivity and activity coefficient of the aromatic/aliphatic mixture, the ionic liquid was suggested for the extractions. The application of ILs for the extraction processes are promising because of their non volatile nature and require less step and energy consumption because it had a negligible vapour pressure (Meindersma *et al*., 2005).

## *2.1 Ionic Liquids*

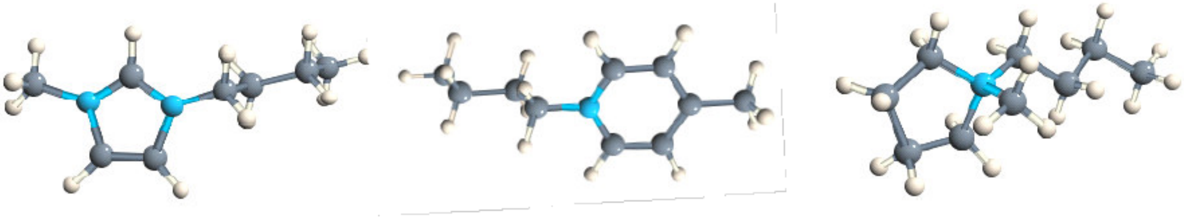
Extraction of aromatic from mixed aromatic and aliphatic streams with the ionic liquids are expected to require less process steps and less energy consumption compare to extraction with conventional solvents because ionic liquids have a negligible vapor pressure (Meindersma *et al*., 2005). In development of extraction solvent, ionic liquids offer new opportunities. The ionic liquids that has known today are based on the different large, which are the organic cation combined with a great variety of organic and inorganic anions. Compared with other solvent like molecular solvent, ionic liquids have advantages of being liquids over a wide range of temperature and having a non-volatile nature.

The latter property has been the reason to call ionic liquids as a green solvent and to start the development as a alternative, environmental friendly solvents. Actually the properties of the ionic liquids are determined by the combination of the cation and anion. Due to the large number of possible ion combination which gives the opportunity to tailor a specific solvent for a particular separation, ionic liquids are also called designer solvents. Recently, the ionic liquids become more famous and gained more interest for many different fields of application. From the journal that was written by Maase (2008), he suggested the ionic liquids need to classified for the process chemical, performance chemical and also for engineering fluids.



tetrafluoroborat methylsulfate p-toluene-4-sulfonate bis(trifluoromethyl-sulfonyl)imide

Anions



1-methyl-3-butyl-imidazolium 4-methyl-N-butyl-pyridinium 1-methyl-1-butyl-pyrrolidinium

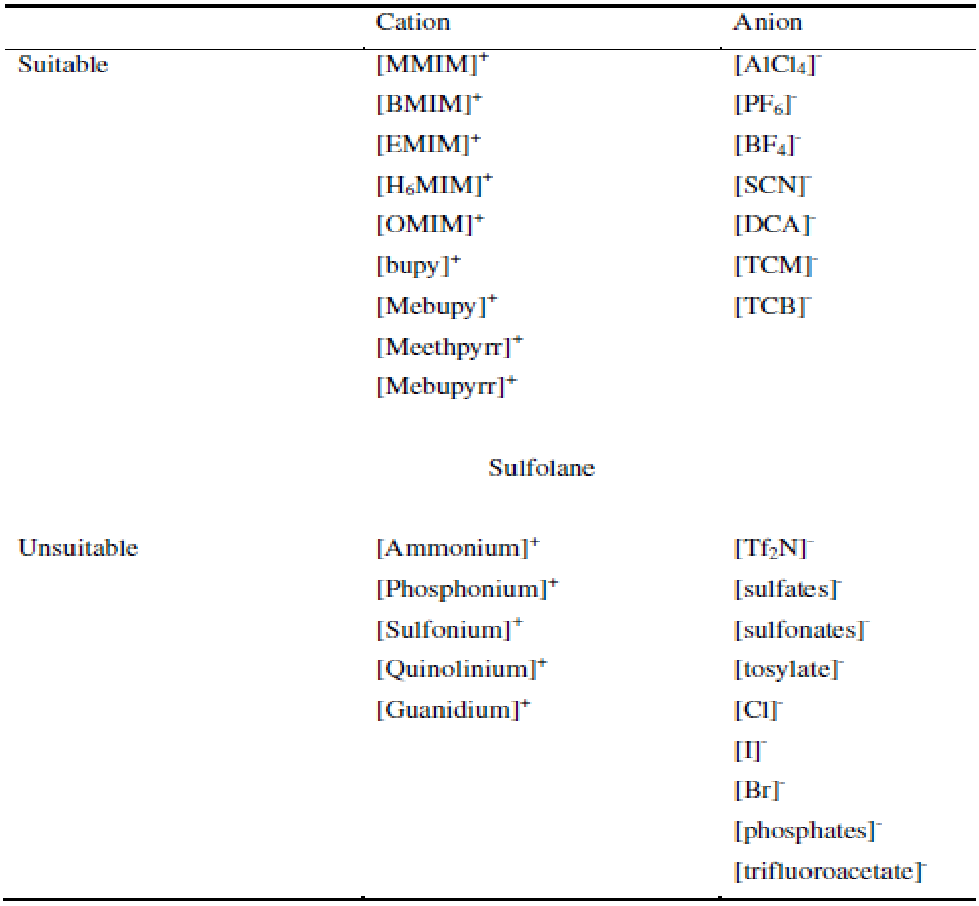
Cations

**Figure 2.1** Typical ionic liquids anions and cations. (Hansmeier, 2010)

Actually this ionic liquid has been mentioned for the first time in the open literature in 19 century. Ionic liquids develop mainly by the electrochemists in their researched of ideal electrolytes for batteries, that has been used initially for those that are related application like semiconductor (Oliver and Magna, 2002). According to Wilke and Zaworotko (1992), in 90's, the first water stable ionic liquids was reported, the signal had been given for many other applications outside the field of electrochemistry. Difasol, the first ionic liquid based process on the pilot scale has been the dimerization of olefins with biphasic that are homogeneous catalyst developed by the *Institute Française du Pétrole (IFP)* (Weyershausen & Lehmann, 2005).

In selection of the ionic liquids for the separation of the aromatic from aliphatic hydrocarbon need to give more intentions. The selection of the ionic liquid has been made according to the hypothesis from the journal that has been written by Hansmeier (2010). From the hypothesis, the cation such as imidazolium, pyridinium, and pyrrolidinium are suitable cation where this thing a not aromatic in nature. For the selection of anions, they are typically small, linear components with the explicit charge distribution like dicyanamide, thiocyanate, tetracyanoborate and tricyanomethanide.

**Table 2.1** Overview theoretically suitable and unsuitable cations and anions.



| | Cation | Anion |
|---|---|---|
| Suitable | [MMIM]$^+$ | [AlCl$_4$]$^-$ |
| | [BMIM]$^+$ | [PF$_6$]$^-$ |
| | [EMIM]$^+$ | [BF$_4$]$^-$ |
| | [H$_6$MIM]$^+$ | [SCN]$^-$ |
| | [OMIM]$^+$ | [DCA]$^-$ |
| | [bupy]$^+$ | [TCM]$^-$ |
| | [Mebupy]$^+$ | [TCB]$^-$ |
| | [Meethpyrr]$^+$ | |
| | [Mebupyrr]$^+$ | |
| | Sulfolane | |
| Unsuitable | [Ammonium]$^+$ | [Tf$_2$N]$^-$ |
| | [Phosphonium]$^+$ | [sulfates]$^-$ |
| | [Sulfonium]$^+$ | [sulfonates]$^-$ |
| | [Quinolinium]$^+$ | [tosylate]$^-$ |
| | [Guanidium]$^+$ | [Cl]$^-$ |
| | | [I]$^-$ |
| | | [Br]$^-$ |
| | | [phosphates]$^-$ |
| | | [trifluoroacetate]$^-$ |

## 2.2 *Extraction Based on Ionic Liquids*

Extraction of aromatics from the mixed aromatic and aliphatic hydrocarbon streams with the ionic liquids are expected to required less process step and less the energy consumption. Differences separation of aromatic/aliphatic mixture by using extraction with ionic liquid and conventional solvent, ionic liquid had a negligible vapour pressure and has different behaviour in capacity depending on the aromatics concentration compared to solvent like sulfolane (Meindersma *et al*., 2005). Other than that, because of the properties of ionic liquids are non- volatile nature, the extraction processes are really promising and the facilities solvent recovery as simple as flash distillation or stripping. According to Meindersma *et al.* (2005), the requirements of suitable extraction solvent for the separation of aromatic and aliphatic hydrocarbon are:

- High solubility of aromatic hydrocarbons in the ILs.
- No or low solubility of aliphatic hydrocarbon in the ILs.
- High separation factor and a high distribution coefficient.
- Simple recovery of the ILs from both the extract and raffinate phase.
- Fast mass transport from the feed phase to the ILs phase.

Toluene from aromatic hydrocarbon and heptane from the aliphatic hydrocarbon group was chosen as a model for the separation between aromatic/ aliphatic hydrocarbon. According to Weissermal and Arpe (2003), no feasible processes are available for the separation of aromatic and aliphatic hydrocarbon in the range below 20 percent of aromatic in the feed mixture. Because of that reason, the large number of ionic liquids with different cations and anions were tested with a mixture of 10 (v/v) percent toluene in heptane as a reference for the selection of suitable ionic liquids for the separation (Meindersma *et al*., 2007). Extraction of this hydrocarbons experiment will be performed with the most suitable ionic liquid. In the industries, sulfolane are conventional in extraction processes because of that reason this solvent are used as a benchmark for this separation ($S_{tol/hep}$= 30.9, $D_{tol}$=0.31 at 40 °C). To make sure this experiment come out with the good results, the suitable ionic liquids for this separation must show $S_{tol/hep} \geq 30.9$, $D_{tol} \geq 0.31$.

Aromatics hydrocarbon has low activity coefficients at infinite solution in several ionic liquids. Krummen *et al* (2002) have measured activity coefficient at infinite dilution for several solutes in ionic liquids like [mmim]Tf$_2$N, [emim]Tf$_2$N, [bmim]Tf$_2$N and [emim] ethyl-sulfate. From the data that was collected from the activities, the distribution coefficient and selectivity of these solutes can be calculated. From the calculations that was performed, the results showed that the ionic liquid [emim] ethylsulfate have highest selectivity where S=36.4 at 40 °C for separation toluene/ n-heptane, where the selectivity higher than selectivity from sulfolanes (Krummen et al., 2002). For the ionic liquids like [bmim]Tf$_2$N, it showed a lower selectivity but had higher capacity or distribution coefficient than the ILs with the cation [emim]$^+$ and [mmim]$^+$. This result also showed when do the separations for the aromatic/aliphatic hydrocarbon like benzene/cyclohexanes and benzene/hexane. From this data also, it can be conclude that the length of the R-group also affected because the shorter the R-group, it favourable for the aromatic/aliphatic hydrocarbon selectivity but it will decrease in the capacity.

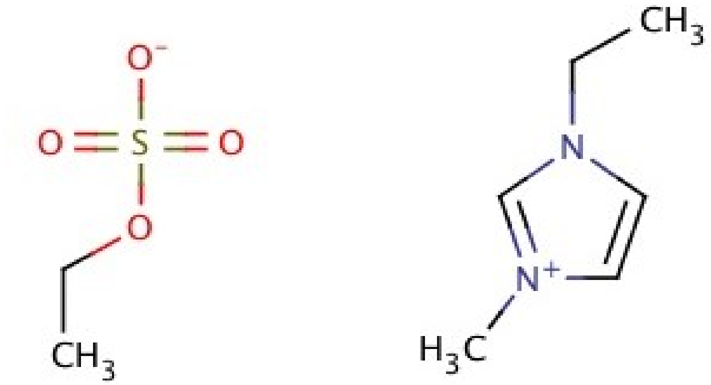


**Figure 2.2** 3-ethylimidazolium-ethylsulfate structures.

**Table 2.2** Physical and chemical properties 3-ethylimidazolium-ethylsulfate ([EIM][$EtSO_4$]). (Material Safety Data Sheet, 2009)

| **General Information** | |
|---|---|
| **Form** | Liquid |
| **Colour** | Pale Yellow |
| **Odour** | Not determine |
| **Change in condition** | |
| **Melting point/Melting range** | Less than -30°C |
| **Boiling point/Boiling range** | Not determined |
| **Sublimation temp/ start** | Not determined |
| **Flash point** | 162°C |
| **Ignition temperature** | Not determined |
| **Decomposition temperature** | Not determined |
| **Danger of explosion** | Do not present an explosion hazard |
| **Explosion limit** | |
| **Lower** | Not determined |
| **Upper** | Not determined |
| **Vapor pressure** | Not determined |
| **Density at 20°C** | 1.24 g/$cm^3$ |

## *2.3 Fourier Transform Infra- Red Spectroscopy (FTIR)*

Fourier transform infrared spectroscopy is the one method to analyze the sample in industries. This technique is to obtain an infrared spectrum of some phenomenon like absorption, emission, photoconductivity or Raman scattering of solid, liquids or gas. An FTIR spectrometer simultaneously collects spectral data in wide range. In this spectroscopy, IR radiation is passed through a sample and some of the infrared radiation is absorbed by the sample and some of it will pass through the transmitter. From the results, spectrum that developed will represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures was produce at the same infrared spectrum. Because of the FTIR ability, that makes this spectroscopy useful for several types of analysis like:

- It can identify unknown material.
- It can determine the quality or consistency of a sample.
- It can determine the amount of components in a mixtures

FTIR has been used as a workhouse technique for materials analysis in the laboratory for over seventy years. The infrared spectrum that was developed by FTIR will represent a fingerprint of a sample with the absorption peaks which are corresponds to the frequencies of the vibrations between the bonds of the atoms that are making up the materials. The sample that was analyzed will contained several combinations of materials and each of the materials will have different unique combination of atoms that are no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy ca results in a positive identification or qualitative analysis of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With modern software algorithms, infrared is an excellent tool for qualitative analysis. There are some major advantages of using FTIR over the disperse technique included in **Table 2.3**.

**Table 2.3** Advantages by using Fourier Transform Infra-Red spectroscopy (Thermo Nicolet, 2001)

| | |
|---|---|
| **Speed** | • Because all of the frequencies are measured simultaneously, mist measurements by FTIR are made in a matter of seconds rather than several minutes. This is sometimes referred to as the Felgett Advantages. |
| **Sensitivity** | • Sensitivity is dramatically improved with FTIR for many reasons. The detectors employed are much more sensitive the optical throughout is much higher (referred to as the Jacquinot Advantages) which results in much lower noise levels, and the fast scans enable the co-addition for several scans in order to reduce the random measurement noise to any desired level. |
| **Mechanical Simplicity** | • The moving mirror in the interferometer is the only continues moving part in the instrument. Thus, there is very little possibility of mechanical breakdown. |
| **Internally Calibrated** | • These instruments employ a HeNe laser as an on internal wavelength calibration standard (referred to as the Conned Advantages) |

# 3 MATERIALS AND METHODS

## *3.0 Chemicals*

Toluene (≥99.7 wt %) and n-Heptane (≥99.5 wt %) over molecular sieve were purchased from Sigma-Aldrich and used as received, without further purification. The ILs used is 3-ethylimidazolium-ethylslfate [EIM][EtSO$_4$] where obtained from the previous study.

## *3.1 FTIR Analysis*

There are several processes that need to follows in order to analyzing the ionic liquids that was used in this experimental and in order to characterize the ionic liquid, it was tested on Fourier Transform Infra-Red (FTIR) where an infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of the vibrations between the bonds of the atoms making up the material. This equipment was used to detect the functional group in ionic liquid, 3-ethylimidazoilum-ethylsulfate.

## *3.2 HPLC Analysis*

High Performance Liquids Chromatography (HPLC) was used in order to detect the percentage of the toluene before and after the extraction process with ionic liquids. This equipment (HPLC AGILENT TECH model 1200 SERIES and used a DAD UV detector that was set at 280 nm with the temperature was set at 30°C) was used for calibration curve establishment. The column that was used in high performance liquid chromatography is a column C18 with 5 micron (460 × 250 mm) analytical column. To analyze the samples, HPLC need the mobile phase to carry the sample pass through analytical column. For the sample aromatic/aliphatic mixtures, water- methanol mixtures was used as a mobile phase with the percentages 10 percent water and 90 percent methanol HPLC grade and the flow rate was set at one ml/minute. To avoid from the column jammed or the HPLC broken, the mobile phase need to filtered and degassed for the 30 minutes. This process is to make sure that no bubbles in the tube when the HPLC pumped the mobile phase into the column.

### 3.3 *Calibration Curve*

By using the HPLC, the calibration curve was developed in order to comparing the data that was collected from the samples. From the **Figure 3.1**, it shows that the graph for the toluene (v/v) % versus the Area (mAU*s) that represent the calibration curve for this experiment and the data for this graph was shown in the **APPENDICES B.**

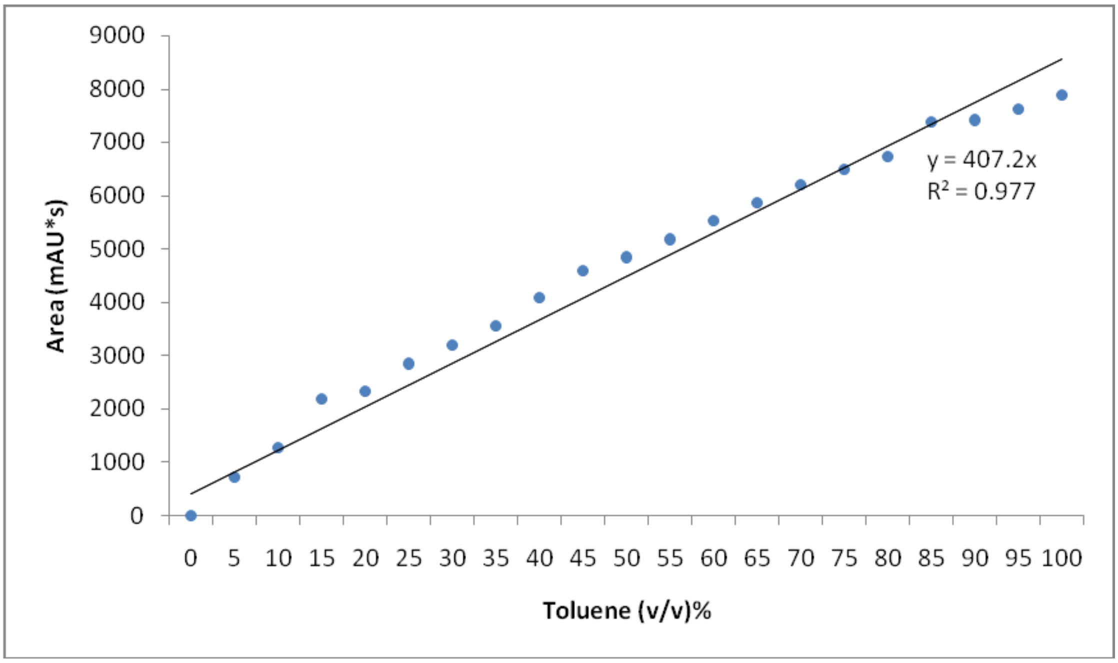


**Figure 3.1** Calibration Curve

By analyzing the data and the graph, it showed that the increasing pattern of the area with the volume ratio of toluene in mixtures. It means that the more the amount of toluene volume in the mixtures was detected by the analysis by HPLC, the area became increasing. To compare the toluene/heptanes mixture after the extraction, one straight line graph was developed by using MICROSOFT EXCEL in order to calculate how much the ionic liquid will extract the toluene in the mixture. In the straight line, the equation for the straight line are y= 407.2x and the value best fits data, $R^2$ = 0.977 where when the value closed to 1, it means the straight line was perfect fits between the data and the line drawn through them.

## *3.4 Analysis of Extraction*

For the extraction of toluene from the n-heptane, the mixtures need to extract with the 3-ethylimidazolium-ethylsulfate. To compare the results, six samples are chosen to make the extraction by sample volume ratios (toluene/n-heptane) are:

**Table 3.1** Ratios toluene and n-heptane.

| **Toluene (v/v)%** | **n- Heptane (v/v)%** |
|---|---|
| 100 | 0 |
| 80 | 20 |
| 60 | 40 |
| 50 | 50 |
| 40 | 60 |
| 20 | 80 |

Before start the extraction, the samples need to stir for 5 minutes to make sure it well mixing. By using ratios 1:1 for the mixture and ionic liquid, each sample mixtures was taken 2 ml and added with 2 ml of [EIM][EtSO$_4$] for the extraction. After that, the sample was stirred for 5 minutes to make sure the separation occurs and 10 minute for the samples to settling down. To calculate the distribution coefficient and selectivity for separation aromatic/aliphatic mixture with the ionic liquid, sample with ratio 50:50 toluene/n-heptane with the total volume 20 ml were stir for 120 minutes and every 5 min, 10 min, 15 min, 30 min, 60 min and 120 min, the sample was taken for 2 ml and mixed to 2 ml of ionic liquid. Like the method was using before, this sample also need to stir for 5 min and settle down for 10 min. To analyze and to tabulate the data, the sample that was extract with ionic liquid was injected into HPLC with the same setting when doing the calibration curve. For regenerated back the ionic liquid that was used for extraction, the rotary evaporator was used to get back the ionic liquid. To regenerate back, the ionic liquid was rotary for 2 hours with the temperature 111 °C with rotation 8 rpm. For the comparison, the sulfolane that a conventional solvent in industries was used as a benchmark with the selectivity, Stol/hept=30.9 and distribution coefficient, Dtol=0.31.

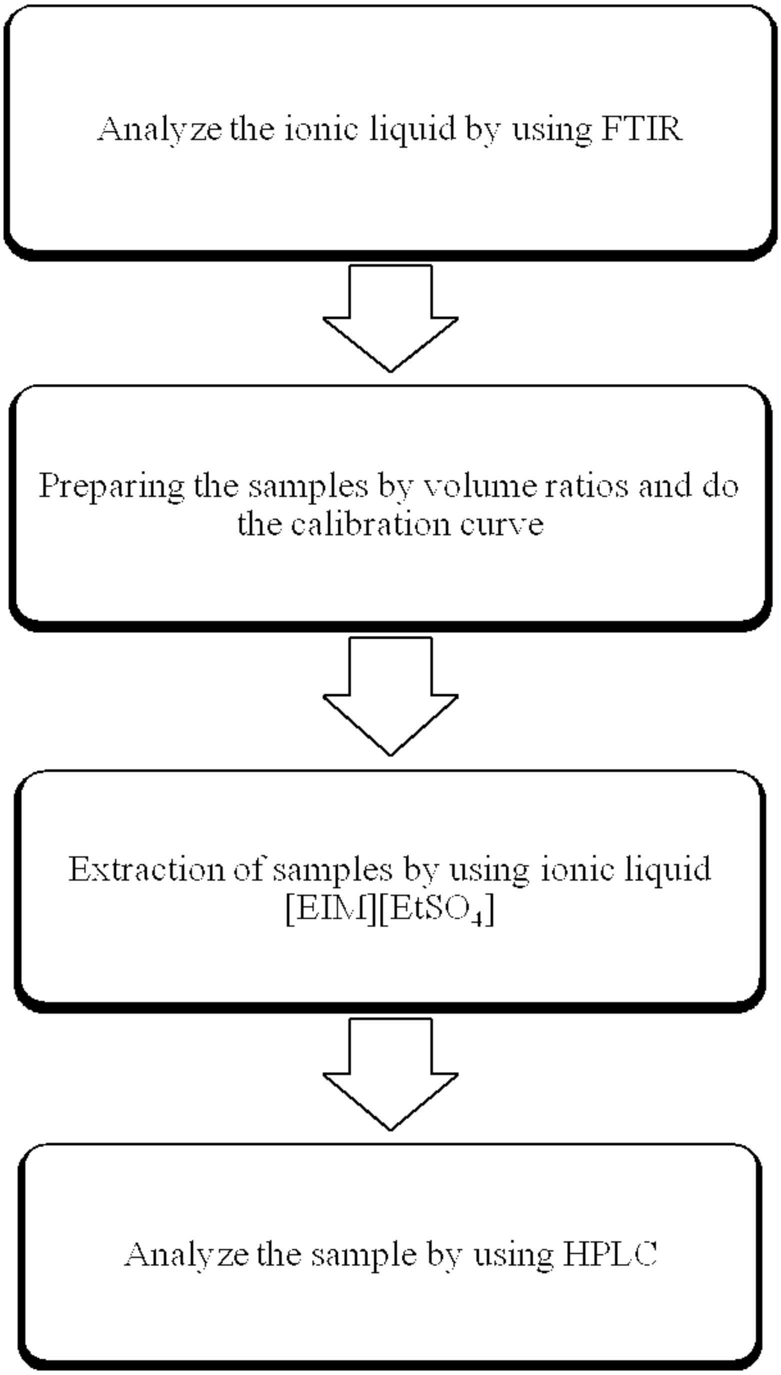


**Figure 3.2** Summary of Methodology

# 4 EXTRACTION OF AROMATIC FROM ALIPHATIC COMPOUNDS

## *4.0 Functional Group in Ionic Liquid*

From the analysis using Fourier Transform Infra Red (FTIR), the spectrum data for the ionic liquid [EIM][EtSO$_4$] was determined. **Figure 4.1** is a spectrum data that was developed in order to characterize the functional group in the ionic liquid 3-ethylimidazolium-ethylsulfate. In this spectrum data, there are several peaks that was appeared when the ionic liquids was analyzed. The functional group for the ionic liquid was characterized by comparing the wave number that was developed in FTIR with the standard infrared absorption frequencies.

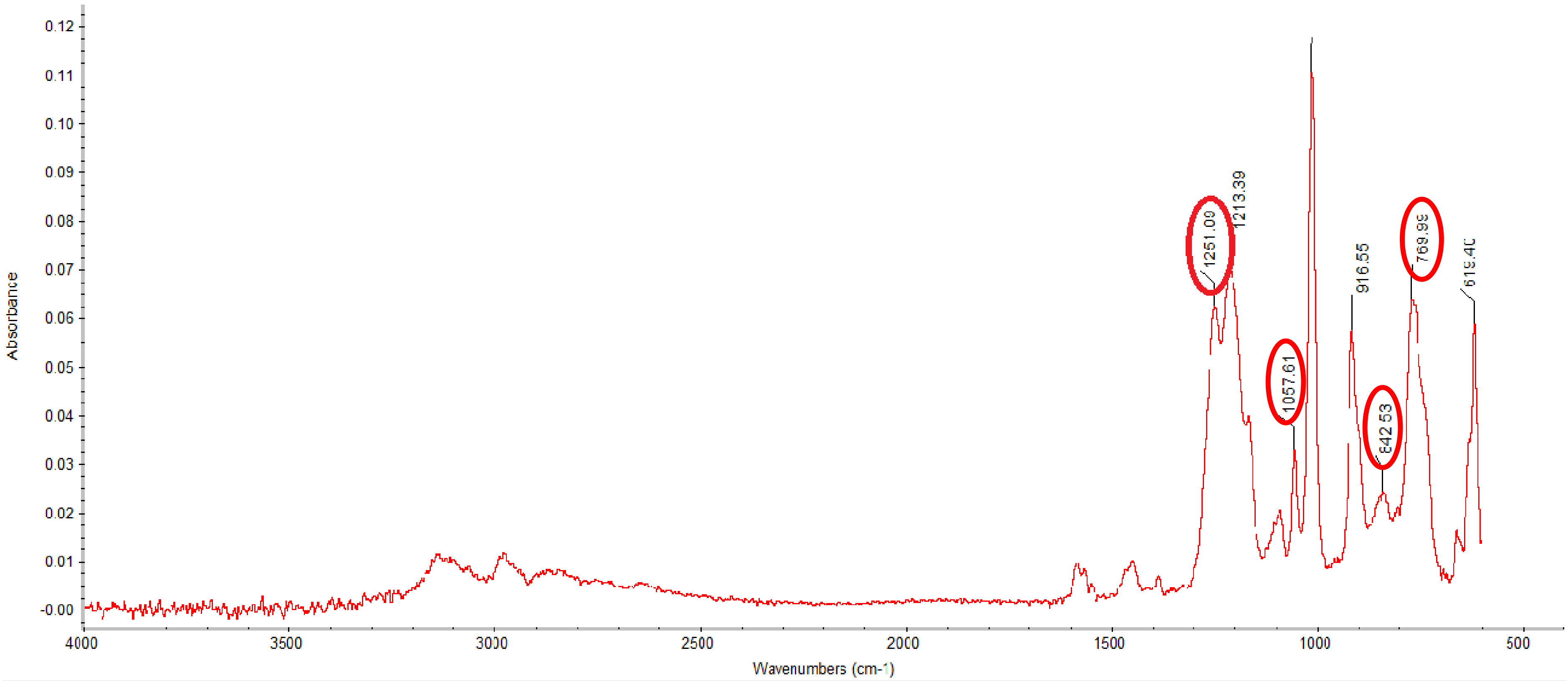


**Figure 4.1** Spectrum graph for determination of functional group in the ionic liquid.

**Table 4.1** List of Functional Group for Ionic Liquid [EIM][ESO$_4$]

| WAVENUMBERS (1/cm) | BONDING | RANGE |
|---|---|---|
| 1251.09 | (C-N stretch) | 1360-1250 |
| 1057.61 | (S=O stretch) | ~1050 |
| 842.53<br>769.99 | (S-O stretch) | 1000-750 |

From the data in **Figure 4.1**, there are three types of functional group that were determined in this ionic liquid. The first wave number that was founds in the analysis are 1251.09 cm$^{-1}$ where this wave number belongs to amine groups that had C-N stretch bond that in range 1360- 1250 cm$^{-1}$. For the second group with the wave number 1057.61 cm$^{-1}$, this wavelength belongs to sulfoxides group that had S=O stretch bond where the range approximately to 1050 cm$^{-1}$ and for the last group, with the wave number 842.53 cm$^{-1}$ and 769.99 cm$^{-1}$ are belongs to sulfonates group that had S-O stretch with the range between 1000- 750 cm$^{-1}$ . From the comparison with the ionic liquid structure, the amine group is belongs to the cation imidazolium base ionic liquids and for the sulfoxides and sulfonates belongs to anion ethylsulfate that was contains in the [EIM][EtSO$_4$].

## *4.1 Extraction of Toluene*

Extraction of the mixture of toluene/ n- heptanes as model oil samples by using a 3-ethylimidazolium-ethylsulfate ionic liquid is the one of the objective that need to achieve and the data need to analyze in order to know the behaviour of the ionic liquids. For this experiment, 6 samples was choose in order to know the effectiveness of the [EIM][EtSO$_4$] ionic liquids in extraction of the toluene from the mixture. There are 6 samples that are chosen for the extraction which is volume ratios of 20, 40, 50, 60, 80, and also 100 percent of toluene.

**Table 4.2** Extraction of Toluene

| Toluene (v/v) % | % Removal |
|---|---|
| 20 | 8.07 |
| 40 | 20.73 |
| 50 | 27.76 |
| 60 | 34.77 |
| 80 | 52.17 |
| 100 | 65.8 |

From the data that was collected, **Table 4.2** shows that the experimental and calculated data of the extraction with the ionic liquids [EIM][$EtSO_4$] are shown at 30°C. From the calibration curve, the value or the percentage of the toluene removal from the toluene/n-heptane mixture was calculated and it was illustrate in the **Figure 4.1.**

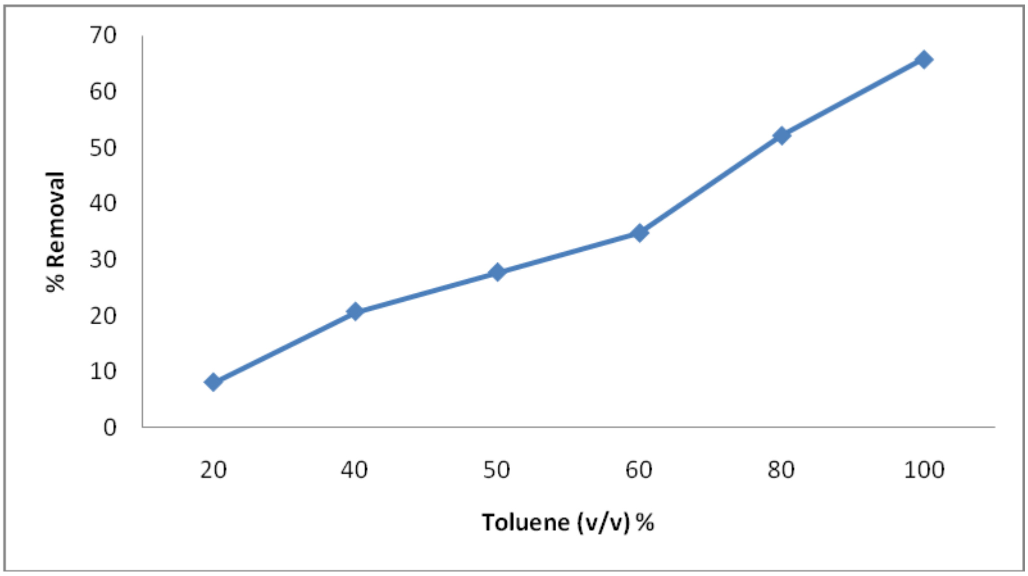


**Figure 4.2** Removal of the Toluene after Extraction at 30°C

From the **Figure 4.2**, it shows that the percentage of the removal of toluene after the extraction. From the data that was collected, the graph was showed the percentage removal is in increasing pattern where it was proportionally with the volume ratio of the toluene and n-heptane. From the observation, the percentage or the amount of the toluene that was removed from the mixture depends on the how much the percentage of the toluene in the mixture. For the examples, for the 20 percent of toluene the percentage of the toluene that was removed much lowered compared to the 100 percent of toluene. Another reason is the effect of the loading capacity for the ionic liquid to attract the toluene in the mixture. For this experiment, the amount of the ionic liquids to extract the mixture was limited to 2mL for each extraction processes. This was effected the extraction of toluene in the mixture. The effect of the alkyl chain also can give different results because of the shorter alkyl chain on the imidazolium ion is favourable for higher aromatic/ aliphatic selectivity (Krummen *et al*., 2002).

## *4.2 Distribution Coefficient and Selectivity*

**Table 4.3** Distribution Coefficient Data

| Time (min) | $C^{org}$tol | $C^{IL}$tol | $C^{org}$hept | $C^{IL}$hept |
|---|---|---|---|---|
| 5 | 0.2318 | 0.1159 | 0.7085 | 0.8841 |
| 10 | 0.2264 | 0.0869 | 0.7736 | 0.9131 |
| 15 | 0.227 | 0.0675 | 0.773 | 0.9459 |
| 30 | 0.2355 | 0.0541 | 0.7645 | 0.9459 |
| 60 | 0.2497 | 0.0438 | 0.703 | 0.9562 |
| 120 | 0.251 | 0.0331 | 0.749 | 0.967 |

From the data that was collected, in **Table 4.3**, the experimental and calculated data of the extraction with the ionic liquids [EIM][EtSO$_4$] are shown at 30°C. The distribution coefficients, Di, are directly calculated from the ratio of the mole fraction in the extract and raffinate phases. The distribution coefficient of the toluene and n-heptane are defined by the ratio of the mole fraction of the solute in the extract (IL) phase and in the raffinate (organic) phases, according to:

$$D_{tol} = C^{IL}{}_{tol}/C^{org}{}_{tol} \text{ and } D_{hept} = C^{IL}{}_{hept}/C^{org}{}_{hept} \quad (4.1)$$

And for the selectivity, $S_{tol/hept}$, of toluene/n-heptane is defined as the ratio of the distribution coefficients of toluene and n-heptane:

$$S_{tol/hept} = D_{tol}/ D_{hept} = (C^{IL}{}_{tol}/C^{org}{}_{tol})/(C^{IL}{}_{hep}t/C^{org}{}_{hept}) \quad (4.2)$$

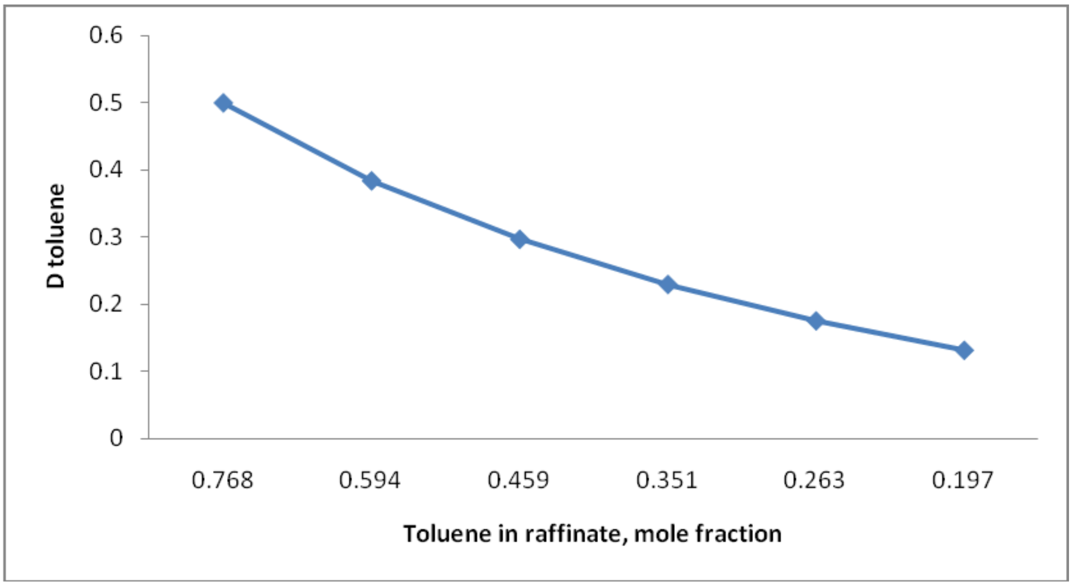


**Figure 4.3** Distribution coefficient for toluene, T = 30°C

From **Figure 4.3**, it can be seen that the distribution coefficient of the toluene that using 3-ethylimidazolium-ethylsulfate as the extractant is about 0.5 over the entire concentration range at 30°C. From this results, it showed that ionic liquid [EIM][$EtSO_4$] had higher distribution coefficient compared with the sulfolane where Dtol=0.31. Ionic liquid with higher distribution coefficient requires a lower solvent to feed ratios (Meindersma *et al*., 2005 &2007).

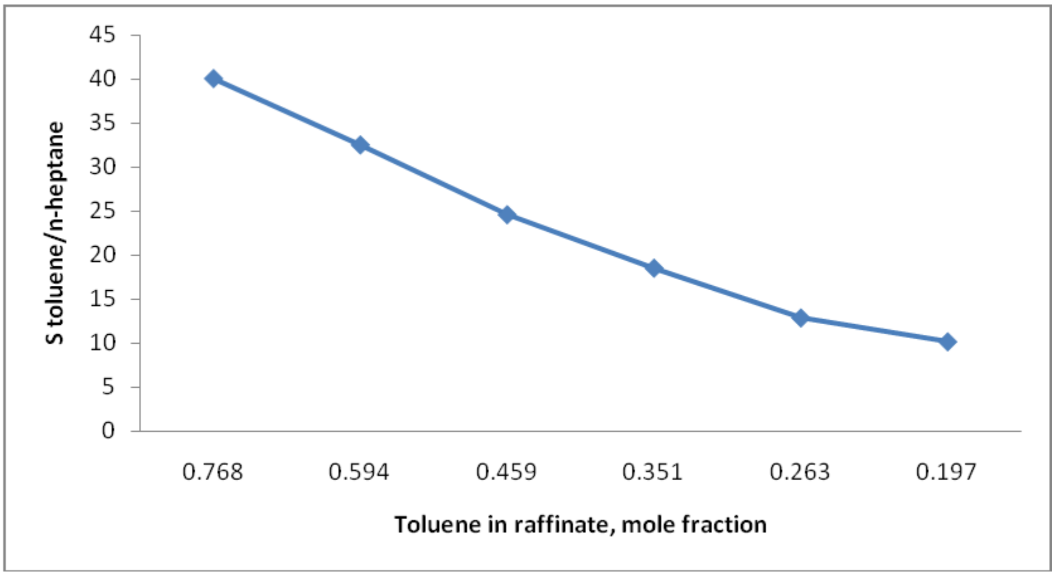


**Figure 4.4** Toluene/n-Heptane Selectivities, T = 30°C

In **Figure 4.4,** it showed that the selectivity of toluene/n-heptane selectivity at 30°C after the extraction with the ionic liquid. From the figure, the selectivity was decreases from 40.1 to 10.2 with the decreasing toluene content in mixture from 76.8 percent of toluene to 19.7 percent. When this results was compared with the sulfolane, the selectivity of 3-ethylimidazolium-ethylsulfate (Stol/hept= 40.1) higher than sulfolane ((Stol/hept= 30.9). In this study, the ionic liquid with the shorter alkyl chain that was attached to imidazolium ion also contributed for higher aromatic/aliphatic selectivity but it was affected to the lower contribution coefficient (Krummen *et al*., 2002). Other than that, for better effectiveness in extraction of toluene from n-heptane mixture, anion in the ionic liquid also affected. According to Meindersma *et al* (2002), anion like $HSO_4^-$, $C_2H_4SO_4^-$, $BF_4^-$, $CH_3SO_3^-$, and $(C_2H_5)_2PO_4^-$ (at 40°C) was more effective in increasing order and that effected to the distribution coefficient of both toluene and n-heptane with imidazolium as a base in ionic liquid. All the data for distribution coefficient and selectivity showed in **APPENDICES C**.

# 5 CONCLUSION

## *5.0 Conclusion*

The objective of this research is to study and characterized the ionic liquid and also to analyze the content of aromatic from aliphatic hydrocarbon after the extraction. For the first objective, by analyzing the ionic liquid on the FTIR, the wave number and the peak that was developed during the test shows that the ionic liquid, 3-ethylimidazolium-ethylsulfate consist of amine, sulfoxide, and sulfonates group and from the analysis this ionic liquids is from the amine group. For the second objective, to analyze the contents of the aromatic/aliphatic compound where it is a mixture of toluene and n- heptane. To analyze the data of the extraction, the calibration curve was developed to find the equation for the straight line where it is **$y = 407.3\ x$.** For the calculations, 6 sample that was chosen and it was extracted with the [EIM][$EtSO_4$] and from the results, it showed the increasing of the toluene removal that depends on the amount or the percentages of the toluene volume ratios in the mixtures. In this researched also, the distribution coefficient and selectivity of toluene in the toluene/n-heptane mixture was calculated in order to compared with conventional solvent in industry, sulfolane with selectivity, Stol/hept=30.9 and distribution coefficient, Dtol=0.31. After the extraction, the data was showed that, the ionic liquid [EIM][$EtSO_4$] are more effective compare with the sulfolane because after the calculation, the selectivity (Stol/hept=40.1) and distribution coefficient (Dt0l=0.5) for ionic liquid at 30°C are higher than sulfolane.

## *5.1 Future work*

The research carried in this project (liquid- liquid extraction) is currently being expended in order to separated the aromatic from aliphatic that was had the close range of the boiling point. The extraction using ionic liquids has more advantages to the industrial application because of the separation is less and the recovery facilities for this process are using technique as simple as flash distillation or stripping compare to the other conventional separation that need more equipment and steps. Other than that, because of ionic liquids have a negligible vapour pressure, it can recovered back by evaporating the extracted hydrocarbon from the ionic liquid phase and this process promising less investment cost and also energy consumptions compared to the sulfolane that was common solvent in the industries for separation process.

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# APPENDICES

## Gantt Chart for Undergraduate Research Project

| Subject/week | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Getting topic from coordinator | 🟦 | | | | | | | | | | | | |
| Meeting and discussion with supervisor | | 🟦 | 🟦 | | 🟦 | 🟦 | 🟦 | | | | | | |
| Finding journal and other information | | 🟦 | 🟦 | 🟦 | 🟦 | 🟦 | | | | | | | |
| Writing proposal (draft) | | | 🟦 | 🟦 | 🟦 | 🟦 | | | | | | | |
| Prepare slide presentation | | | | 🟦 | 🟦 | 🟦 | | | | | | | |
| Presentation | | | | | | 🟦 | 🟫 | | | | | | |
| Finalize proposal report | | | | | | 🟦 | 🟫 | | | | | | |
| Seminar methodology | | | | | | | | 🟦 | | | | | |
| Prepare for URP II | | | | | | | | 🟦 | 🟦 | 🟦 | 🟦 | 🟦 | 🟦 |

🟫 Actual Progress

## Gantt Chart for Undergraduate Research Project II

| Subject/week | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Literature Research | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ |  |
| Experiment Familiarization | ■ | ■ | ■ |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Equipment Setup | ■ | ■ | ■ | ■ |  |  |  |  |  |  |  |  |  |  |  |  |
| Experiment Work |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| a) Calibration Curve |  |  | ■ | ■ | ■ | ■ |  |  |  |  |  |  |  |  |  |  |
| b) Extraction Method |  |  | ■ | ■ | ■ | ■ | ■ | ■ |  |  |  |  |  |  |  |  |
| c) Analysis Method |  |  | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ |  |  |  |  |  |
| Discussion with Supervisor |  |  | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ |  |  |  |  |
| Preparation of Full Thesis |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Preparation of Technical Paper |  |  |  |  |  |  |  |  |  |  |  | ■ |  |  |  |  |
| Submission of Draft Thesis |  |  |  |  |  |  |  |  |  |  |  | ■ |  |  |  |  |
| Correction for Draft |  |  |  |  |  |  |  |  |  |  |  | ■ | ■ |  |  |  |
| Submission of Final Draft Thesis |  |  |  |  |  |  |  |  |  |  |  |  |  | ■ |  |  |
| Submission of Full Thesis |  |  |  |  |  |  |  |  |  |  |  |  |  |  | ■ | ■ |

## APPENDICES A

## EQUIPMENT AND PROCESS

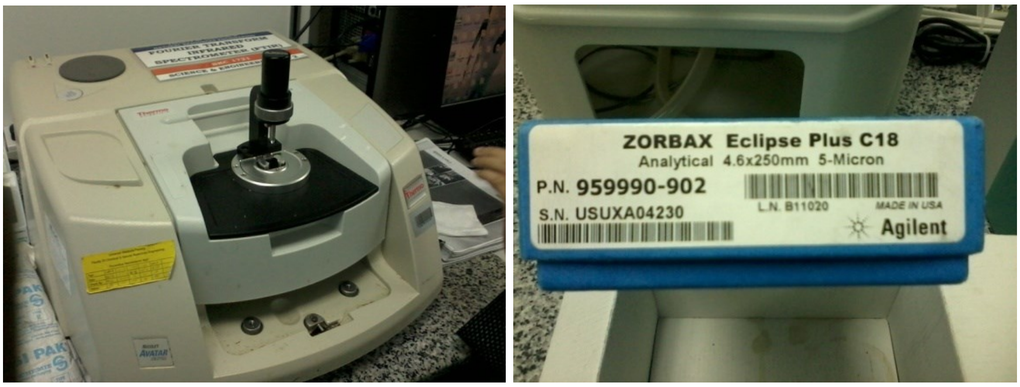

**Figure A.1** Fourier Transform Infra Red and High Performance Liquid Chromatography column

**Figure A.2** Preparing the mobile phase (Degassed and filtered process)

## APPENDICES B

### Calculation:

### Calibration curve

To find the toluene volume ratios in the toluene/heptanes mixtures:

Total volume mixtures = 6 mL

First: 5 % toluene by volume ratio = 0.05 × 6 mL

= 5.7 mL

- The volume of heptane are = 6 mL – 5.7 mL = 0.3 mL

**Unit conversion:**

1 mL = 1000 microliter

**Table B.1** The volume ratios of the of the toluene/heptanes mixtures

| **Percentage of the volume ratios of the mixtures (v/v) %** | | **Total volume (mL)** | |
|---|---|---|---|
| **Toluene** | **Heptane** | **Toluene** | **Heptane** |
| 95 | 5 | 5.7 | 0.3 |
| 90 | 10 | 5.4 | 0.6 |
| 85 | 15 | 5.1 | 0.9 |
| 80 | 20 | 4.8 | 1.2 |
| 75 | 25 | 4.5 | 1.5 |
| 70 | 30 | 4.2 | 1.8 |
| 65 | 35 | 3.9 | 2.1 |
| 60 | 40 | 3.6 | 2.4 |
| 55 | 45 | 3.3 | 2.7 |
| 50 | 50 | 3.0 | 3.0 |
| 45 | 55 | 2.7 | 3.3 |
| 40 | 60 | 2.4 | 3.6 |
| 35 | 65 | 2.1 | 3.9 |
| 30 | 70 | 1.8 | 4.2 |
| 25 | 75 | 1.5 | 4.5 |
| 20 | 80 | 1.2 | 4.8 |
| 15 | 85 | 0.9 | 5.1 |
| 10 | 90 | 0.6 | 5.4 |
| 5 | 95 | 0.3 | 5.7 |

**Table B.2** The analysis data from the HPLC

| **Volume ratio toluene (v/v)%** | **Area (mAU*s)** | **Retention time (min)** |
|---|---|---|
| 5 | 717.63037 | 3.92 |
| 10 | 1274.34326 | 3.923 |
| 15 | 2187.43237 | 3.968 |
| 20 | 2329.5354 | 3.953 |
| 25 | 2846.08105 | 3.94 |
| 30 | 3195.80249 | 3.931 |
| 35 | 3562.30762 | 3.926 |
| 40 | 4086.91772 | 3.924 |
| 45 | 4583.31055 | 3.924 |
| 50 | 4841.10645 | 3.956 |
| 55 | 5179.73584 | 3.93 |
| 60 | 5531.71631 | 3.934 |
| 65 | 5862.71875 | 3.935 |
| 70 | 6194.69336 | 3.932 |
| 75 | 6494.91455 | 3.934 |
| 80 | 6729.42236 | 3.911 |
| 85 | 7417.38379 | 3.915 |
| 90 | 7379.39648 | 3.936 |
| 95 | 7620.01611 | 3.932 |
| 100 | 7878.37695 | 3.932 |
|  | 95912.84178 | 3.9328 |

**Total Area (mAU*s)** = 95912.84178 mAU*s

**Average Retention Time** = 3.9328 min

## APPENDICES C

## Extraction

From the calibration curve, the straight line equation is **$y = 407.3\ x$**

Where:

Y: Area (mAU*s)
X: Toluene (v/v) %

For extraction data, the % removal of toluene was calculated.

**Table C.1** Percentage of Toluene Before and After the Extraction

| Toluene (v/v) % (Before Extraction) | Toluene (v/v) % (After Extraction) |
|---|---|
| 20 | 11.93 |
| 40 | 19.27 |
| 50 | 22.24 |
| 60 | 25.23 |
| 80 | 27.83 |
| 100 | 34.20 |

**To calculate the percentage of removal:**

20% - 11.93% = 8.07 %

**Table C.2** Percentage of Toluene Removal from the mixture

| Toluene (v/v) % (Before Extraction) | % Toluene Removal |
|---|---|
| 20 | 8.07 |
| 40 | 20.73 |
| 50 | 27.76 |
| 60 | 34.77 |
| 80 | 52.17 |
| 100 | 65.8 |

**Table C.3** Distribution Coefficient

| Toluene in raffinate | Dtol | Dhept |
|---|---|---|
| 0.768 | 0.5 | 1.2479 |
| 0.594 | 0.384 | 1.1802 |
| 0.459 | 0.297 | 1.2063 |
| 0.351 | 0.2297 | 1.2373 |
| 0.263 | 0.1755 | 1.3602 |
| 0.197 | 0.1317 | 1.2912 |

**Table C.4** Selectivities

| $C^{org}$tol | Stol/hept |
|---|---|
| 0.2318 | 40.07 |
| 0.2264 | 32.54 |
| 0.227 | 24.62 |
| 0.2355 | 18.56 |
| 0.2497 | 12.91 |
| 0.251 | 10.2 |

# APPENDICES D

## PEAKS FROM HPLC (Calibration Curve)

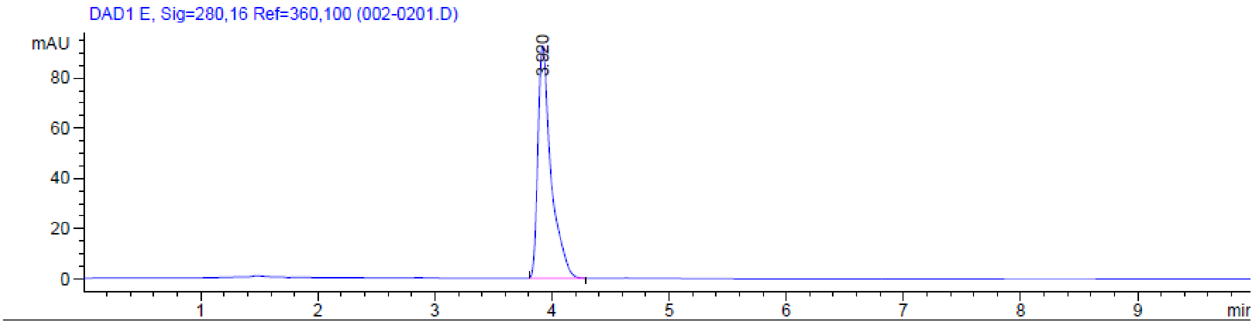

**Figure D.1** 5% toluene

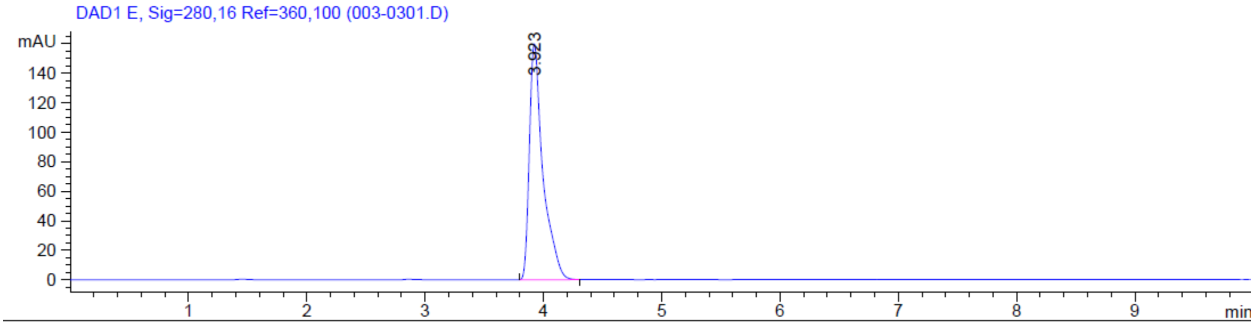

**Figure D.2** 10% toluene

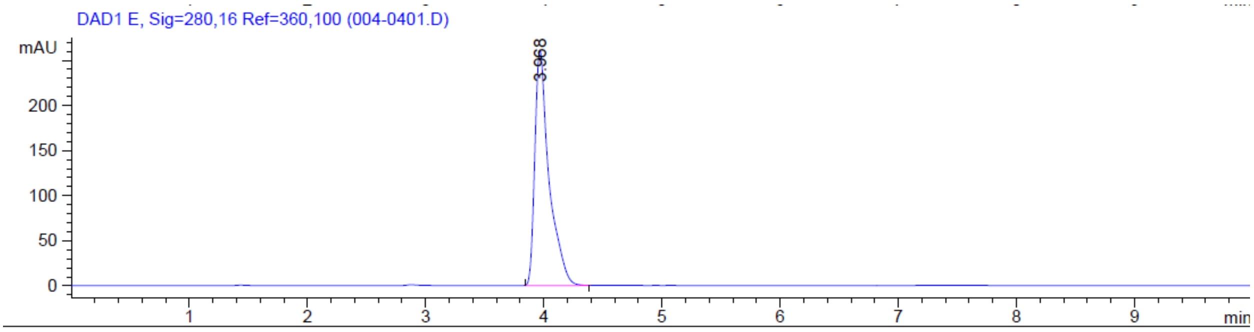

**Figure D.3** 15% toluene

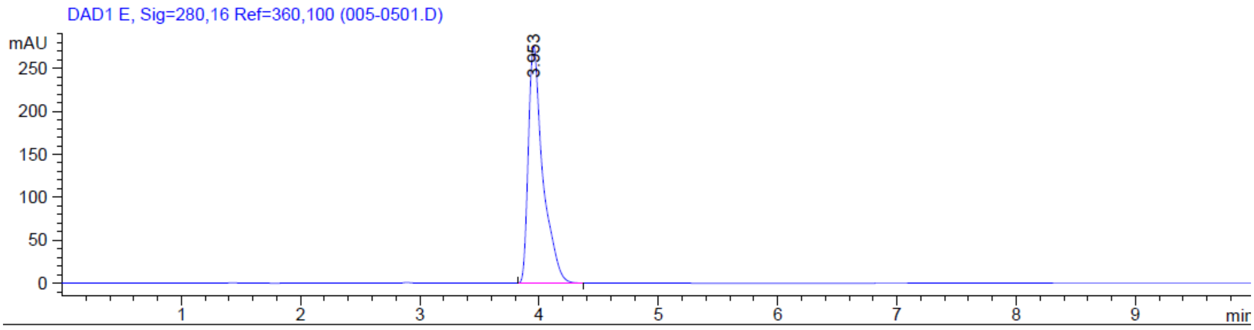

**Figure D.4** 20% toluene

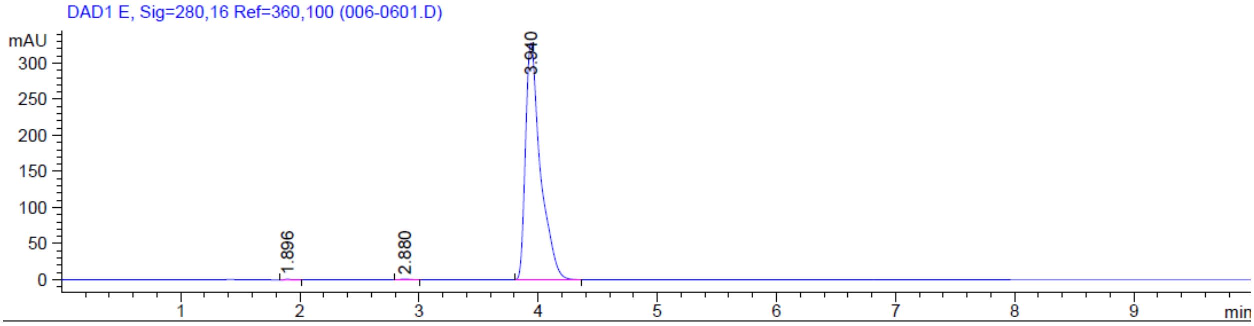

**Figure D.5** 25% toluene

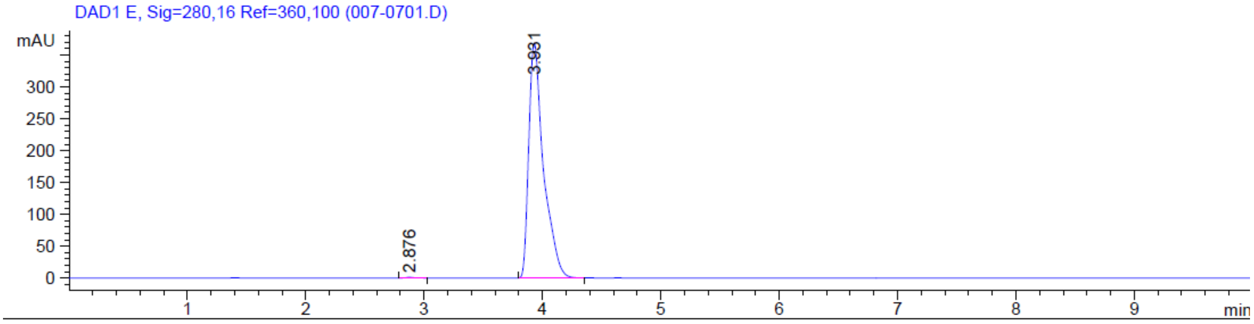

**Figure D.6** 30% toluene

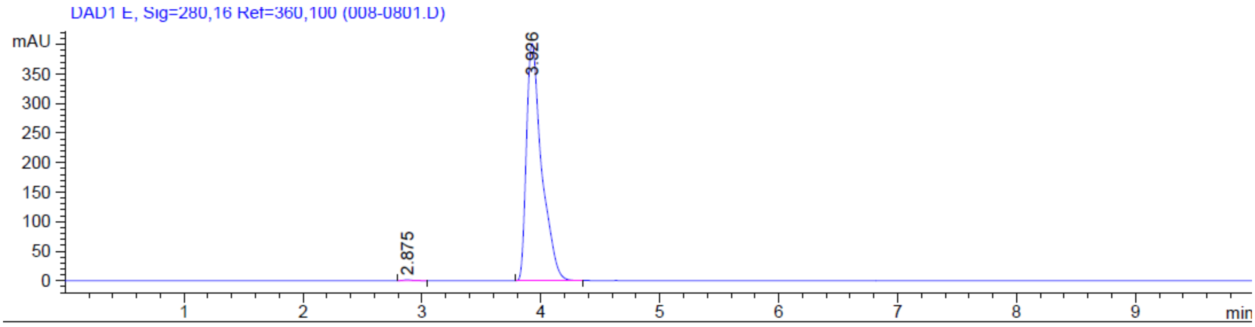

**Figure D.7** 35% toluene

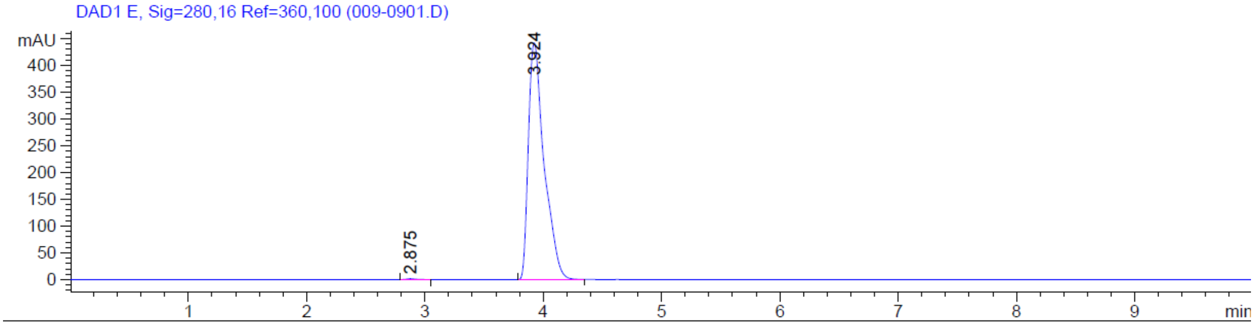

**Figure D.8** 40% toluene

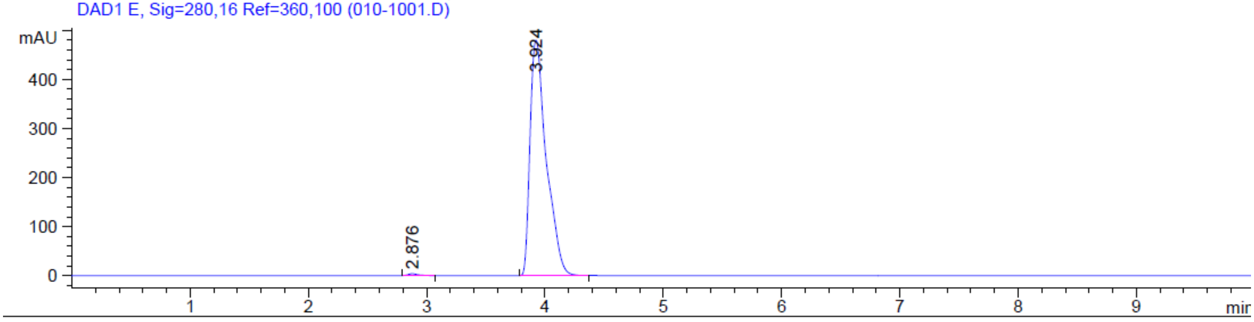

**Figure D.9** 45% toluene

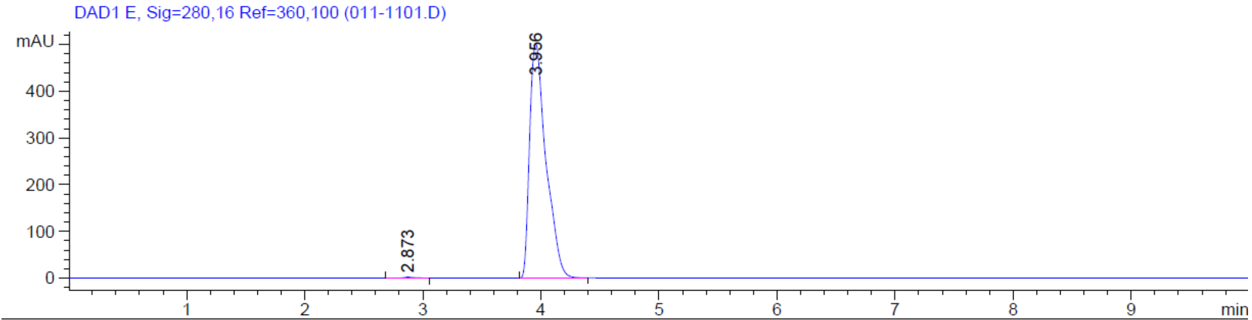

**Figure D.10** 50% toluene

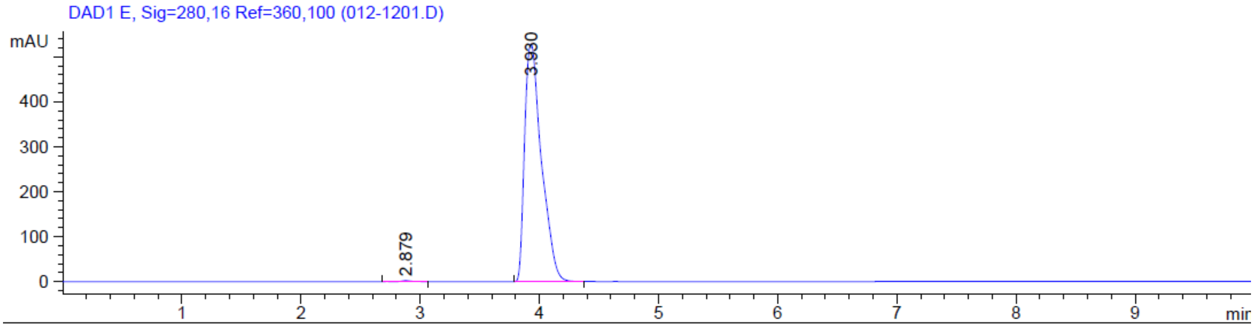

**Figure D.11** 55% toluene

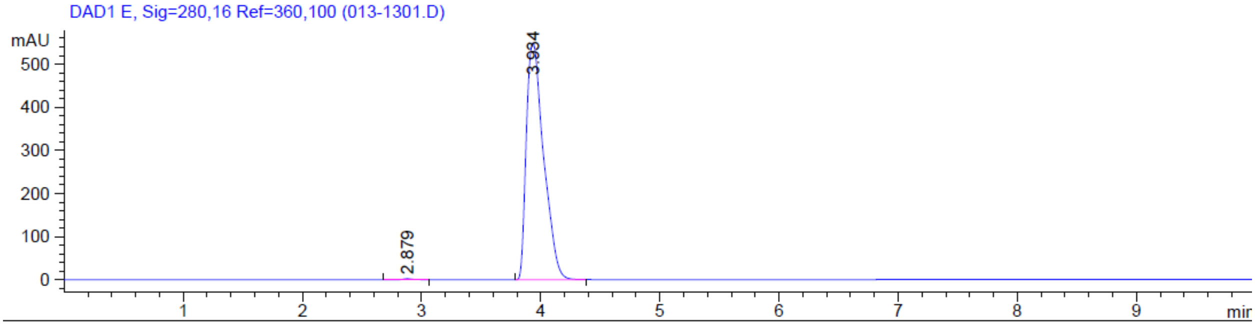

**Figure D.12** 60% toluene

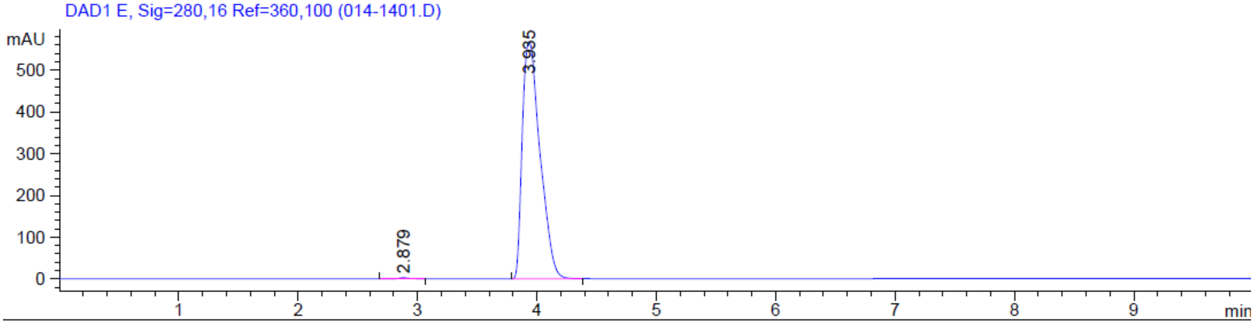

**Figure D.13** 65% toluene

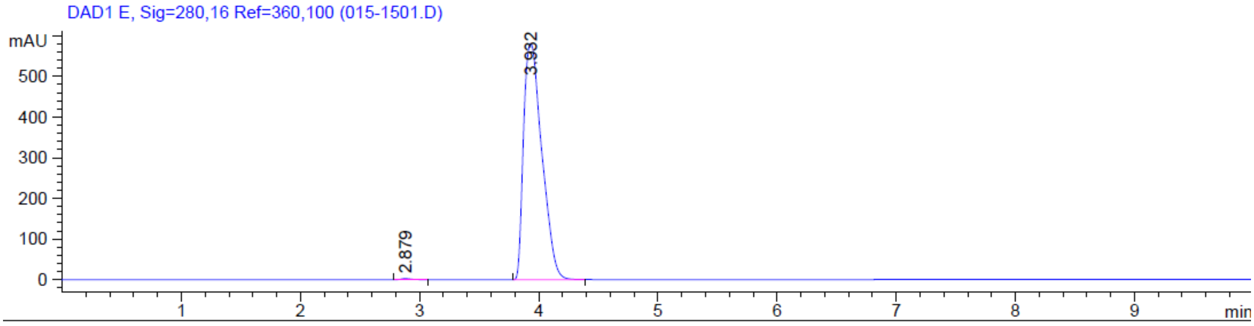

**Figure D.14** 70% toluene

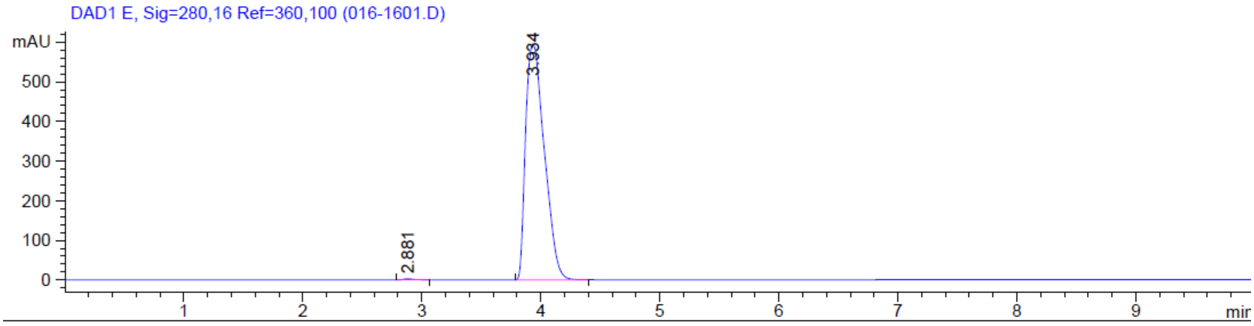

**Figure D.15** 75% toluene

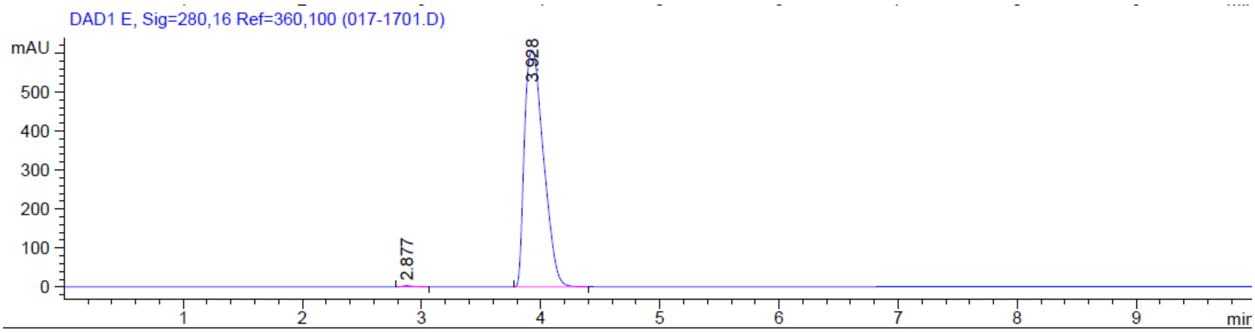

**Figure D.16** 80% toluene

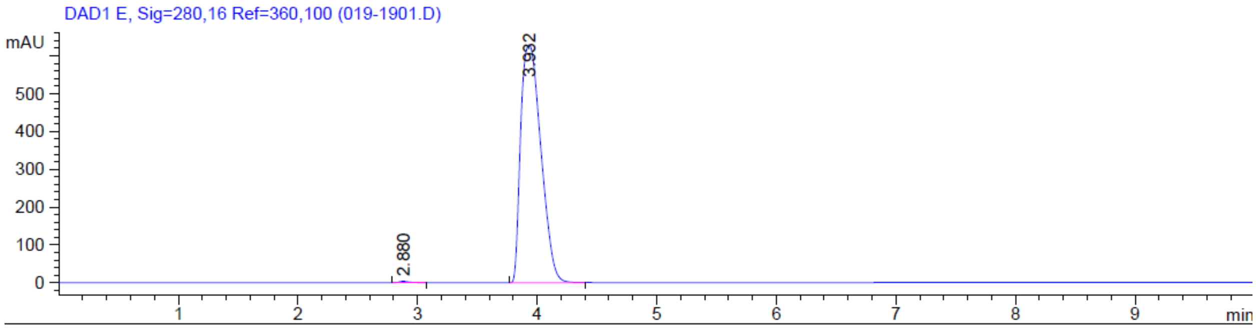

**Figure D.17** 85% toluene

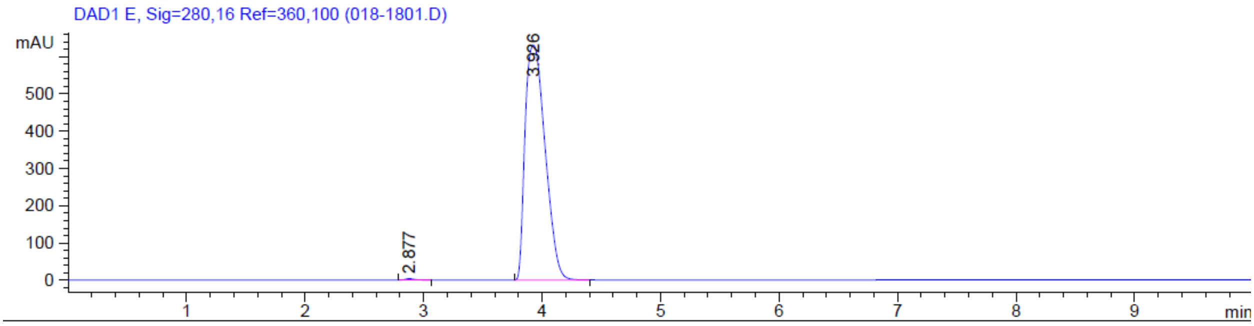

**Figure D.18** 90% toluene

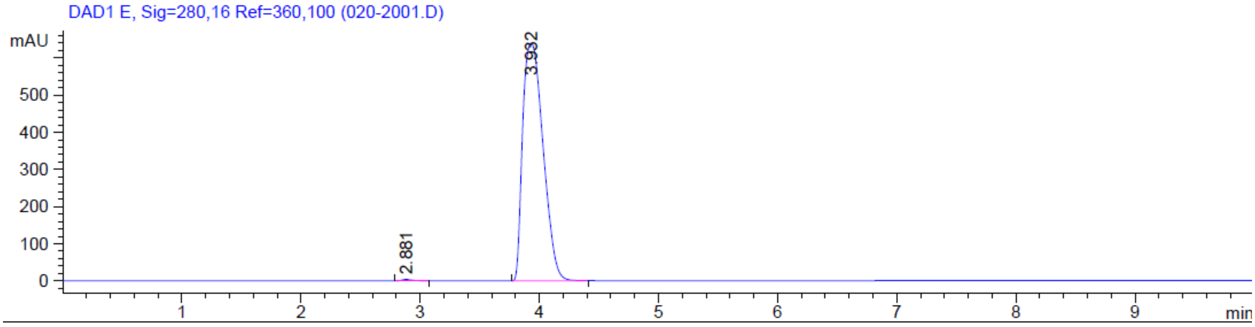

**Figure D.19** 95% toluene

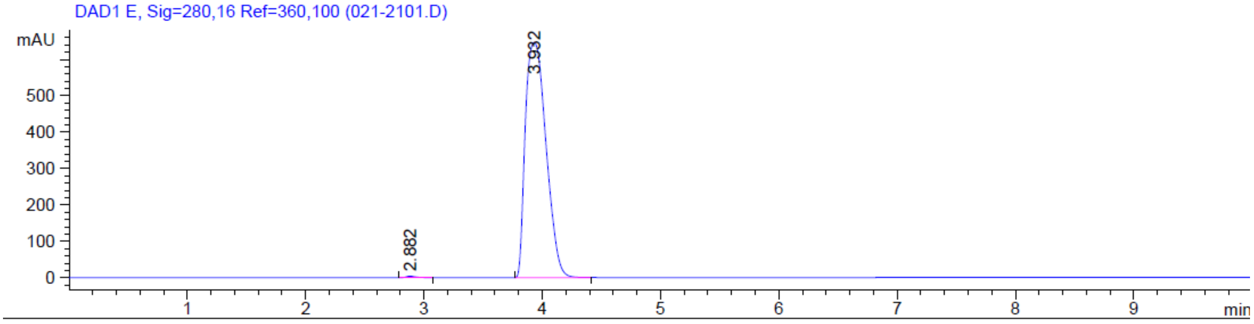

**Figure D.20** 100% toluene

**PEAKS FROM HPLC (Extraction)**

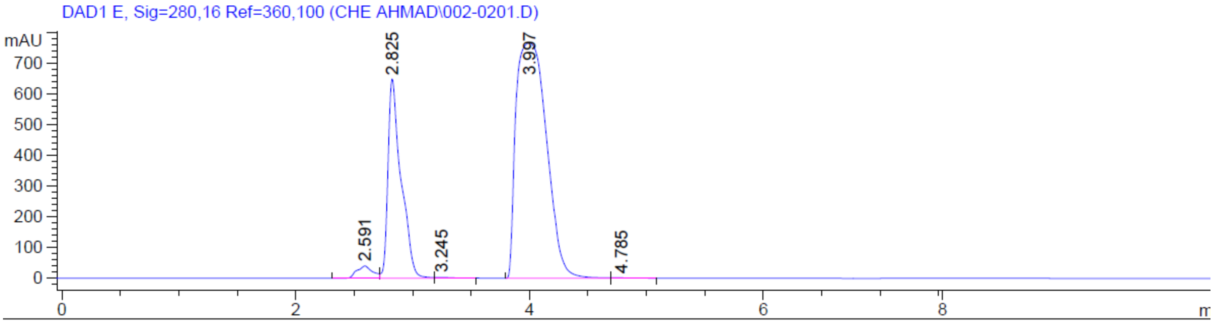

**Figure D.21** 100% toluene (Extraction)

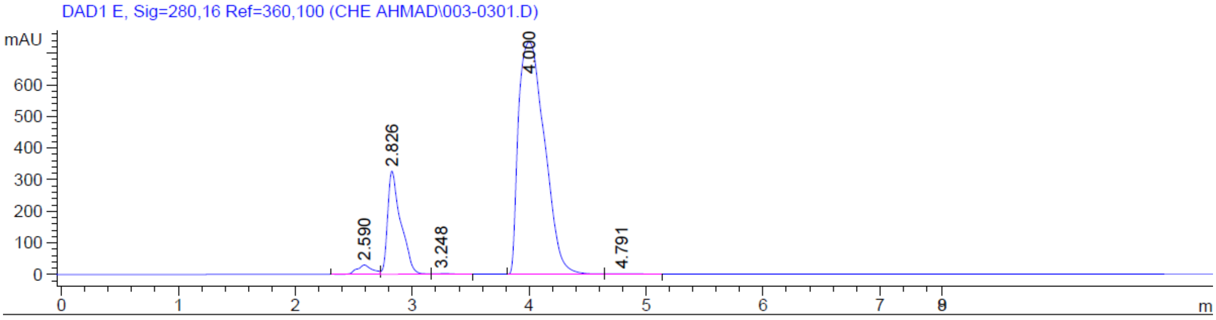

**Figure D.22** 80% toluene (Extraction)

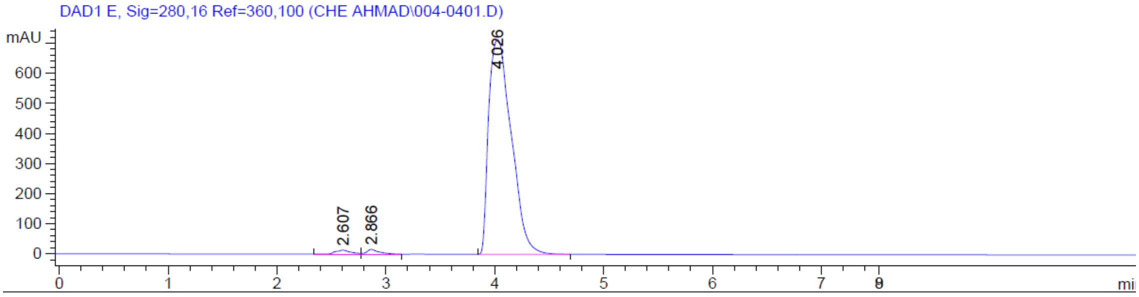

**Figure D.23** 60% toluene (Extraction)

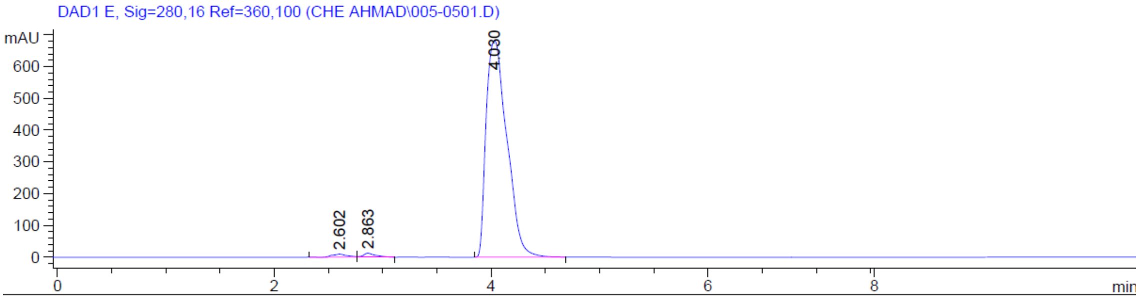

**Figure D.24** 50% toluene (Extraction)

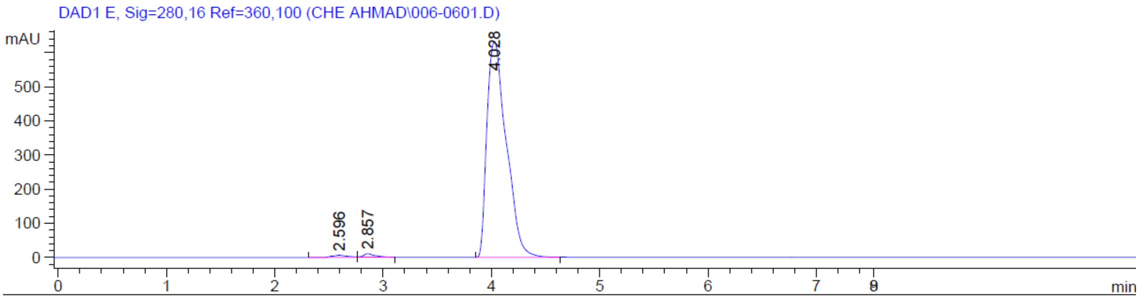

**Figure D.25** 40% toluene (Extraction)

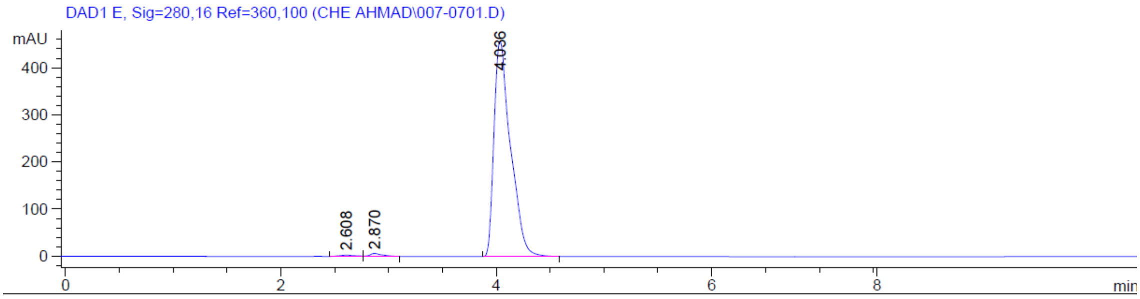

**Figure D.26** 20% toluene (Extraction)

## PEAKS FROM HPLC (Stirring Effect)

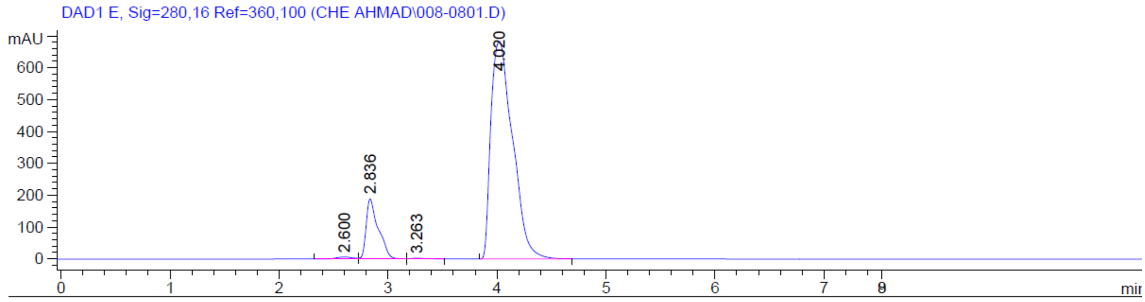
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**Figure D.27** 5 min

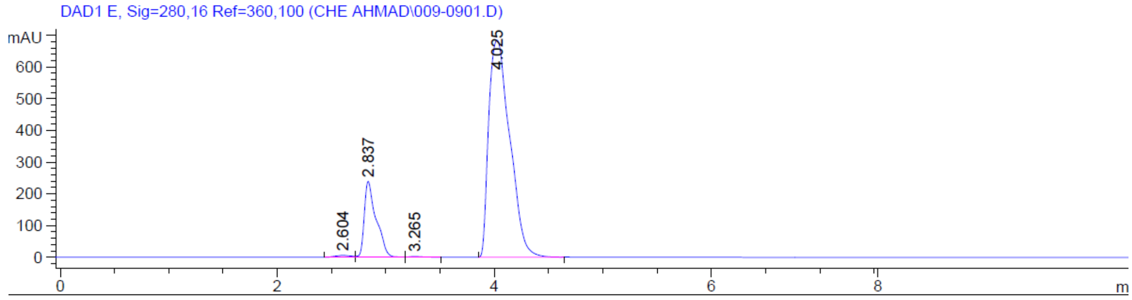
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**Figure D.28** 10 min

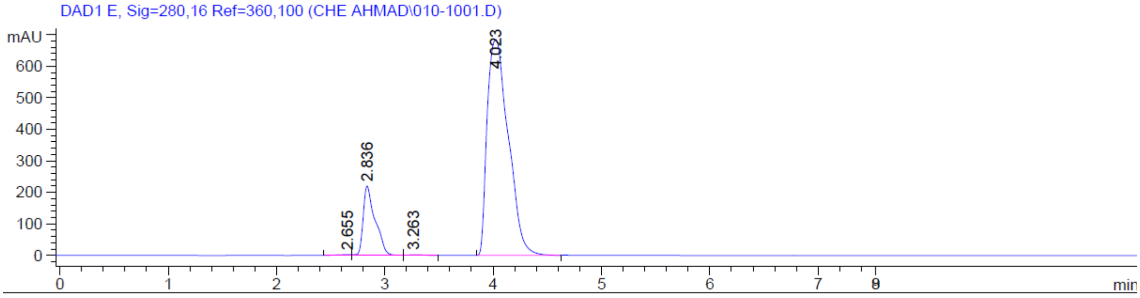
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**Figure D.29** 15 min

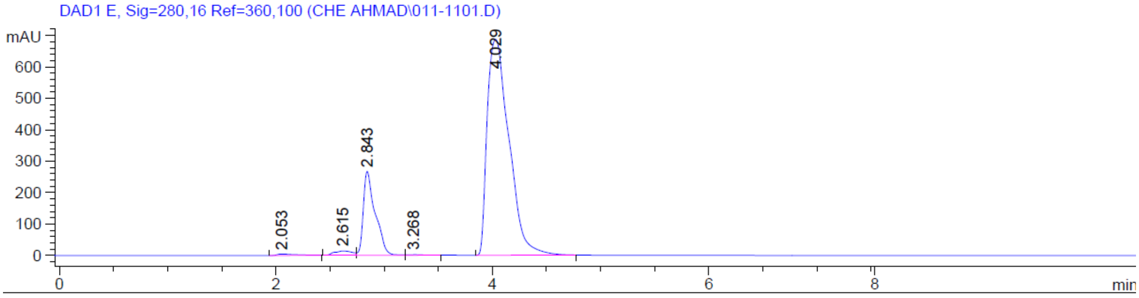
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**Figure D.30** 30 min

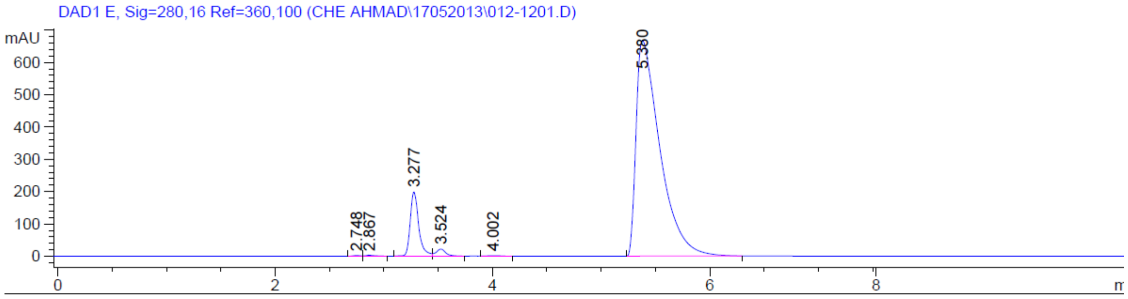

**Figure D.31** 60 min

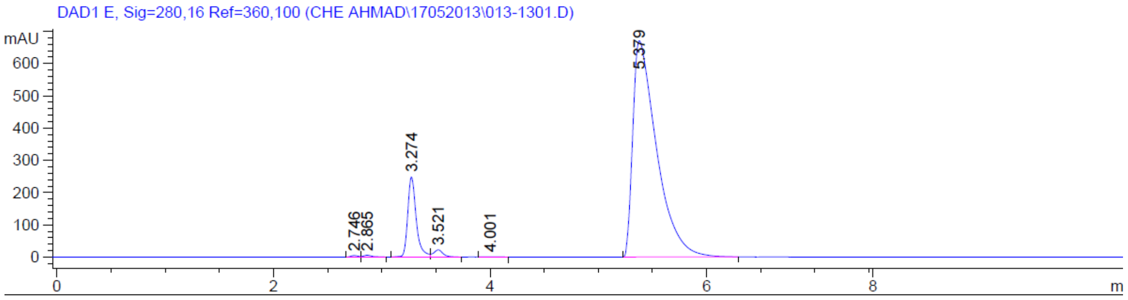

**Figure D.32** 120 min

# SEPARATION OF AROMATIC FROM ALIPHATIC BY USING [EIM][EtSO$_4$] IONIC LIQUIDS

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## ABSTARCT

This paper presents the separation of aromatic from the aliphatic hydrocarbon mixtures. The separation of this mixture is very challenging since these hydrocarbons have boiling point in a close range and several combination form an azeotrope. Toluene and *n*-heptane are known to have a very close boiling point, thus difficult to separate by fractionation with distillation. The present studies focusing on separating toluene from *n*-heptane using 3-ethylimidazolium-ethylsulfate [EIM][EtSO$_4$]. From the analysis of data by using the FTIR and HPLC, the functional group of ionic liquid can be determined as amine group and for the analyzing the data for the extraction, the removal of the toluene from the mixture shows the positive results where the toluene was separated from the aromatic/aliphatic mixtures increases and it depends on the amount or percentages of the volume ratios of the toluene compound in the mixtures. From the results of stirring, it shows that the distribution coefficient of toluene was decreasing with the increasing of the removal of the toluene from the toluene/n-heptane and the selectivities at the temperature 30°C was increasing with decreasing toluene content in the feed.

*Keywords:* Separation, Toluene/n-Heptane mixture, Azeotrope, Ionic Liquids, 3-ethylimidazolium-ethylsulfate [EIM][EtSO$_4$].

## INTRODUCTION

Separation of aromatic form aliphatic hydrocarbon by using ionic liquids (ILs) have achieved much attention and more improving to be valuable and useful in a multitude of different application since separation of aromatic hydrocarbon (benzene, toluene, ethyl benzene, and xylene) from the $C_4$ and $C_{10}$ aliphatic hydrocarbon mixtures is very challenging because of these hydrocarbon have close ranged boiling point and several of the combination form azeotrope. From the Meindersma et al (2005), the most conventional process for the separation of hydrocarbon mixtures are liquids extraction that suitable for the range 20-65 wt.% aromatic content, extractive distillation for the range 65-90 wt.% aromatics and azeotropic distillation for the high aromatic content, >90 wt.% and for the liquid-liquid separation, the common solvent used in the industries are polar component such as sulfolane. The types of solvent require additional distillation steps to separate the extraction solvent from the extract and raffinate streams that cost more investment and energy consumption (Pereiro and Rodriguez., 2009).

According to Weissermel and Arpe, no feasible processes are available for the separation of aromatic and aliphatic hydrocarbons in range below 20% aromatic in the feed mixture. Since the extraction with the conventional solvent is not of option, the application of ionic liquids was develop. The extraction processes using the ionic liquid is better because of their non-volatile in nature and the facilities of recovery using technique as simple as flash distillation or stripping compared to the complicated recovery for the sulfolane. In addition, extraction of aromatic from mixed aromatic/aliphatic stream with the ionic liquids is expected ti required less process step and less energy consumption because of ionic liquids have a negligible vapor pressure. The variability of the anion and R group in the imidazolium, pyridinium, ammonium or phosponium cations may be used to adjust the properties of the ionic liquids. Because of the inic liquids have a wide liquids range (~300°C), it was allowed a better kinetic control on the reactions.

For the selection of the type of the ionic liquids, it is remarkable that most of the ionic liquids used for the extraction of the hydrocarbon compounds mention imidazolium-based ionic liquids. The reason is that these ionic liquids a very versatile and easy to prepare, although HF formation is likely, as reported by Swatloski et al (2003). The requirements of a suitable ionic liquid for the separation of aromatic from aliphatic hydrocarbon are:

- High solubility of aromatic hydrocarbon in the ionic liquid
- No or low solubility of aliphatic hydrocarbon in ionic liquid
- High separation factor and a high distribution coefficient
- Simple recovery of the ILs from both the extract and raffinate phase
- Fast mass transport from the feed phase to ILs phase

A higher selectivity means the purer product and less extraction of aliphatic and a higher distribution coefficient requires a lower solvent to feed ratio.

## MATERIALS AND METHODS

### Chemicals

Toluene (≥99.7 wt %) and n-Heptane (≥99.5 wt %) over molecular sieve were purchased from Sigma-Aldrich and used as received, without further purification. The ILs 3-ethylimidazolium-ethylslfate [EIM][EtSO$_4$] (≥97.0 wt %) where obtained from the previous study.

### Sample Preparation

For this experiment, for the first step, toluene and n-heptane was mixed together with the different volume ratios between the liquids. There are 6 samples which is the toluene ratios for each sample is 20%, 40%, 50%, 60%, 80%, and 100 % where the total volume is 6mL. For the second step which is to determine the results for the stirring effect, the volume ratio for toluene and n-heptane is 50:50 where the total volume is 20mL and each period, the sample was taken after 5 min, 10 min, 15 min, 30 min, 60 min and 120 min stirring.

## FTIR Analysis

Fourier Transform Infra Red (FTIR) was used to determine and characterize the functional group in the ionic liquid 3-ethylimidazolium-ethylsulfate. In this FTIR, the ionic liquid was tested and the data that produced in infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of the vibrations between the bonds of the atoms making up the material. Because of the unique combination of atoms in each different material, no two compounds produce the exact same infrared spectrum and in addition, the size of the peaks in the spectrum ia a direct indication of the amount of material present. So, this equipment was used to detect the functional group in ionic liquid, 3-ethylimidazoilum-ethylsulfate.

## HPLC Analysis

High Performance Liquids Chromatography (HPLC) was used in order to detect the percentage of the toluene before and after the extraction process with ionic liquids. This equipment (HPLC AGILENT TECH model 1200 SERIES and used a DAD UV detector that was set at 280 nm with the temperature was set at 30°C) was used for calibration curve establishment. The column that was used in high performance liquid chromatography is a column C18 with 5 micron (460 × 250 mm) analytical column. To analyze the samples, HPLC need the mobile phase to carry the sample pass through analytical column. For the sample aromatic/aliphatic mixtures, water- methanol mixtures was used as a mobile phase with the percentages 10 percent water and 90 percent methanol HPLC grade and the flow rate was set at one ml/minute. To avoid from the column jammed or the HPLC broken, the mobile phase need to filtered and degassed for the 30 minutes. This process is to make sure that no bubbles in the tube when the HPLC pumped the mobile phase into the column.

In order to determine the percentage of toluene removal, the calibration curve was developed to finding the standard for the volume ratios mixture of toluene/n-heptane as shown as in Figure 1. For the purpose of quantitative, standard curve were constructed using a line fit forced through zero where the equation and correlation for the curve was $y = 407.2\ x$ and $r^2 = 0.977$.

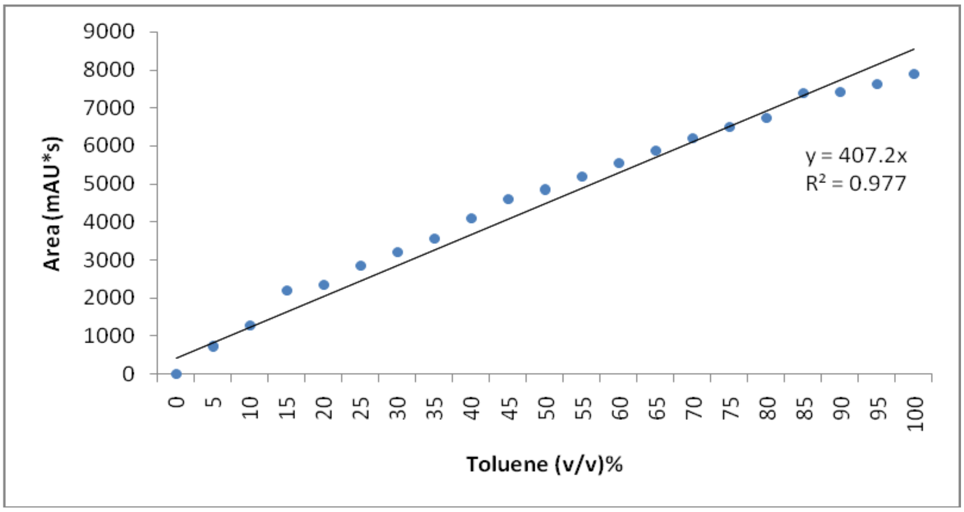

Figure 1: Calibration Curve for Toluene (v/v) %

## RESULTS AND DICUSSION

### Functional Group in Ionic Liquid

From the analysis using Fourier Transform Infra Red (FTIR), the spectrum data for the ionic liquid [EIM][EtSO$_4$] was determined. Figure 2 is a spectrum data that was developed in order to characterize the functional group in the ionic liquid 3-ethylimidazolium-ethylsulfate that was used in the extractions of toluene from the mixture. In this spectrum data, there are several peaks that was appeared when the ionic liquids was analyzed. The functional group for the ionic liquid was characterized by comparing the wave number that was developed in FTIR with the standard infrared absorption frequencies.

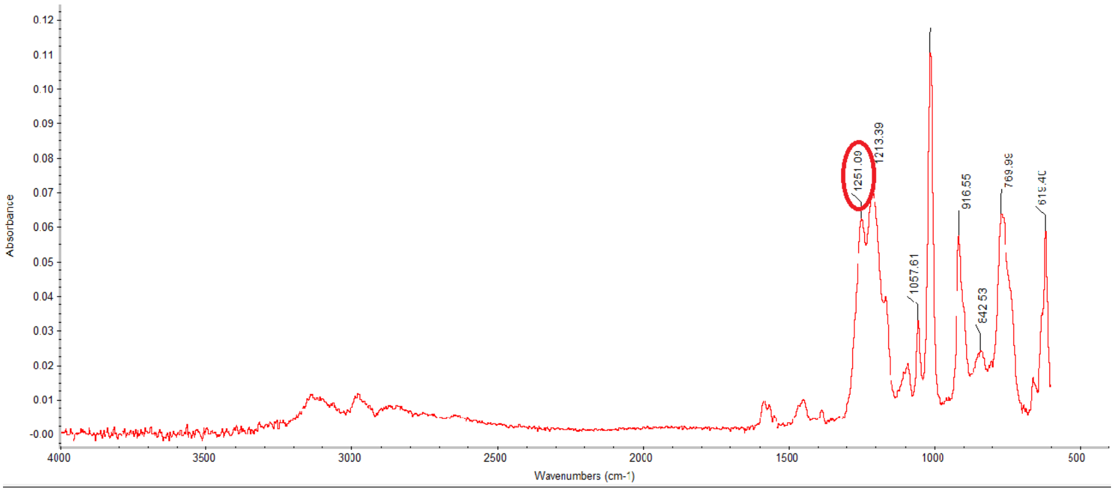

Figure 2: Spectrum graph for determination of functional group in the ionic liquid

From the data in Figure 2, there are three types of functional group that were determined in this ionic liquid. The first wave number that was founds in the analysis are 1251.09 cm$^{-1}$ where this wave number belongs to amine groups that had C-N stretch bond that in range 1360- 1250 cm$^{-1}$. For the second group with the wave number 1057.61 cm$^{-1}$, this wavelength belongs to sulfoxides group that had S=O stretch bond where the range approximately to 1050 cm$^{-1}$ and for the last group, with the wave number 842.53 cm$^{-1}$ and 769.99 cm$^{-1}$ are belongs to sulfonates group that had S-O stretch with the range between 1000- 750 cm$^{-1}$ . From the wavelength or wave number that was analyzed by the FTIR, this ionic liquid is belongs to amine group.

### Extraction of Toluene

Extraction of the samples that is mixture of toluene/ n- heptanes as model oil by using a 3-ethylimidazolium-ethylsulfate, [EIM][EtSO$_4$] ionic liquid is the one of the objective that need to achieved and to analyzed the data. For this experiment, 6 samples was choose in order to know the effectiveness of the [EIM][EtSO$_4$] ionic liquids in extraction of the toluene from the model oil. The 7 samples that was choose for the extraction are 100 percent of n- heptane, volume ratios of 20, 40, 50, 60, 80, and also 100 percent of toluene. From the data that was collected, the experimental and calculated data of extraction with the ionic liquid are shown. From the equation that was developed in the calibration curve, the percentage of the toluene removal from the mixture was calculated and it was illustrated in Figure 3.

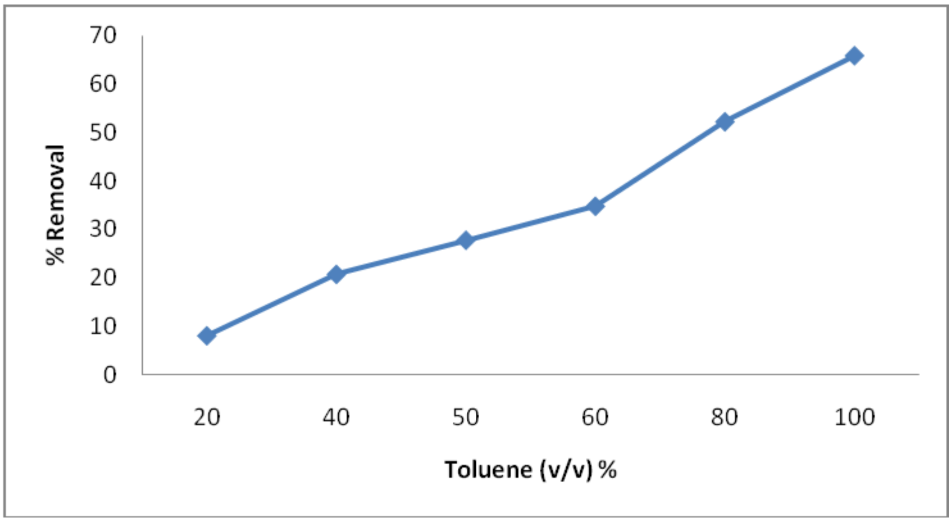

Figure 3: Removal of the Toluene after Extraction at 30°C

From the Figure 3, it shows that the percentage of the removal of toluene after the extraction. From the data that was collected, the graph shows the percentage removal is in increasing pattern where it was proportionally with the volume ratio of the toluene and n-heptane. From the observation, the percentage or the amount of the toluene that was remove from the mixture is depends on the how much the percentage of the toluene in the mixture. For the examples, for the 20 percent of toluene the percentage of the toluene that was remove is much lower compared to the 100 percent of toluene. Another reason is the effect of the loading capacity for the ionic liquid to attract the toluene in the mixture. For this experiment, the amount of the ionic liquids to extract the mixture was limited to 2mL for each extraction process. This may effect the extraction of toluene in the mixture. The effect of the alkyl chain also can give different results because of the shorter alkyl chain on the imidazolium ion is favorable for higher aromatic/ aliphatic selectivity (Krummen *et al*., 2002).

## Distribution Coefficient and Selectivity

The distribution coefficients, Di, are directly calculated from the ratio of the mole fraction in the extract and raffinate phases. The distribution coefficient of the toluene and n-heptane are defined by the ratio of the mole fraction of the solute in the extract (IL) phase and in the raffinate (organic) phases, according to:

$$D_{tol} = C^{IL}_{tol}/C^{org}_{tol} \text{ and } D_{hept} = C^{IL}_{hept}/C^{org}_{hept} \qquad \text{eq. (1)}$$

And for the selectivity, $S_{tol/hept}$, of toluene/n-heptane is defined as the ratio of the distribution coefficients of toluene and n-heptane:

$$S_{tol/hept} = D_{tol}/ D_{hept} = (C^{IL}_{tol}/C^{org}_{tol})/(C^{IL}_{hep}t/C^{org}_{hept}) \qquad \text{eq. (2)}$$

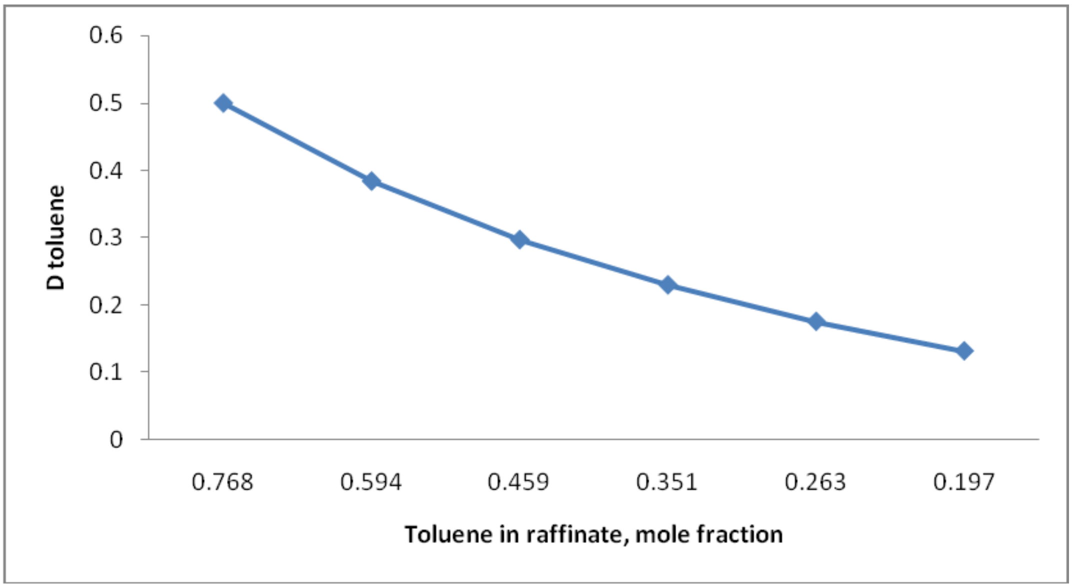

Figure 4: Distribution coefficient for toluene, T = 30°C

From Figure 4, it can be seen that the distribution coefficient of the toluene that using 3-ethylimidazolium-ethylsulfate as the extractant is about 0.5 over the entire concentration range at 30°C. From this results, it showed that ionic liquid [EIM][EtSO$_4$] had higher distribution coefficient compared with the sulfolane where Dtol=0.31. Ionic liquid with higher distribution coefficient requires a lower solvent to feed ratios (Meindersma *et al.*, 2005 &2007).

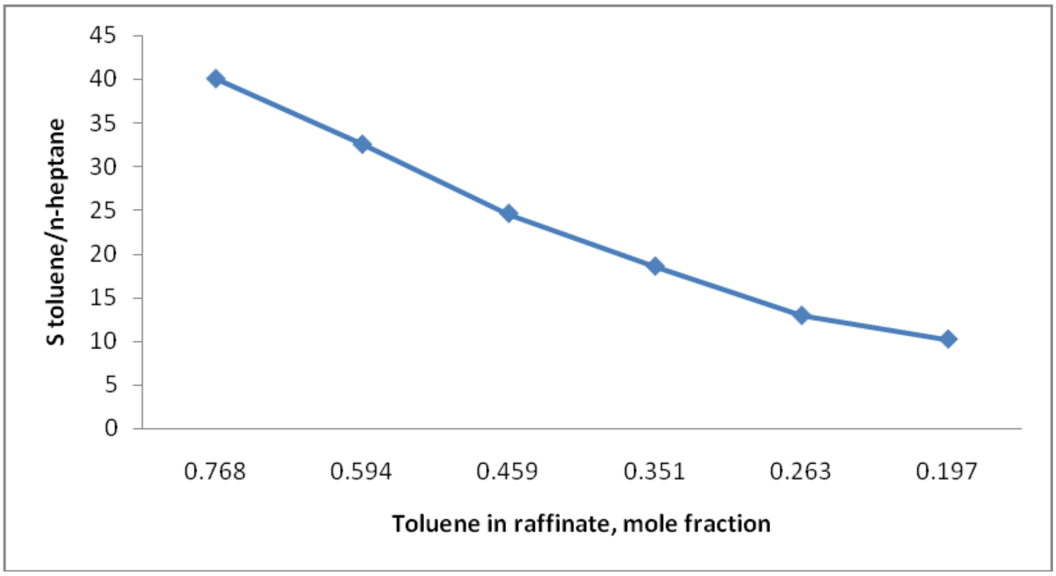

Figure 5: Toluene/n-Heptane Selectivities, T = 30°C

In Figure 5, it showed that the selectivity of toluene/n-heptane selectivity at 30°C after the extraction with the ionic liquid. From the figure, the selectivity was decreases from 40.1 to 10.2 with the decreasing toluene content in mixture from 76.8 percent of toluene to 19.7 percent. When this results was compared with the sulfolane, the selectivity of 3-ethylimidazolium-ethylsulfate (Stol/hept= 40.1) higher than sulfolane ((Stol/hept= 30.9). In this study, the ionic liquid with the shorter alkyl chain that was attached to imidazolium ion also contributed for higher aromatic/aliphatic selectivity but it was affected to the lower contribution coefficient (Krummen *et al.*, 2002). Other than that, for better effectiveness in extraction of toluene from n-heptane mixture, anion in the ionic liquid also affected. According to Meindersma *et al* (2002), anion like $HSO_4^-$, $C_2H_4SO_4^-$, $BF_4^-$, $CH_3SO_3^-$, and $(C_2H_5)_2PO_4^-$ (at 40°C) was more effective in increasing order and that effected to the distribution coefficient of both toluene and n-heptane with imidazolium as a base in ionic liquid.

## CONCLUSION

The objective of this research is to study and characterized the ionic liquid and also to analyze the content of aromatic from aliphatic hydrocarbon after the extraction. For the first objective, by analyzing the ionic liquid on the FTIR, the wave number and the peak that was developed during the test shows that the ionic liquid, 3-ethylimidazolium-ethylsulfate consist of amine, sulfoxide, and sulfonates group and from the analysis this ionic liquids is from the amine group. For the second objective, to analyze the contents of the aromatic/aliphatic compound where it is a mixture of toluene and n- heptane. To analyze the data of the extraction, the calibration curve was developed to find the equation for the straight line where it is **y = 407.3 x.** For the calculations, 6 sample that was chosen and it was extracted with the [EIM][$EtSO_4$] and from the results, it showed the increasing of the toluene removal that depends on the amount or the percentages of the toluene volume ratios in the mixtures. In this researched also, the distribution coefficient and selectivity of toluene in the toluene/n-heptane mixture was calculated in order to compared with conventional solvent in industry, sulfolane with selectivity, Stol/hept=30.9 and distribution coefficient, Dtol=0.31. After the extraction, the data was showed that, the ionic liquid [EIM][$EtSO_4$] are more effective compare with the sulfolane because after the calculation, the selectivity (Stol/hept=40.1) and distribution coefficient (Dt0l=0.5) for ionic liquid at 30°C are higher than sulfolane.

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# APPENDICES

**A .1:** The analysis data from the HPLC (Calibration Curve)

| Volume ratio toluene (v/v)% | Area (mAU*s) | Retention time (min) |
|---|---|---|
| 5 | 717.63037 | 3.92 |
| 10 | 1274.34326 | 3.923 |
| 15 | 2187.43237 | 3.968 |
| 20 | 2329.5354 | 3.953 |
| 25 | 2846.08105 | 3.94 |
| 30 | 3195.80249 | 3.931 |
| 35 | 3562.30762 | 3.926 |
| 40 | 4086.91772 | 3.924 |
| 45 | 4583.31055 | 3.924 |
| 50 | 4841.10645 | 3.956 |
| 55 | 5179.73584 | 3.93 |
| 60 | 5531.71631 | 3.934 |
| 65 | 5862.71875 | 3.935 |
| 70 | 6194.69336 | 3.932 |
| 75 | 6494.91455 | 3.934 |
| 80 | 6729.42236 | 3.911 |
| 85 | 7417.38379 | 3.915 |
| 90 | 7379.39648 | 3.936 |
| 95 | 7620.01611 | 3.932 |
| 100 | 7878.37695 | 3.932 |
|  | 95912.84178 | 3.9328 |

**A.2**: Percentage of Toluene Removal from the mixture

| Toluene (v/v) % (Before Extraction) | % Toluene Removal |
|---|---|
| 20 | 8.07 |
| 40 | 20.73 |
| 50 | 27.76 |
| 60 | 34.77 |
| 80 | 52.17 |
| 100 | 65.8 |

**A.3**: Distribution Coefficient data

| Toluene in raffinate | Dtol | Dhept |
|---|---|---|
| 0.768 | 0.5 | 1.2479 |
| 0.594 | 0.384 | 1.1802 |
| 0.459 | 0.297 | 1.2063 |
| 0.351 | 0.2297 | 1.2373 |
| 0.263 | 0.1755 | 1.3602 |
| 0.197 | 0.1317 | 1.2912 |

**A.4**: Selectivity data

| $C^{org}$tol | Stol/hept |
|---|---|
| 0.2318 | 40.07 |
| 0.2264 | 32.54 |
| 0.227 | 24.62 |
| 0.2355 | 18.56 |
| 0.2497 | 12.91 |
| 0.251 | 10.2 |