

**LIQUID-LIQUID EXTRACTION OF NAPHTHENIC ACID  
USING THIOCYANATE BASED IONIC LIQUIDS**

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**CHEMICAL ENGINEERING  
UNIVERSITI TEKNOLOGI PETRONAS  
SEPTEMBER 2015**

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by

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15659

Dissertation submitted in partial fulfilment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

SEPTEMBER 2015

Universiti Teknologi PETRONAS,

32610, Bandar Seri Iskandar,

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

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(Prof. Dr. Mohamed Ibrahim Abdul Mutalib)

UNIVERSITI TEKNOLOGI PETRONAS

BANDAR SERI ISKANDAR, PERAK

September 2015

## CERTIFICATION OF ORIGINALITY

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

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RABIATUL ADAWIYAH BINTI NAJMUDDIN

## ABSTRACT

The presence of carboxylic acids in the form of naphthenic acid in crude oil could cause severe corrosion problem during oil refinery. Therefore, this study is to investigate the potential of using ionic liquid as a non-volatile solvent for the extraction of naphthenic acid from a model hydrocarbon liquid that is dodecane. In this study, ionic liquid based on 1,8-diazobicyclo[5.4.0]undec-7-ene-hexyl [DBU-Hex] cation with anion thiocyanate [SCN] was synthesized for the naphthenic acid extraction. Liquid-liquid extraction for ternary system {dodecane + naphthenic acid + [DBU-Hex][SCN]} will be performed at constant temperature 25 °C within the specified feed compositions. Finally, the ternary phase diagrams will be developed and the experimental data will be compared with the tie lines correlated using NRTL or UNIQUAC model.

## **ACKNOWLEDGEMENT**

I would like to take this opportunity to express my gratitude to the following person who have support and guide me through my Final Year Project (FYP). First and foremost, I would like to take this opportunity to express my gratitude to both of my parents Najmuddin bin Ahmad and Bedah binti Abd Razak for their continuous moral support.

Thank you to my FYP supervisor Prof. Dr. Mohamed Ibrahim Abdul Mutalib and post graduate student Syed Nasir Shah for their guidance and support. They are the person behind the success of this project. Their feedbacks help me to improve further for my technical report and presentation.

Thank you to all Research Officers and Lab Executives from Centre of Research in Ionic Liquids for their great assistance throughout my lab experiment. Last but not least, thanks to my friends and everyone that helped me directly or indirectly in completing my project.

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# CHAPTER 1

## INTRODUCTION

### 1.1 Background Study

Petroleum or crude oil consists of paraffinic, naphthenic and aromatic hydrocarbons ranging in carbon number from C1 to more than C60 (Screening-Level Hazard Identification, 2011). Carboxylic acid is naturally presence in crude oil in the form of naphthenic acids with chemical formula  $C_nH_{2n+z}O_2$ , where  $n$  indicates the carbon number and  $z$  indicates hydrogen deficiency as a result from ring formation. This crude oil is also known also known as sour crude oil meaning the crude oil that contains some impurities. The value of  $z$  could be zero or even negative (Clemente & Fedorak, 2005). These naphthenic acids can be retrieved from petroleum refining begins with several distillation fractions of crude oil such as kerosene, gas oil, heavy naphtha's and light lubricating oil. Further alteration of physical and molecular structure of distillation's products via cracking and reforming process, naphthenic acid can be converted into more usable products for various applications, such as wood preservative, paint driers, lubricants and fuel additives (Shah et al., 2014).

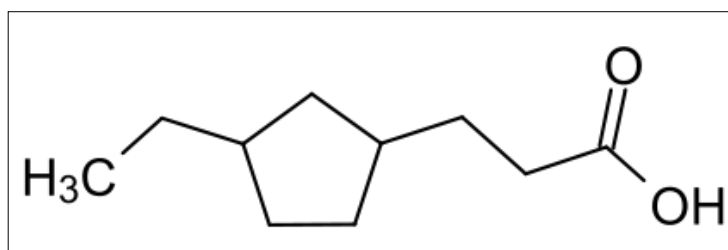


FIGURE 1.1 Example of Naphthenic Acid

In other cases, existence of naphthenic acid can have effects on the production equipment, storage, transport facilities and also the performance of oil. Complication towards operation system may also occur like foaming in various units and also leaching of cations during desalting process where it may lead to the deactivation of the catalyst (Shah et al., 2014). Additionally, crude oil with total acid number (TAN) greater than 0.5 mg KOH/g may cause corrosion towards refinery units (Becerra et al., 2012). TAN is generally a measurement that is expressed in milligrams of KOH necessary to neutralize 1 g of crude oil (Shah et al., 2014). In other words, TAN was developed to indicate a composite of acids present in crude oil. Around 220°C, naphthenic acids start to become corrosive and reach their highest activity at 350 °C. However, there is no evidence of naphthenic acid corrosion when the temperature is over 400 °C due to naphthenic acid decomposition at high temperature (Bota et al., 2010). Moreover, naphthenic acids lead to formation of stable emulsions by forming metallic naphthenates that reduces interfacial tensions which affect phase separation stages (Becerra et al., 2012). Considering multiple problems that can arise as above, it is necessary to extract the naphthenic acid.

Numerous ways have been studied by researchers in order to harness the energy source nature that has been provided namely neutralization, adsorption, thermal decomposition, catalytic decarboxylation and esterification (Lethesh et al., 2014). Another possible way is using ionic liquids as a potential solvent in liquid-liquid extraction. Ionic liquids are simply composed of heterocyclic organic cations and various anions (Dharaskar, 2012). The main advantage of ionic liquids is the ionic liquid's environment is very different from all molecular polar and non-polar organic solvents. The ionic liquids have extremely low vapour pressure and wide range temperature for liquid phase. To be part of the ionic liquid family, the melting point of a given salts must be below 100 °C. If the salts melting point are below room temperature that is around 25 °C, it is considered as a room-temperature ionic liquid (RTIL) (Berthod et al., 2008). Due to ionic liquids unique properties, ionic liquids have been regarded as the green solvent for petroleum industries by all scientists and engineers. Therefore, this study will be focusing on the liquid-liquid extraction of naphthenic acids using thiocyanate based ionic liquid at constant room temperature and within specified feed compositions.

## 1.2 Problem Statement

Recently, every chemical industry is concerned with the environmental issues and the need for more greener and sustainable technologies. In petroleum and hydrocarbon industries, various solvents have been used such as esters, amines, alcohol and other volatile organic compounds for the extraction. However, these solvents may give negative impacts towards health and environment (Dharaskar, 2012). Due to limitations of these solvents, the application of ionic liquids as green solvent for separation of aromatic and non-aromatic compounds has been an explosion of interest in various industries in order to minimize the environmental impact.

Characterization of liquid-liquid equilibrium (LLE) is important in evaluating ionic liquid as potential substitute for traditional extraction and separation solvents. However, the problem of this project is on how to characterize the LLE because it is impossible to characterize the LLE that contain ionic liquid through experimental observation alone. In order to evaluate ionic liquid as a potential candidate for solvent, a proper modelling of LLE data that involve ionic liquid will be compared with standard excess Gibbs energy model to predict ternary LLE exclusively from binary measurements. In this study, Gibbs free energy model that will be evaluated is non-random two liquid (NRTL) or universal quasi chemical (UNIQUAC) model.

### 1.3 Objectives and Scope of Study

The scope of study is mainly focus on liquid-liquid extraction of naphthenic acid from dodecane using synthesized ionic liquid [DBU-Hex][SCN]. The liquid-liquid extraction will be done under constant conditions of temperature and pressure with different feed compositions.

Therefore the main objectives of this project are:

- i. To synthesize ionic liquid [DBU-Hex][SCN]
- ii. To develop ternary phase diagram of {dodecane + naphthenic acid + [DBU-Hex][SCN]} by correlating liquid-liquid equilibrium data with NRTL or UNIQUAC model

## **CHAPTER 2**

### **LITERATURE REVIEW AND THEORY**

#### **2.1 Synthesis of Ionic Liquids**

Ionic liquids are synthesized through formation of the cation and anion exchange. In some cases, only cation exchanged is required. Another option left is to purchase the desired cation at a reasonable cost from market that is already available most commonly as halide salt, making it left only with anion exchange reaction. The anion exchange reactions can be carried out by direct treatment of halide salts with Lewis acids or by anion metathesis (Wasserscheid & Welton, 2002). Aluminium chloride ( $\text{AlCl}_3$ ) is the most used Lewis acid based ionic liquids. The direct treatment results in formation of more than one anionic species depending upon the ratio of quaternary halide salt and Lewis acid. Anion metathesis involves treatment of halide salt with silver, sodium or potassium salts or with the free acid of appropriate anion (Ratti, 2014). In addition, the ionic liquids can be designed specifically so that it can be use to dissolve a certain chemical or to extract a certain material from a solution (Keskin et al., 2007). However, the designed anion and cation of ionic liquids can affect the physiochemical properties of ionic liquids.

## 2.2 Physiochemical Properties of Ionic Liquids

The physiochemical properties of ionic liquid depend mostly on the nature of the cations and anions. For example, ionic liquids containing bis-(trifluoromethylsulfonyl)imide ( $\text{Tf}_2\text{N}$ ) anion would be water immiscible (hydrophobic) while acetate anion will form water soluble (hydrophilic) ionic liquids (Lethesh et al., 2014). According to Berthod et al. the alkyl chain in the cation or symmetry of the shape may affect density, viscosity and surface tension while anion can affect selected properties such as thermal stability and miscibility. Thus, the combination of different anions and cations has expanded more than two thousand ionic liquids at possible low melting temperature that are known today.

Ionic liquid is known for having extremely low vapour pressure in green chemistry. In another study of Berthod et al., vapour pressure of two ionic liquids 1-ethyl-3-methyl imidazolium bis(trifluoromethylsulfonyl) amide (EMIM NTfO<sub>2</sub>) and 1-butyl-3-methyl imidazolium dicyanamide (BMIM DCA) were compared with three liquids namely mercury, nonacosane and water as reference liquid. FIGURE 2.1 below show the vapour pressure of the two ionic liquids were determined between 180 and 260 °C. To determine parameters of the equation for the ionic liquid molar enthalpy of vaporization, thermo chemical measurements were used. The calculated vapour pressure of ionic liquids EMIM NTfO<sub>2</sub> and BMIM DCA at room temperature are 12 and 2  $\mu\text{Pa}$  while the corresponding vapour pressure of water, mercury and nonacosane are 2500, 0.27 and 0.01 Pa. This has proven that ionic liquids have extremely low volatility.

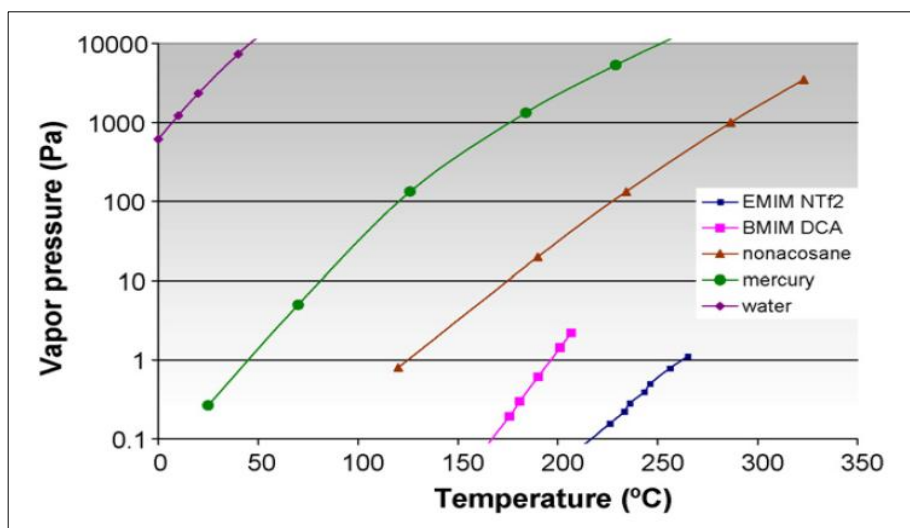


FIGURE 2.1 Vapour Pressure of Molecular Liquids Compared to Ionic Liquids (Berthod et al., 2008)

Since ionic liquids have extremely low volatility, this green solvent has non-flammable properties (Berthod et al., 2008). Due to unique properties of ionic liquids, they are a suitable candidate to replace organic pollutant solvents and can be applied for removing undesirable impurities within a single processing step, which is called liquid-liquid extraction (LLE).

### 2.3 Limitation of Liquid-Liquid Extraction

Liquid-liquid extraction (LLE) is widely used in industry for separation of aromatic hydrocarbon and purification because of mild operating conditions and due to its simplicity (Kareem et al., 2012). LLE is a mass transfer process between two phases which are feed and solvent. The extraction is a transfer of the solute from the feed to the solvent. By the end of the extraction process, the feed deprived of solute becomes a raffinate and the solvent turns into extract. The aim of this extraction process is to purify the feed or to recover one or more compounds from it (Koncsag & Barbulescu, 2011). However, there are various conditions or limitations that need to be considered for the LLE solvent such as:



### **2.3.1 Immiscibility and Density**

One of the conditions for LLE is immiscibility between the two liquids in contact. Technically, the extraction of dissolved chemical component X from liquid phase A is accomplished by bringing the liquid solution of X in contact with a second liquid phase, B. After distribution of analyte between the immiscible phases occurs, the extracted analyte is recovered from phase B for subsequent extraction procedures. Another consideration need to be considered is the density of the extraction solvent to help determine the position of the layers.

### **2.3.2 Pressure and Temperature**

The effectiveness of the separation is also affected by the pressure and temperature conditions. These conditions are to ensure that mixtures remain in the two-phase liquid region and soluble with one another. Nevertheless, these conditions are insignificant in isothermal and isobaric process where heating and pressure is not required and where the objective is to attain phase stability of the system. Phase stability is temperature and pressure dependent. Since these conditions are not changing, the stability of the phase will not change. Generally the extraction process can just be done at ambient pressure and temperature.

### **2.3.3 Alkyl Chain in Ionic Liquids**

Liquid-liquid extraction process can be affected by the length of alkyl chain in ionic liquids too. Previous study by Garcia et al. on liquid-liquid extraction of toluene from heptanes was to observe the effect of alkyl chain length in the ionic liquid on the efficiency separation by using 1-Alkyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide ionic liquids ( $[x\text{mim}][\text{Tf}_2\text{N}]$ ) where x refers to methyl, ethyl, butyl and hexyl group. The result of the experiment showed that  $[\text{mmim}][\text{Tf}_2\text{N}]$  and  $[\text{emim}][\text{Tf}_2\text{N}]$  ionic liquids which had shorter alkyl chain has

better separation of toluene from heptanes compared to [bmim][Tf<sub>2</sub>N] and [hmim][Tf<sub>2</sub>N] ionic liquids.

This finding is also supported by Dominguez et al. in the study of separation for ternary mixture {cyclohexane + benzene + 1-Propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([PMim][NTf<sub>2</sub>]) or 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMim][NTf<sub>2</sub>])}, {cyclohexane + benzene + 1-Ethyl-3-methylpyridinium ethylsulfate ([EMpy][ESO<sub>4</sub>]) or 1-Ethylpyridinium ethylsulfate ([Epy][ESO<sub>4</sub>])}, and {cyclohexane + benzene + 4-Methyl-N-butylpyridinium tetrafluoroborate ([BMpy][BF<sub>4</sub>]) or 1-Butylpyridinium tetrafluoroborate ([Bpy][BF<sub>4</sub>])}. The experimental result showed that increase of the alkyl chain length results in a major selectivity drop due to the interaction of the aliphatic hydrocarbon with the alkyl group of cation. As the alkyl chain length increases, the electron donation from the alkyl group to the cation of ionic liquid increases resulting in a decrease in the positive character of the cation. Hence, weakened the interaction between cation and aromatic hydrocarbon and resulting in decreasing of selectivity.

Both of the case studies above conclude that LLE is affected by alkyl chain of ionic liquid. As the length of alkyl chain increases, it will decrease the selectivity. LLE is also limited by the immiscibility, density, pressure and temperature of the solvent. In this study, experimental LLE data for the ternary system {dodecane + naphthenic acid + [DBU-Hex][SCN]} were determined at T = 25 °C and atmospheric pressure. The results from the research work are expected to be benefit for extraction process in order to upgrade the quality of crude oil.

## CHAPTER 3

### METHODOLOGY AND PROJECT WORK

#### 3.1 Project Flow Chart

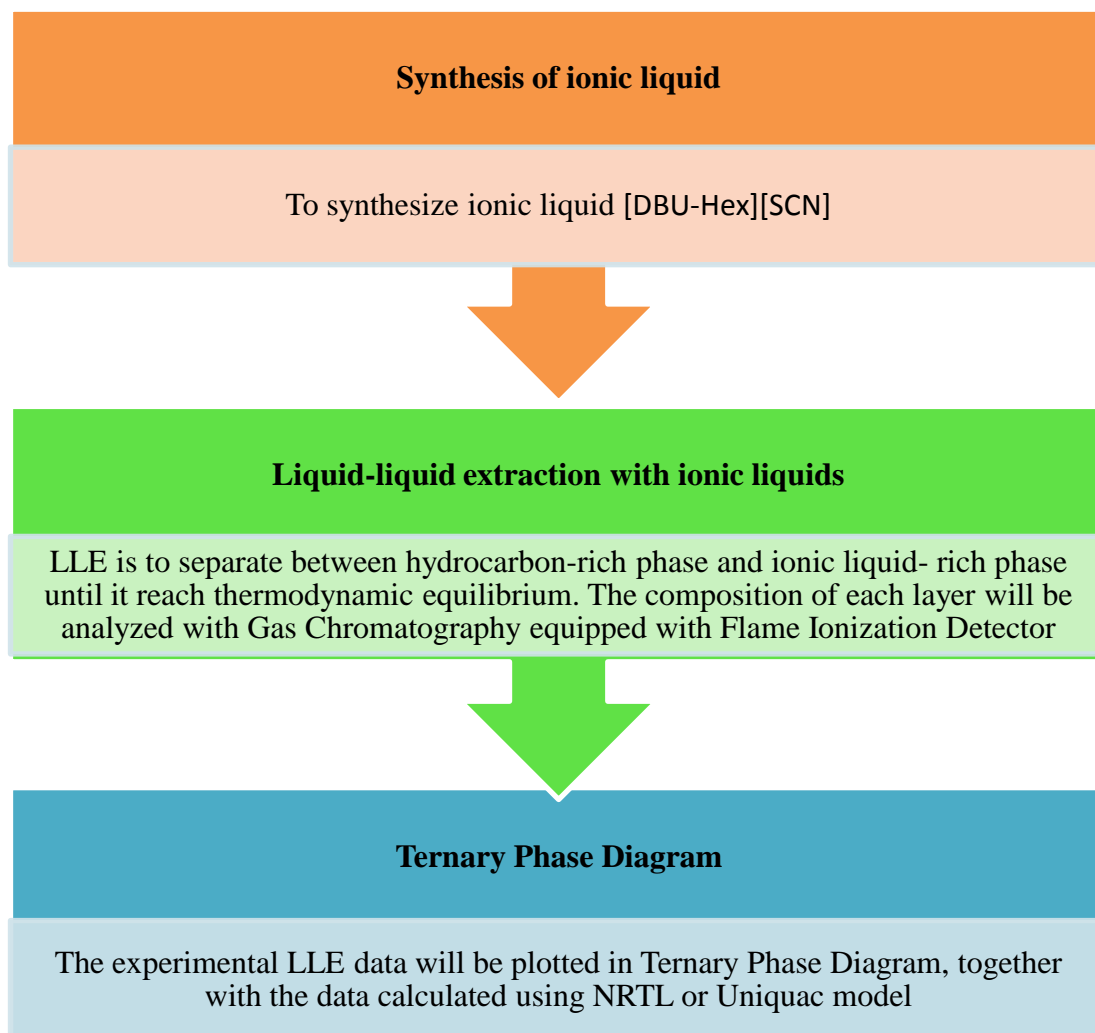


FIGURE 3.1 Project Flow Chart

## 3.2 Methodology

### 3.2.1 Synthesis of Halide Salts

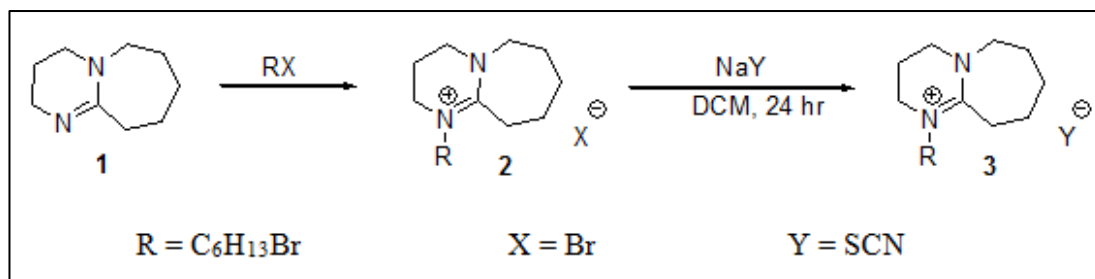


FIGURE 3.2 Synthesis of DBU Based Ionic Liquids

To a 5 g solution of 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU) in a 35 mL acetonitrile, 6.5 g of 1-bromohexane is added into a round bottom flask and stirred at rate 500 rpm on a hot plate that is set to 50 °C for 48 h. The reaction mixture is cooled using ice bath and the acetonitrile is removed using a rotary evaporator. Cyclohexane is used to wash away white solid (chloride salt) obtained and is dried in a vacuum oven at 70 °C for 24 h.

### 3.2.2 Synthesis of 1, 8-diazobicyclo [5.4.0] eundec-7-ene (DBU) based Ionic Liquid

After the halide salts 1-hexyl-1, 8-diazobicyclo [5.4.0] undec-7-ene Bromide [DBU-Hex] [Br] has been prepared, sodium thiocyanate is added in a dichloromethane and the reaction is stirred vigorously using a mechanical stirrer at 25 °C for 24 hours. The precipitate formed is filtered off, and the dichloromethane layer is washed with cold water. Dichloromethane is evaporated under vacuum to give [DBU-Hex][SCN] as a pale yellow liquid. The ionic liquid (IL) is further dried in a vacuum oven at 60 °C for 24 h. FIGURE 3.2 shows the mechanism representing the above reaction synthesis.

### 3.2.3 Density and Viscosity Measurement

An Anton Paar viscometer (model SVM3000) was used to measure the viscosity of ionic liquids. Density measurement was carried out using Anton Paar densitometer (DMA 5000). Standard uncertainties are:  $u(\rho) = \pm 0.00001 \text{ g.cm}^{-3}$ ,  $u(\eta) = \pm 0.32 \%$  mPa.s and  $u(T) = \pm 0.01\text{K}$ .

### 3.2.4 Liquid-Liquid Extraction

The model acid oil was prepared by mixing together dodecane and benzoic acid (to represent the naphthenic acid) until it is soluble. The LLE experiments were performed in 8 mL vials with screw caps. Mixture of known masses of dodecane, benzoic acid and ionic liquid [DBU-Hex][SCN] were transferred to tared vials. The vials were then placed on a shaker with a shaking speed of 800 rpm for 5 h at 25 °C to reach the thermodynamic equilibrium. Finally, the vials were left to settle overnight at room temperature to ensure complete phase separation.

Approximately 50  $\mu\text{L}$  samples from the lower and upper layers were carefully taken with disposable Pasteur micropipets. Then, gas chromatograph (model Agilent) equipped with a flame ionization detector (FID) fitted with a 30-m DB-5 capillary column will analyse each layer. The carrier gas was helium and was set to maintain capillary pressure of 10 psi. The initial temperature of 100 °C was held for 3 min, followed by an increase of 8 °C/min to a final temperature of 300 °C.

### 3.2.5 Development of Ternary Diagram

After the experimental LLE data was analyzed by using a gas chromatograph, ternary systems dodecane + naphthenic acid + ionic liquid will be developed as shown in figure below with the data calculated using non-random two liquid (NRTL) or universal quasi chemical (UNIQUAC) model.

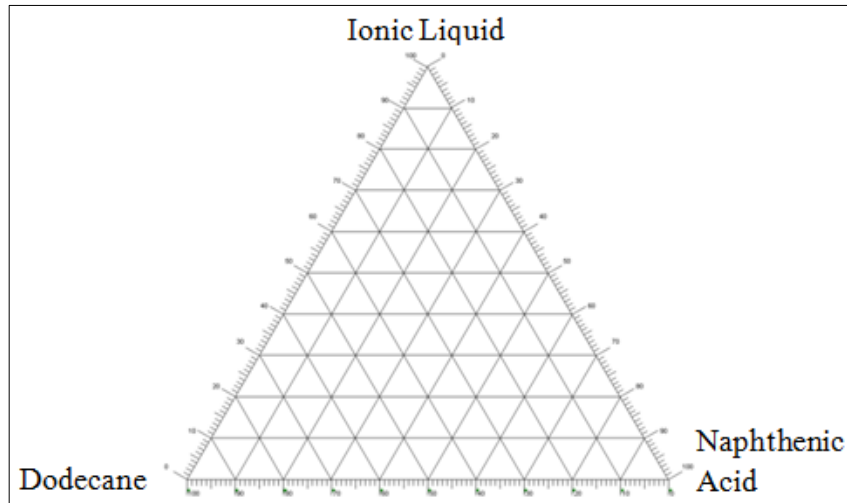


FIGURE 3.3 Ternary Phase Diagram

For these two models, it is assumed that each cation is completely paired with anion and the pair is considered a single molecular species in the solution. In addition, the reference states are considered to be pure liquids of all species at system temperature  $T$  and pressure  $P$  (Simoni et al., 2008). Therefore the total Gibbs energy of mixing  $g^M$  is

$$\frac{g^M}{RT} = \sum_{i=1}^n x_i \ln(x_i) + \frac{g^E}{RT} \quad (1)$$

Where,

$g^E$  = molar excess Gibbs energy

$x_i$  = mole fraction of component  $i$

$R$  = universal gas constant

$T$  = Temperature

$n$  = number of species present

The Gibbs energy equation was further derived to give the NRTL equation. The NRTL model is commonly predicts large heat of mixing and characteristic of solutions (Simoni et al., 2007). The equation for NRTL model is,

$$\frac{g^E}{RT} = \sum_{i=1}^n x_i \frac{\sum_{j=1}^n \tau_{ji} G_{ji} x_j}{\sum_{k=1}^n G_{ki} x_k} \quad (2)$$

$$G_{ji} = \exp(-\alpha_{ij} \tau_{ij}) \quad (3)$$

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} = \frac{\Delta g_{ij}}{RT} \quad (4)$$

Where,

$g_{ij}$  = energy parameter that characterizes the interaction of species  $i$  and  $j$

$\alpha_{ij}$  = non-randomness in mixture which equal to 0

$\tau_{ij}$  = binary interaction parameters

Most of the time, for ionic liquid solvent or co-solvent, the binary of LLE data is used for parameter estimation. The parameters for the binary can be determined by using the equal activity equations. However, there will be no parameter solutions to this equation system if a model does not permit liquid-liquid phase splitting (Simoni et al., 2008).

For UNIQUAC model, even if all binary interaction parameters are equal to 0, it still will be able to predict the LLE by only considering the combinatorial contribution to molar excess Gibbs free energy ( $g_C^E$ ). The combinatorial contribution is predicted based on the values of  $r$  and  $q$  of the substances (Simoni et al., 2007). The UNIQUAC model is given by the following formulae,

$$\frac{g_C^E}{RT} = \sum_{i=1}^N \ln \left( \frac{\phi_i}{x_i} \right) + 5 \sum_{i=1}^N q_i x_i \ln \left( \frac{\theta_i}{x_i} \right) \quad (5)$$

$$\phi_i = \frac{x_i r_i}{\sum_{j=1}^N x_j r_j} \quad (6)$$

$$\theta_i = \frac{x_i q_i}{\sum_{j=1}^N x_j q_j} \quad (7)$$

Where,

$x_i$  = mole fraction

$r_i$  = volume parameter

$q_i$  = surface area of component  $i$

$\phi_i$  = volume fraction

$\theta_i$  = surface area fraction

$R$  = universal gas constant

$T$  = temperature



## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 Synthesis of Ionic Liquid [DBU-Hex][SCN]

Synthesis of ionic liquid involves two steps. Firstly, alkyl halide salts was prepared by quaternization of 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU) with alkyl halide at 50 °C for 48 h in acetonitrile. After removal of solvent, ionic liquid was washed with cyclohexane and dried under vacuum to give halide salts. Next step is anion metathesis with sodium thiocyanate, Na[SCN], resulted in SCN anion based hydrophilic DBU based ionic liquid. About 7.33 g of pale yellow ionic liquid [DBU-Hex][SCN] was obtained from the synthesis reaction. The synthesized ionic liquid will be use for liquid-liquid extraction of naphthenic acid from dodecane.

Balance equations:

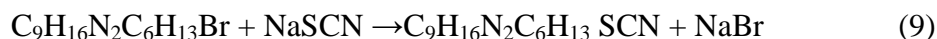


TABLE 4.1 Mass of Components

Component	Chemical formula	Molar mass (g/mol)	Mass (g)
DBU	$\text{C}_9\text{H}_{16}\text{N}_2$	152.24	5
Bromo Hexane	$\text{C}_6\text{H}_{13}\text{Br}$	165.07	6.5
[DBU-Hex]Br	$\text{C}_9\text{H}_{16}\text{N}_2\text{C}_6\text{H}_{13}\text{Br}$	317.31	9.63
Sodium Thiocyanate	NaSCN	81.07	2.706
[DBU-Hex][SCN]	$\text{C}_9\text{H}_{16}\text{N}_2\text{C}_6\text{H}_{13}\text{SCN}$	295.45	7.33

- i. Calculation Mass of Bromo Hexane (C<sub>6</sub>H<sub>13</sub>Br):

$$\text{Mass} = \text{Mol of DBU} \times 1.2 \times \text{Molar Mass of Bromo Hexane} \quad (10)$$

$$\text{Mass} = \frac{5 \text{ g}}{152.24 \frac{\text{g}}{\text{mol}}} \times 1.2 \times 165.07 \frac{\text{g}}{\text{mol}} = 6.5 \text{ g} \quad (11)$$

- ii. Calculation Mass of Sodium Thiocyanate (NaSCN):

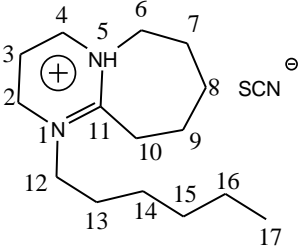
$$\begin{aligned} \text{Mass} &= \text{Mol of [DBU - Hex]Br} \times 1.1 \\ &\times \text{Molar Mass of Sodium Thiocyanate} \end{aligned} \quad (12)$$

$$\text{Mass} = \frac{9.63 \text{ g}}{317.31 \frac{\text{g}}{\text{mol}}} \times 1.1 \times 81.07 \frac{\text{g}}{\text{mol}} = 2.706 \text{ g} \quad (13)$$

#### 4.2 H NMR data of Ionic Liquid [DBU-Hex][SCN]

Based on the H NMR chemical shift ( $\delta$ ) values for ionic liquid [DBU-Hex][SCN] in TABLE 4.2, the value at  $\delta = 0.87$  ppm corresponds to the three hydrogen atom on C<sub>17</sub>. At  $\delta = 1.30$  ppm, the six hydrogen atom corresponds to the protons on carbon atoms on C<sub>7</sub>, C<sub>8</sub>, C<sub>16</sub>. The two hydrogen at multiplet  $\delta = 1.54$  ppm corresponds to the protons on carbon atoms C<sub>4</sub>. The multiplet at  $\delta = 1.67$  ppm correspond to six hydrogen atoms from C<sub>6</sub>, C<sub>14</sub> and C<sub>15</sub>. The two multiplet at  $\delta = 1.97$  ppm corresponds to hydrogen atoms on C<sub>3</sub>. Another multiplet at  $\delta = 2.86$  ppm represents proton on C<sub>9</sub> carbon atom. The multiplet at  $\delta = 3.36$  ppm is related to the two hydrogen on C<sub>13</sub> while multiplet at  $\delta = 3.45$  represents the hydrogen on C<sub>2</sub> and C<sub>10</sub> respectively. The multiplet at  $\delta = 3.63$  ppm represents the two hydrogen on C<sub>12</sub>.

TABLE 4.2 HNMR Data and CHNS details of DBU-Hex][Hex]

Structure code	Structure of ILs	$^1\text{H}$ NMR $\delta$ (300 MHz)
[DBU-Hex][SCN]		$\text{C}_{17} = 0.87$ (t, 3H) $\text{C}_7, \text{C}_8, \text{C}_{16} = 1.30$ (m, 6H) $\text{C}_4 = 1.54$ (m, 2H) $\text{C}_6, \text{C}_{14}, \text{C}_{15} = 1.67$ (m, 6H) $\text{C}_3 = 1.97$ (m, 2H) $\text{C}_9 = 2.86$ (m, 2H) $\text{C}_{13} = 3.36$ (m, 2H) $\text{C}_2, \text{C}_{10} = 3.45$ (m, 4H) $\text{C}_{12} = 3.63$ (m, 2H)

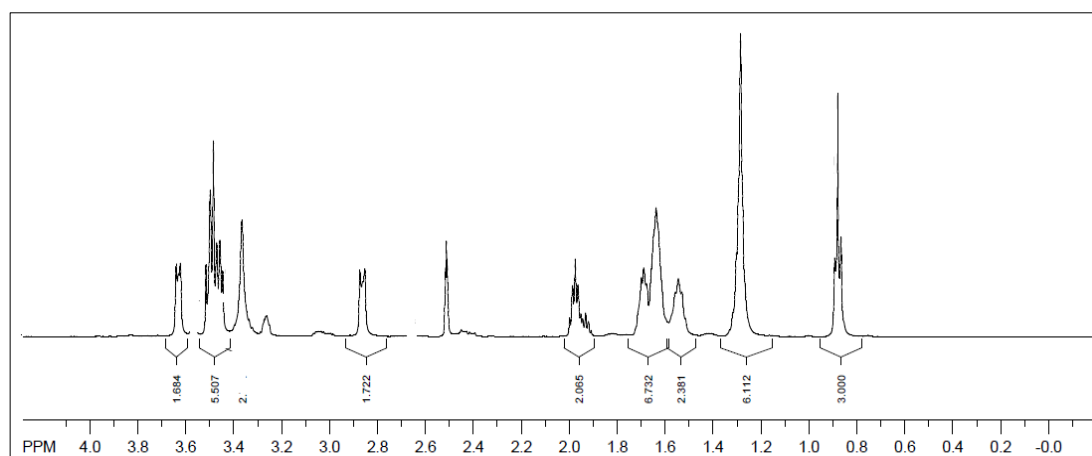


FIGURE 4.1  $^1\text{H}$  NMR Spectrum of 1-Hexyl-1, 8-Diazobicyclo [5.4.0] undec-7-ene Thiocyanate [DBU-Hex] [SCN]

### 4.3 Density and Viscosity of [DBU-Hex][SCN]

Viscosity and density measurement was performed in a temperature range from 293.15 K to 373.15 K. The viscosity and density decreased as temperature increased. The corresponding data is summarized in TABLE 4.3, FIGURE 4.2 and FIGURE 4.3 as a function of temperature. The alkyl length of ionic liquid has impact on the viscosity and density of ionic liquid [DBU-Hex][SCN]. Ionic liquid with alkyl group six is room temperature ionic liquid.

TABLE 4.3 Experimental Viscosity ( $\eta$ ) and Density ( $\rho$ ) of Ionic Liquid as a Function of Temperature

T (K)	Viscosity, $\eta$ / (mPa.s)	Density, $\rho$ / (g cm <sup>-3</sup> )
293.15	4198.8	1.0618
303.15	1504.3	1.0564
313.15	635.21	1.0509
323.15	306.06	1.0451
333.15	164.15	1.0395
343.15	96.185	1.0399
353.15	60.575	1.0284
363.15	40.353	1.0229
373.15	28.295	1.0174

Standard uncertainties:  $u(\eta) = \pm 0.32 \%$  mPa.s;  $u(\rho) = \pm 0.00001$  g.cm<sup>-3</sup>;  $u(T) = \pm 0.01$ K

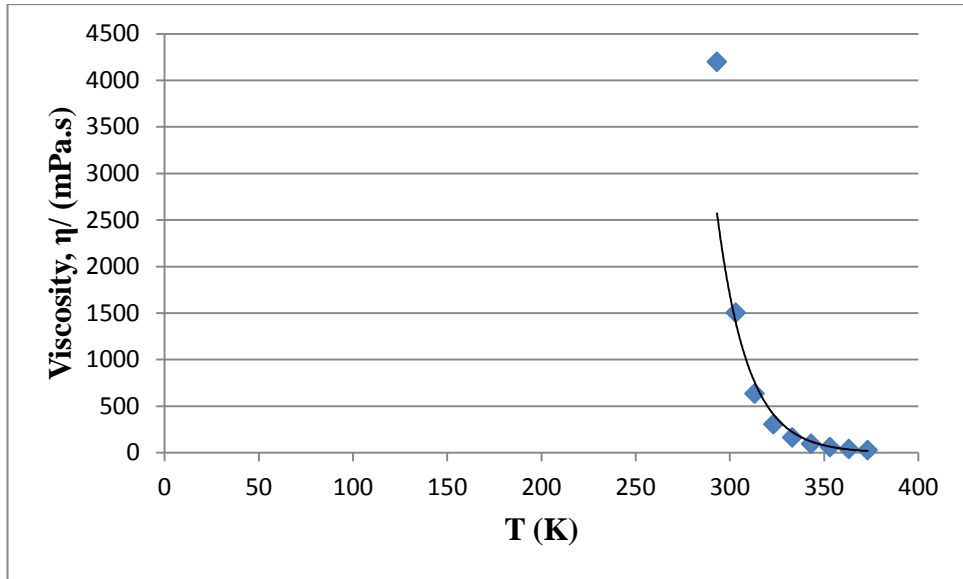


FIGURE 4.2 Graph of Viscosity as a Function of Temperature

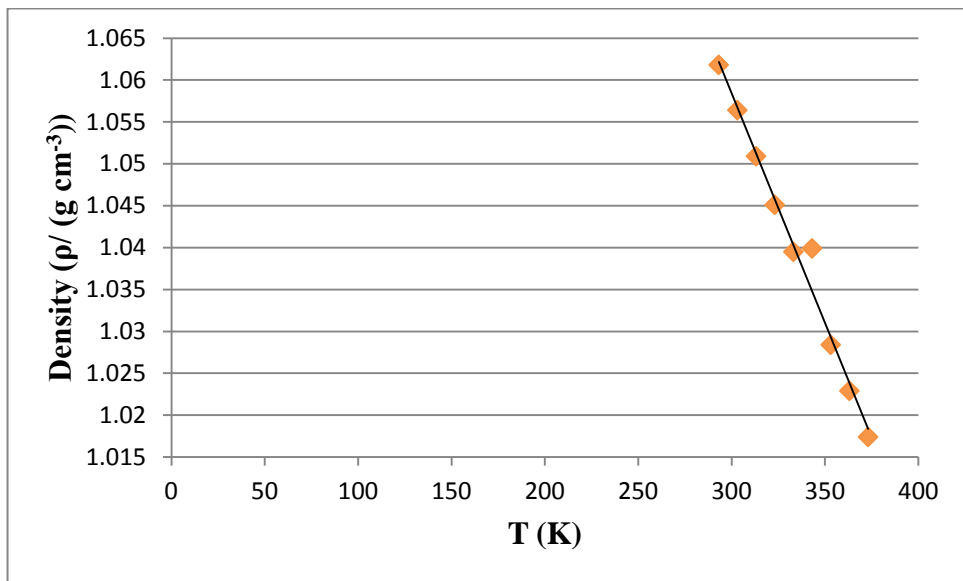


FIGURE 4.3 Graph of Density as a Function of Temperature

#### 4.4 Liquid-Liquid Extraction (LLE)

Solubility test was done prior LLE for known amount of naphthenic acid that is 0.5 g to dissolve completely in dodecane. The solubility test showed that about 45 g of dodecane is needed. Thus, the solubility ratio of dodecane to naphthenic acid is 90:1. Based on the solubility ratio, the mole fraction compositions for the dodecane, naphthenic acid and ionic liquid [DBU-Hex][SCN] with total feed of 2 g was calculated. The experimental LLE data on mole fraction of dodecane is decreasing from 0.7828 until 0.7772, the mole fraction of naphthenic acid is increasing from 0.004 until 0.012 and the mole fraction of ionic liquid is decreasing from 0.2132 until 0.2108.

TABLE 4.4 Feed Compositions

Feed Composition in mg			Feed Composition in moles		
Dodecane	Naphthenic acid	[DBU-Hex][SCN]	Dodecane	Naphthenic acid	[DBU-Hex][SCN]
$X_1$	$X_2$	$X_3$	$X_1$	$X_2$	$X_3$
1355	5	640	7.9551	0.0409	2.1662
1354.375	6.25	639.375	7.9515	0.0512	2.1641
1353.75	7.5	638.75	7.9478	0.0614	2.1620
1353.125	8.75	638.125	7.9441	0.0717	2.1598
1352.5	10	637.5	7.9405	0.0819	2.1577
1351.875	11.25	636.875	7.9368	0.0921	2.1556
1351.25	12.5	636.25	7.9331	0.1024	2.1535
1350.625	13.75	635.625	7.9295	0.1126	2.1514
1350	15	635	7.9258	0.1228	2.1493

TABLE 4.5 Feed Compositions in Mole Fraction (x) at T = 25 °C

Feed compositions		
$x_1$ (Dodecane)	$x_2$ (Naphthenic acid)	$x_3$ (Ionic Liquid)
0.7828	0.0040	0.2132
0.7821	0.0050	0.2129
0.7814	0.0060	0.2126
0.7807	0.0070	0.2123
0.7800	0.0080	0.2120
0.7793	0.0090	0.2117
0.7786	0.0100	0.2114
0.7779	0.0110	0.2111
0.7772	0.0120	0.2108

Formula for Calculation Number of Moles:

$$\text{Number of Moles} = \text{Feed Mass} \div \text{Molar Mass} \quad (14)$$

$$= \text{Number of Moles} \div \text{Total Number of Moles} \quad (15)$$

Based on equation (14), following are the examples on calculating number of moles for:

i. Dodecane:

$$= 1355 \text{ mg} \div 170.33 \frac{\text{mg}}{\text{mol}} = 7.9551 \text{ mol} \quad (16)$$

ii. Naphthenic acid:

$$= 5 \text{ mg} \div 122.12 \frac{\text{mg}}{\text{mol}} = 0.0409 \text{ mol} \quad (17)$$

iii. Ionic liquid:

$$= 640 \text{ mg} \div 295.45 \frac{\text{mg}}{\text{mol}} = 2.1662 \text{ mol} \quad (18)$$

Based on equation (15), below is the example for calculation of moles fraction of dodecane:

$$\text{Mole fractions} = 7.9551 \div (7.9551 + 0.0409 + 2.1662) = 0.7828 \quad (19)$$

The experimental LLE data for the ternary system {dodecane + naphthenic acid + [DBU-Hex][SCN]} at T = 25 °C and atmospheric pressure are plotted in triangular diagram in **Error! Reference source not found.**. The feasibility of using ionic liquid [DBU-Hex][SCN] as solvent for liquid-liquid extraction of naphthenic acid from dodecane was evaluated using distribution ratios ( $D_i$ ) and separation factors ( $\alpha_{2,1}$ )'s formulae, where  $x$  is the mole fraction, superscript 1 and 2 refer to the hydrocarbon-rich and ionic liquid-rich phase respectively. The calculated values of  $D_i$  and  $\alpha_{2,1}$  are tabulated in TABLE 4.6.

$$D_1 = \frac{x_1^2}{x_1^1} \quad (20)$$

$$D_2 = \frac{x_2^2}{x_2^1} \quad (21)$$

$$\alpha_{2,1} = \frac{D_2}{D_1} \quad (22)$$

TABLE 4.6 Experimental LLE Data on Mole Fraction ( $x$ ), Distribution Ratios ( $D_i$ ) and Separation Factors ( $\alpha_{2,1}$ )

Hydrocarbon-rich phase (upper layer)		IL-rich phase (lower layer)		$D_1$	$D_2$	$\alpha_{2,1}$
$x_1^1$	$x_2^1$	$x_1^2$	$x_2^2$			
0.99982	0.00018	0.565855	0.00788	0.56595	44.54130	78.70117
0.99987	0.00013	0.564384	0.009938	0.56446	77.17270	136.72021
0.99982	0.00018	0.563042	0.011898	0.56314	67.07805	119.11389
0.99983	0.00017	0.561633	0.013907	0.56173	79.89573	142.23129
0.99978	0.00022	0.560296	0.015861	0.56042	70.76912	126.27844
0.99976	0.00024	0.558918	0.017845	0.55905	73.61055	131.67004
0.99967	0.00033	0.557633	0.019757	0.55782	59.67019	106.97070
0.99964	0.00036	0.556272	0.021726	0.55647	60.34660	108.44494
0.99973	0.00027	0.554757	0.023813	0.55491	87.67820	158.00501



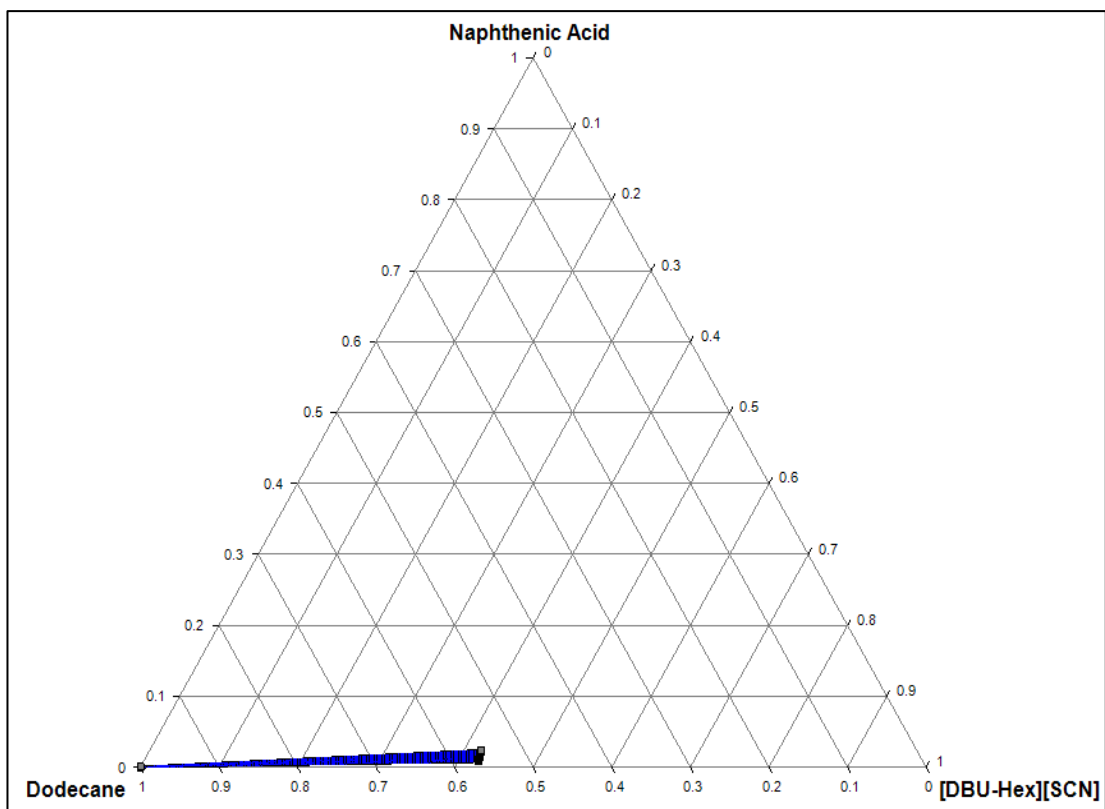


FIGURE 4.4 Experimental LLE Data for Ternary System {dodecane (1) + naphthenic acid (2) + [DBU-Hex][SCN](3)}

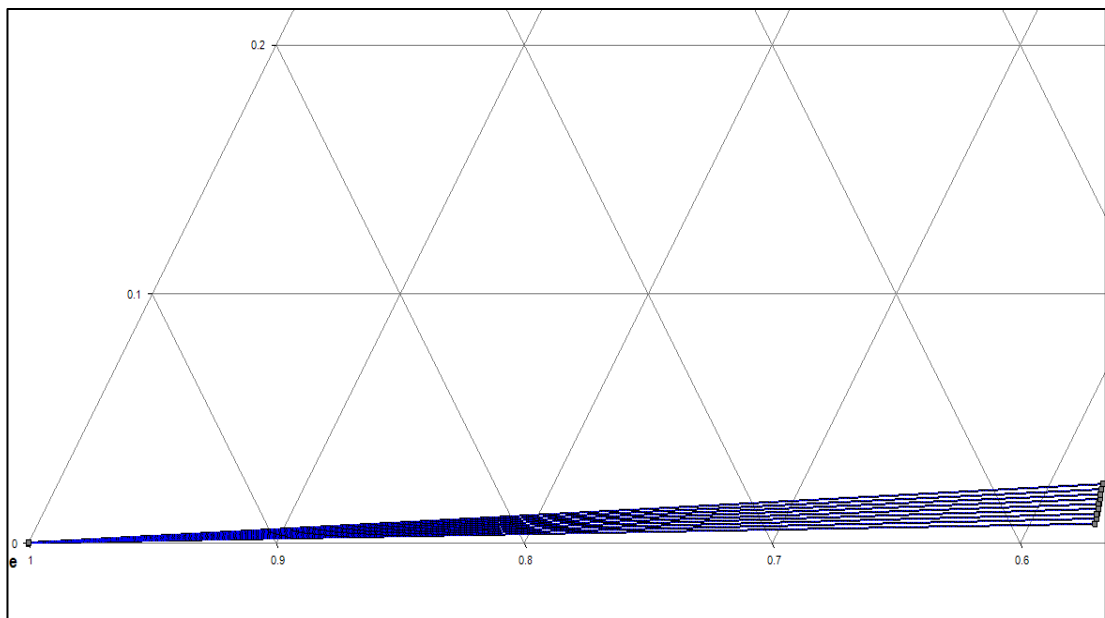


FIGURE 4.5 Closer View of Experimental LLE Data for Ternary System {dodecane (1) + naphthenic acid (2) + [DBU-Hex][SCN](3)}

As can be seen from FIGURE 4.4, the ternary phase diagram is to represent the mole fractions of all three components namely dodecane, naphthenic acid and ionic liquid [DBU-Hex][SCN] in each hydrocarbon and ionic liquid rich-phase layer. The result showed that ionic liquid [DBU-Hex][SCN] is able to extract naphthenic acid from the hydrocarbon rich-phase into the ionic liquid rich-phase. The separation factor is also affected by the naphthenic acid concentration. The increase of  $D_1$  and  $D_2$  is expressed by a decrease in  $\alpha_{2,1}$ . This indicates that as the concentration of naphthenic acid increase, the separation will become difficult.

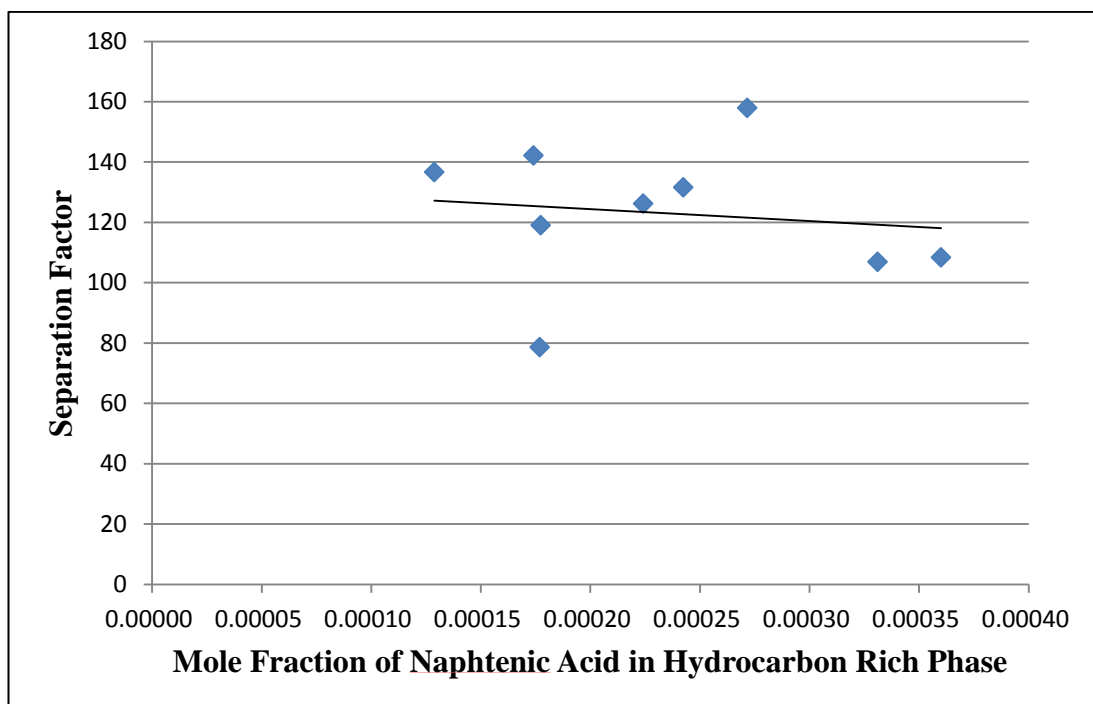


FIGURE 4.6 Graph of Separation factor for the ternary system at  $T = 25\text{ }^{\circ}\text{C}$  {dodecane (1) + naphthenic acid (2) + [DBU-Hex][SCN](3)}

## **CHAPTER 5**

### **CONCLUSION AND RECOMMENDATION**

The liquid-liquid extraction (LLE) data for the ternary systems {dodecane (1) + naphthenic acid (2) + [DBU-Hex][SCN](3)} were determined experimentally at 25 °C and atmospheric pressure. The respective values of distribution ratios and separation factor were calculated. The results distribution ratio and separation factor is affected by the naphthenic acid mole fraction in hydrocarbon-rich phase. The solubility ratio of dodecane to naphthenic acid is also affecting the feed compositions for LLE and thus affecting the whole LLE experimental data.

As a conclusion, from the finding of this research, the author hopes it can bring more benefits in the industry. For future research, the author recommends to compare the LLE data with different alkyl chains based on thiocyanate ionic liquids. The reason is so that more variety of ionic liquids with the same based thiocyanate ionic liquid can be compared.

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