CERTIFICATION OF APPROVAL

Extractive Distillation of Benzene and Cyclohexane by Using 1-propyronitrile-3-butylimidazolium dicyanamide

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

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CERTIFICATION OF ORIGINALITY

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

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This page is especially dedicated to all who have contributed to the success this two semester Final Year Project on the topic of Extractive Distillation of Benzene and Cyclohexane by Using 1-propyronitrile-3-butylimidazolium dicyanamide.

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ABSTRACT

Due to very close boiling point of benzene and cyclohexane ($\Delta T_b = 0.6^{\circ}C$), separation of them is one of the most challenging processes in the chemical industry and it is not practical to separate such a binary mixture by conventional distillation process. The separation efficiency of ionic liquid as a solvent in the extractive distillation process, COSMO-RS generated the information of potentially applicable ionic liquid of 1-propyronitrile-3-butylimidazolium dicvanamide [C₂CNBim]N(CN)₂ with aromatic compound and aliphatic compound is studied at temperature range (293.15 to 323.15) K and at atmospheric pressure. Firstly, the ionic liquid is synthesized and its property measurements is characterized. Then study on thermophysical properties of ionic liquid is done by preparing 1-propyronitrile-3butylimidazolium dicyanamide added with benzene at different compositions and their density and refractive indices are measured at the stated temperature and pressure. Thermal expansion coefficients are estimated using the measured density values. Secondly, headspace-gas chromatography (HSGC) experiments are done at the stated conditions to calculate the relative volatility of the sytstem by measuring and observing vapor-liquid equilibrium (VLE) data for the ternary systems (benzene+cyclohexane) with the ionic liquid. So far there is no available thermophysical data of 1-propyronitrile-3-butylimidazolium dicyanamide with aromatic compound yet and there is no available data on relative volatility of this ionic liquid with benzene and cyclohexane. All of these reasons have given me the motivation to carry out this study.

TABLE OF CONTENTS

CERTIFIC	ATION OF APPROVAL1
ACKNOWI	EDGEMENTS
ABSTRAC	۲4
List of Table	s7
List of Figur	es7
CHAPTER	18
INTRODUC	CTION
1.1 Bac	kground8
1.1.1 P	roperties of benzene and cyclohexane9
1.1.2 Prod	uction of benzene and cyclohexane10
Benzene	
Cyclohe	xane10
1.1.3 Se	paration for Benzene/Cyclohexane11
1.1.4 En	trainer characteristics12
1.2 Problem	m Statement14
1.3 Object	ives14
1.4 Scope	of study14
CHAPTER	2 16
LITERATU	RE REVIEW16
CHAPTER	320
METHODO	LOGY
3.1 Experi	mental procedure
3.1.1 Sy [C ₂ CN	nthesis of ILs. 1-propyronitrile-3-butylimidazolium dicyanamide, Bim]N(CN) ₂ 21
3.1.2	Ionic liquid characterization (FTIR, NMR and TGA)21
3.1.3	Ionic Liquid thermophysical properties measurement
3.1.4	Vapor-Liquid Equilibrium (Head-space Gas Chromatography)22
3.2 Chemi	cals Required23
3.3 Equipn	nent/Instruments required23

CHAPTER 4	24
RESULT AND DISCUSSION	24
4.1 Characterization of 1-propyronitrile-3-butylimidazolium dicyanamide	24
4.2 Thermophysical properties of 1-propyronitrile-3-butylimidazolium	27
CHAPTER 5	34
CONCLUSION AND RECOMMENDATION	34
REFERENCES	35
APPENDICES	37

List of Tables

Table 1: Physical properties of benzene	9
Table 2: List of ionic liquids and their selectivity	13
Table 3: Parameters that will be tested in the experiment	15
Table 4: Water Content (mass fraction) for [C2CN Bim]N(CN)2	24
Table 5: Summary of NMR result	25
Table 6: Experimental Densities for [C2CN Bim]R as a function of temperature	27
Table 7: Experimental Refractive Indices for [C2CN Bim]R as a function of	
temperature	28
Table 8: Experimental dynamic viscosities, n for [C2CNBim]R as a function of	
temperature	29
Table 9: Thermal Expansion Coefficient Values of Presented Ionic Liquid as a	
Function of Temperature.	31

List of Figures

Figure 1: Selected uses of benzene compound	9
Figure 2: VLE of Benzene and Cyclohexane before present of entrainer	11
Figure 3: VLE of Benzene and Cyclohexane after the presence of entrainer(IL)	12
Figure 4: UOP Sulfolane Process(www.uop.com/aromatics/3000.html)	18
Figure 5: [C ₂ CN Bim]N(CN) ₂ FTIR Spectrum	25
Figure 6: [C ₂ CN Bim]N(CN) ₂ NMR Spectrum (H)	26
Figure 7: [C ₂ CN Bim]N(CN) ₂ NMR Spectrum (C)	26
Figure 8: Graph of density of ionic liquid vs temperature	28
Figure 9: Graph of refractive index of ionic liquid vs temperature	29
Figure 10: Graph of viscosity of ionic liquid vs temperature	30
Figure 11: X-Y plot of pure benzene and cyclohexane mixture.	32
Figure 12: X-Y plot of benzene and cyclohexane mixture with IL.	32
Figure 13: Relative volatility of pure benzene and cyclohexane mixture with IL	.33
Figure 14: Schematic diagram of industrial extractive distillation process	37

CHAPTER 1 INTRODUCTION

1.1 Background

Separation of benzene and cyclohexane is among the most important and most difficult processes in the petrochemical industry. Cyclohexane is produced by the catalytic hydrogenation of benzene. At the end of the process, unreacted benzene is present in the reactor product stream and it must be removed purely for pure cylohexane. Separation of benzene and cyclohexane is difficult by conventional distillation process because these components form close boiling point mixtures at the entire range of their composition. Among other methods used in separation of azeotropic mixture, extractive distillation process is simple and can deal with large amount of feestock (Zhigang et al.,2006).

Extractive distillation process is a basic operation used to separate compound with close boiling point or mixtures that form azeotropes but it requires the addition of third component (entrainer or agent) that could alter the relative volatility of the compounds of the mixture(J.M Resa et al.,2000). Selection of the suitable solvent is very important to ensure an effection and economical design of extractive distillation. The utilization of ionic liquid as entrainers comprise advantages of both liquid solvents and solid salts(W.Arlt et al., 2001).

In this case study, ionic liquid is used as the entrainer. Ionic liquids are under investigation as replacement solvents for separation as they reveal nearly no vapor pressure and they do not contribute to air pollution(J.D Seader,1998). Based on our preliminary assessment by using conductor-like screening model for real solvent (COSMO-RS) shows new ionic liquid of 1-propyronitrile-3-butylimidazolium dicyanamide has good performance in separation of aromatic hydrocarbon from aliphatic hydrocarbon. The selection criterias considered are the selectivity and capacity of the ionic liquid.

1.1.1 Properties of benzene and cyclohexane

Benzene is an aromatic hydrocarbon with the chemical formula C_6H_6 . It is non-polar, volatile, colourless, flammable liquid and has great thermal stability. Table 1 shows the physical properties of benzene.

Constant .	Value
Freezing point (°C)	5.533
Boiling point (°C)	80.100
Density at 25°C (g/cm ³)	0.8737
Refractive index	1.49792
Viscosity (absolute) at 20°C (cP)	0.6468
Surface tension at 25°C (dyn/cm)	28.18
Critical temperature (°C)	289.45

Table 1: Physical properties of benzene

Benzene is use as a chemical raw material in the synthesis of compounds such as styrene (polystyrene plastics and synthetic rubber), phenol, and cyclohexane (Nylon). It is also used in production of drugs, dyes, insecticides and plastics. Figure 1 shows the selected application of benzene in different chemical product.



Figure 1: Selected uses of benzene compound

Cyclohexane is a aliphatic hydrocarbon with the chemical formula C_6H_{12} . It is volatile, colourless, flammable, water insoluble, non-corrosive and non-polar liquid. Cyclohexane is used in paints and varnishes, as a solvent in plastic industry particularly for resins used in wire coating and for the extraction of essential oils.

1.1.2 Production of benzene and cyclohexane

Benzene

On account of the increasing demand for plastics detergents and organic chemicals, the production of benzene has increased rapidly since 1950. There are many roots to the production of benzene including :

- Extraction from crude oil or coal
- Dehydrogenation of cycloparaffins
- Dealkylation of chain alkyl aromatics (toluene and xylenes)
- Transalkylation of toluene
- Reforming separation

Cyclohexane

Some processes to produce cyclohexane including :

- Direct fractionation of crude gasoline
- Hydrogenation of benzene
- Direct distillation from naphtha

Among all processes to produce cyclohexane, hydrogenation of benzene process offer the highest purity product. Benzene is hydrogenated catalytically to cyclohexane in liquid or vapor phase in the presence of hydrogen. Some cyclohexane processes use nickel, platinum, or palladium as catalyst (M.L Campbell,1987). About 60% cyclohexane and 40% benzene are obtained as the product purity of the process.

1.1.3 Separation for Benzene/Cyclohexane

Separation of benzene/cyclohexane mixtures is among the most complicated processes in the petrochemical industry as the different boiling points for both compound is only 0.6°C and the interaction parameter between them is small. Figure 2 shows the vapor-liquid equalibrium curve of their binary liquid mixture benzene and cyclohexane before the presence of entrainer.



Figure 2: VLE of Benzene and Cyclohexane before present of entrainer (Scatchard G,1939)

Extractive distillation is widely used by the industry to separate benzene and cyclohexane. The selectivity of this process is limited by the vapor-liquid equalibrium and this process is carry out by adding a third component(entrainer) as solvent to alter the realative voaltility of the mixture. This report will further discusse the extractive distillation by using ionic liquid as entrainer. Figure 3 shows the expected result of VLE in presence of ionic liquid as entrainer.



Figure 3: VLE of Benzene and Cyclohexane after the presence of entrainer (AntjeWesterholt,2009)

1.1.4 Entrainer characteristics

Many factors should be considered in selecting entrainers such as selectivity, solubility, boiling point, thermal stability, corrosion, toxicity, prices and other chemical properties. Among these factors, a good indication of whether or not a certain component is a suitable entrainer from the thermodynamic point of view is the selectivity at infinite dilution. On the other hand, from the point of view of green separation process the amount of entrainer needed has to be minimized. Hence, the entrainer should combine a high selectivity with a high capacity.

$$S_{ij}^{\infty} = \left(\frac{\gamma_2^{\infty}}{\gamma_1^{\infty}}\right)^{L \text{ phase}} \qquad C_{12}^{\infty} = \left(\frac{1}{\gamma_1^{\infty}}\right)^{L \text{ phase}}$$

Where,

S = selectivity of IL

C = capacity of IL

 γ = activity coefficient at infinite dilution

The ionic liquid 1-propyronitrile-3-butylimidazolium dicyanamide is selected based on the selectivity and solvent capacity of the componenets (benzene and cyclohexane) in the ionic liquid. Generally, the performance of ionic liquid in separation of benzene and cyclohexane depends on the interaction of the component with ionic liquid and the strength of the cation and anion interaction. The longer alkyl length chain cation is unfavourable because it increases the Van der Waals interaction of ionic liquid and cyclohexane hence, reduces selectivity. On the other hand, the stronger cation-anion interaction reduces the interaction of benzene and ionic liquid. Therefore, to maximize the benzene-ionic liquid interaction and reduces the cyclohexane ionic liquid interaction, the cation-anion interaction need to be reduced. The introduction of electron withdrawing functional group in the alkyl chain increases the interaction between benzene and ionic liquid. However, the electron withdrawing functional group increases the cation-anion interaction. The cation-anion interaction can be reduced by using weakly coordinating anions such as dicyanamide. Moreover, [C2CNBim]N(CN)2 is selected because it contains electron withdrawing nitrile-functionalized group with weak's coordinating anion, dicyanamide. Table 2 shows the list of ionic liquid and their selectivity based on COSMO-RS.

Ionic liquids	Variation Effect	Selectivity
1-butyl-3-methylimidazolium dicynamide	Effect of alkyl	8.14
1-hexyl-3-methylimidazolium dicynamide	choin length	6.43
1-octyl-3-methylimidazolium dicynamide		5.07
1-propyronitrile-3-butylimidazolium	Effect of nitrile	
dicynamide	functional group	12.36
1-propyronitrile-3-butylimidazolium		
chloride		4.42
1-propyronitrile-3-butylimidazolium	Effect of onion	
ethylsulphate	Effect of amon	8.20
1-propyronitrile-3-butylimidazolium		
octyllsulphate		4.71

 Table 2: List of ionic liquids and their selectivity

1.2 Problem Statement

A lot of researches have been done for the thermophysical properties measurement different type of ionic liquid. But until today, there is no characterization and thermophysical property studies done on 1-propyronitrile-3-butylimidazolium dicyanamide. Thermophysical properties measurement is used to study the interaction of benzene and ionic liquid. In addition., thermophysical properties are important as the side factor in selection of suitable ionic liquid. Moreover, the vapor-liquid equilibrium model of 1-propyronitrile-3-butylimidazolium dicyanamide with benzene and cyclohexane compound is yet to be study in this project.

1.3 Objectives

- To measure thermophysical properties of ionic liquid 1-propyronitrile-3butylimidazolium dicyanamide.
- To evaluate/measure relative volatility of 1-propyronitrile-3butylimidazolium dicyanamide from benzene by using head-space gas chromatography (HS-GC).

1.4 Scope of study

For the present study of extractive distillation by using ionic liquid, the scope is limited to the following and the parameter that will be tested are in Table 1:

- Selection of ionic liquid
- 1-propyronitrile-3-butylimidazolium dicyanamide synthesis
- 1-propyronitrile-3-butylimidazolium dicyanamide charateristics studies (FTR,NMR and TGA)
- Benzene-cyclohexane mixture
- Thermophysical and extractive distillation study of benzene with ionic liquid (1-propyronitrile-3-butylimidazolium dicyanamide).
- Head-space gas chromatography as an efficient method for vapor-liquid (VLE) measurement.

Parameters and testing conditions as in Table 1.

Parameter	Testing condition
Thermopyhsical study	• 293.15 to 353.15 K
(ionic liquid):	Atmospheric pressure
density, p	
viscosity,µ	
refractive indices, η	
Relative volatility, a	At ideal solution

Table 3: Parameters that will be tested in the experiment

CHAPTER 2 LITERATURE REVIEW

Separation process can essentially be term as mass transfer process. The process can be classified as separation, mechanical or chemical. The choice of separation can be based on pros and cons of each. Mechanical separation are usually favored if possible due to lower cost of operations as compared to chemical separation. System that cannot be separated by purely mechanical means, chemical separation is the remaining solution. The mixture could exist as combination of any two or more states such as solid-solid, solid-liquid, solid-gas, liquid-liquid, gas-gas, solid-liquidgas etc. A separation process is any process that can take a combination or mixture of different componenets and extract at least one componenet in a higher purity than in the original mixture. Distillation, evaporation and crystallization are common separation processes in chemcial engineering.

Distillation is a process for isolating components from a mixture based on different boiling point. It is one of the most important separation processes mainly because it allows separating ideal and nonideal mixtures in large scale units. The separation of homogeneous and heterogeneous azeotropic mixture is a great industrial interest (M.A.S.S Ravagnani et al., 2009). Azeotropic mixture is a solution of two or more liquids where the composition of which does not change upon distillation. The composition of the liquid phase at the boiling point is identical to that of the vapor in equilibrium with it, and such mixtures or azeotropes form constant-boiling solutions.

The separation of aromatic hydrocarbons (benzene, toluene, ethylbenzene and xylenes) from C4 – C10 aliphatic hydrocarbon mixtures is challenging since these hydrocarbons have boiling points in a close range and several combinations form azeotropes. The separation of benzene and cyclohexane is one of the most important and most difficult processes in the chemical industry(G.W. Meindersma et al.,1990). Since benzene and cyclohexane form close boiling point mixtures at the entire range of their compositions, the separation is difficult by means of a standard distillation process. Since distillation is not a feasible option for the separation of aromatic hydrocarbons from C4 – C10 aliphatics due to their boiling points in a close range range range of their boiling points and the separation of aromatic hydrocarbons from C4 – C10 aliphatics due to their boiling points in a close range range range range points in a close range range range range points in a close range range point by the separation of a standard distillation process.

and the formation of several azeotropes, separation processes based on differences in interaction or affinity must be used. Examples of such processess are extraction, extractive distillation, adsorption/desorption and membrane permeation.

The selection criteria of separation process for close boiling point mixture are based on:

- Capacity
- Selectivity: >30
- Loss of solvent to raffinate: absent
- Recovery of aromatics: >98%
- Purity of the product streams: >98%
- Increase of investment costs with increased capacity

For each process option, the criterion with regard to capacity must be fixed. The capacity in an extraction process is determined by the distribution coefficient of the aromatics and the capacity of a membrane process is determined by the flux rate through the membrane. The benchmark for the selectivity (>30) is the selectivity obtained in the sulfolane extraction process, which is the most used process for separating aromatic and aliphatic hydrocarbons. The recovery of the aromatics needs not to be complete because of the formation of aromatics during the cracking process. Therefore, the value of 98% is an arbitrary value, just as the requirements of both product streams. For processes like extraction and extractive distillation, the investment cost scale with the capacity to the power 0.6 - 0.65, while the adsorption/desorption and membrane processes are scaled up with a power of 0.85 - 0.95. The higher scale-up factor for adsorption/desorption and membrane processes is directly related to the amount of adsorbent or membrane area. From this it can be stated that extractive distillation is suitable for large-scale processes.



Figure 4: UOP Sulfolane Process(www.uop.com/aromatics/3000.html)

Figure above shows the most commercial extraction process by using sulfolane as solvent but based on Weissermel and Arpe but currently there is no feasible process are available for the separation of aromatic and aliphatic hydrocarbons in the range below 20% aromatics in the feed mixture(G.W. Meindersma et al.,1990). The main reasons being that these processes are highly complex, require high investments and exhibit a large energy consumption due to the unfavourable capacity and selectivity of the solvents used and the need for additional separation steps for solvent recovery and purification of both product streams(Meindersma,2005).

Extractive distillation is used to separate azeotropes and other mixtures that have key components with a relative volatility below 1.1(J.D Seader et al.,1998). Generally, if the feed is a minimum-boiling azeotrope, a solvent, with lower volatility than the key component of the feed mixture is added to a tray above the feed stage and a few trays below the top of the column so that the solvent is present in the down flowing liquid phase to the bottom of the column and little solvent is stripped and lost to the overhead vapor.

Headspace gas chromatography (GC) is an efficient method for the measurement of (vapor-liquid) equilibria (VLE) of volatile compounds. The composition of vapor phase is determined by gas chromatography. The application of ionic liquids as alternative solvent for the separation of aromatics from aliphatic compound have

been investigated recently. Liebert et al. studied the VLE behaviour of the systems (methylcyclohexane+toluene) and (1-octane+octane) in the presence of 1-hexyl-3methyl-imidazolium bis(trifluoromethyl-sulfonyl) imide by headspace gas chromatography. In this work, the influence of ionic liquids on the separation factor for the separation of benzene from cyclohexane is investigated.

Room temperature ionic liquids (RTIL) are liquids that are composed entirely of ions and in this sense alone resemble the ionic melts which may be produced by heating normal metallic salts to high temperature. In fact, ionic liquids can now be produced which remain liquid at room temperature and below (even as low as -96 °C). Ionic liquids possess of a number of properties such as non-volatile component, which are important to be applied as extractive media in liquid/liquid extraction processes. They are liquid at room temperature and, in fact, they have an enormous liquid temperature range of 300 °C, which is larger than that of water (100 °C) and this offers the potential for considerable kinetic control of extractive distillation processes. They are good solvents for a wide range of inorganic, organic and polymeric materials.

Aromatic hydrocarbons are reported to have low activity coefficients at infinite dilution in several ionic liquids, while aliphatic hydrocarbons show high activity coefficients in the same ionic liquids(Huddleston al.et, 1998). This means that ionic liquids can indeed be used as extractants for aromatic hydrocarbons from aliphatic hydrocarbons. For the separation of aromatic hydrocarbons from a mixture of aromatic and aliphatic hydrocarbons, the use of aromatic cations and possibly aromatic anions will have a positive effect on the extraction of aromatic from the mixture. The application hydrocarbons of ionic liquids for extraction/extractive distillation processes is promising because of their non-volatile nature(Huddlestone et al., 1998).

CHAPTER 3 METHODOLOGY



3.1 Experimental procedure

3.1.1 Synthesis of ILs. 1-propyronitrile-3-butylimidazolium dicyanamide, [C₂CN Bim]N(CN)₂.

Imidazolium (1.0 mol) is placed into three-necked round-bottom flask and the system is degassed with nitrogen. Methanol (1.0 mol) is added and stirred thoroughly and then acrylonitrile (1.1 mol) is also added.nThe system is heated to 55°C and stirred vigorously for 10 h under nitrogen atmosphere. The unreacted methanol and acrylonitrile are removed under vacuum at 70°C. Then 1-chlorobutane (1.0 mol) is added by using syringe and the mixture is stirred and maintained at 70°C under nitrogen atmosphere for 48 h. The resulting compound is cooled to room temperature and wash with ethyl acetate for three times . The remaining solvent is removed at 80°C under vacuum for 4 h and then dried in a vacuum for 72 h. 0.8 mol of sodium dicyanamide is prepared and poured into a erlenmeyer flask with screw cap. 0.8 mol methanol is added to dissolve the solid phase sodium dicyanamide. The system is stirred vigourously for 48 h at room temperature (25°C) The resulting compound is filtered to separate the precipitate of sodium chlorice and unreacted sodium dicyanamide from the ionic liquid and methanol. The unreacted methanol is removed under vacuum at 70°C.

3.1.2 Ionic liquid characterization (FTIR, NMR and TGA).

All of the ILs synthesized in this study are characterized using a Shimadzu FTIR-8400S spectrometer with a 4 cm⁻¹ resolution and a wave number range of (350 to 7800) cm⁻¹. H NMR spectra is taken in CDCl₃ solvent and recorded on a Bruker Avance 300 spectrometer. A Perkin-Elmer, Pyris V-3.81 thermal gravimetric analyzer was used to measure the onset temperature and thermal decomposition temperature for the synthesized ionic liquids. The samples were placed in an aluminum pan under a nitrogen atmosphere at a heating rate of 10 °C·min⁻¹ with temperature accuracy better than \pm 3 K.

3.1.3 Ionic Liquid thermophysical properties measurement.

Water content : A coulumetric Karl Fischer titrator, DL 39 (Mettler Toledo) is used to determine the water content of synthesize ILs with benzene using Hydranal coulomat AG reagent (riedel-de Haen). The measurement for each ILs and benzene is made in triplicate and the average values are calculated. Density and Viscosity Measurements : The density and viscosity measurement of the present synthesized ILs are carried out at a temperature range from (293.15 to 323.15) K using an Anton Paar viscometer (model SVM3000). The temperature is controlled to within +- 0.01 °C. The reproducibility of the measurements are 0.35% and $+-5 \times 10^{-4}$ g/cm⁻³ for viscosity and density respectively. Refractive Index Measurements : The refractive indices are measured in the temperature range from (293.15 to 323.15) K using ATAGO programmable digital refractometer (RX-5000a) with a measuring accuracy of $+-4x10^{-5}$. The temperature of the apparatus is calibrated before each series of measurements and checked using pure organic solvents with known refractive indices. The samples are kept dried in desiccators and are directly placed into the measuring cell. The reproducibility of the results are confirmed by performing at least three experiments for each sample in the whole temperature range.

3.1.4 Vapor-Liquid Equilibrium (Head-space Gas Chromatography)

The ternary mixtures are prepared by weighing the appropriate amount of pure ionic liquid, benzene and cyclohexane. The mass of samples are determined using a laboratory balance with the precision of +- 10⁻⁴ g. The liquid samples of the ternary system with known composition are transfered in small vials with a volume of 12 cm³. Then the vials are closed tightly with a cap and a septum. These vials are inserted in the headspace sampler in order to reach the desired temperature and phase equilibrium. After phase equilibrium is reached, a sample from the vapor phase (headspace) is taken by the sampling device of the headspace sampler and analyzed by gas chromatography.

3.2 Chemicals Required

- Immidazole
- Acrylonitrile
- Benzene
- Sodium dicyanamide
- Ethyl acetate
- Methanol

3.3 Equipment/Instruments required

- Density meter
- Viscosity meter
- Analytical balance
- Refractometer
- FTIR-8400S
- NMR-Spectra
- Headspace Gas Chromatography(HSGC)

CHAPTER 4 RESULT AND DISCUSSION

4.1 Characterization of 1-propyronitrile-3-butylimidazolium dicyanamide

A coulometric Karl Fischer titrator, DL 39 (Mettler Toledo), is used to determine the water content of the synthesized ILs, using the Hydranal coulomat AG reagent (Riedel-de Haen). The measurement for each IL was made in triplicate, and the average values are reported in Table 1.

Table 4: Water Content (mass fraction) for [C2CN Bim]N(CN)2

Ionic Liquid	Water Content,	
	ррт	
[C ₂ CN Bim]N(CN) ₂	19820.11(1.99%)	

The structures of the synthesized ionic liquid are characterized by using FTIR (Figure 5), NMR (Figure 6 and 7) to comfirm the desired structure. The main feature in the FTIR spectra shows the characteristic absorption of a C=N group in the range from (2000 to 2245) cm⁻¹ and also C=N at (1550 to 1660) cm⁻¹. The FTIR exhibit C-H bond and weaker C-H bond stretches from (2920 to 3140) cm⁻¹ and from (2840 to 2870) cm⁻¹. The FTIR spectrum of the ionic liquid shown in Table 2 and Figure 5. From the NMR (H) ,the total number of hydorgen molecule observed is 18. Theoretically, 1-propyronitrile-3-butylimidazolium dicyanamide would only contain 16 molecule of hydrogen. Most probably the the other two molecules of hydrogen is from the water compund (H₂O). From the NMR (C) experimental result, the total number of carbon is equal to the theoretical total number of carbon.





Position at spectrum (ppm)	No of hydrogen
3.00	3
2.02	2
1.99	2
0.77	1
2.02	2
0.96	1
1.94	2
0.75	1
1.92	2
1.77	2
Total no of H	18

Table	5:	Summary	of NMR	result
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Figure 7: [C2CN Bim]N(CN)2 NMR Spectrum (C)

4.2 Thermophysical properties of 1-propyronitrile-3-butylimidazolium

Table 3 below shows the experimental densities of nitrile-functionalized ionic liquid with different anion in the temperature range from (298.15 to 353.15) K. The density values decrease after the incorporation of different anion present in the ionic liquid molecule. The density of the present synthesized ionic liquid (C₂CN Bim)N(CN)₂ are lower compared to othe nitrile-functionalized ionic liquid [(C₂CN Bim)Cl. These result might be due to the presence of different electronegativity of anion in the ionic liquid molecule. From the graph plotted, it is observed that density decreases in the order C₂CN Bim]N(CN)₂<[C₂CN Bim]Cl. The correlation that can be produced from the result is the higher the electronegativity present in the ionic liquid compound, the higher the density will be. Similarly, the density of each ionic liquid decreases with increasing temperature. This might be due to expansion of the internal arrangement of anion and cation of the ionic liquid.

		$\rho(g/cm^3)$		
		[C ₂ CN Bim]N(CN) ₂	[C ₂ CN Bim]Cl	
T(°C)	T(K)	(work)	[4]	
25	298.15	1.1197	1.1293	
30	303.15	1.1165	1.1261	
35	308.15	1.1133	1.1229	
40	313.15	1.1100	1.1196	
45	318.15	1.1068	1.1164	
50	323.15	1.1036	1.1133	
55	328.15	1.1004	1.1102	
60	333.15	1.0972	1.1070	
65	338.15	1.0940	1.1039	
70	343.15	1.0909	1.1007	
75	348.15	1.0877	1.0975	
80	353.15	1.0845	1.0944	

Table 6: Experimental Densities for [C2CN Bim]R as a function of temperature



Figure 8: Graph of density of ionic liquid vs temperature

		n _D	
		[C ₂ CN Bim]N(CN) ₂	[C ₂ CN Bim]Cl
T(°C)	T(K)	[work]	[4]
25	298.15	1.51954	1.5243
30	303.15	1.51802	1.5228
35	308.15	1.51616	1.5213
40	313.15	1.51447	1.5199
45	318.15	1.51244	1.5184
50	323.15	1.51056	1.5170
55	328.15	1.50844	1.5156
60	333.15	1.50614	1.5141

 Table 7: Experimental Refractive Indices for [C2CN Bim]R as a function of temperature.





Experimental refractive indices, n_D as a function of temperature for nitrilefunctionalized ionic liquids having similar alkyl length but different anion are presented in Table 4. The measured refractive indices of the present ionic liquids at (298.15 to 333.15) K in the range of (1.50614 to 1.5454). From the result, refractive indices decrease linearly with increasing temperature for each of the ionic liquids and also decrease with decreasing electronegativity of ionic liquid anion.

T(K)	Viscosity, µ(mPa.s)	
	(C ₂ CNBim)N(CN) ₂	(C ₂ CNBim)Cl
	[work]	[4]
293.15	276.26	4707
303.15	139.05	1612
313.15	77.96	668
323.15	47.716	314
333.15	31.355	164
343.15	21.81	94
353.15	15.896	58

Table 8: Experimental dynamic viscosities, η for [C2CNBim]R as a function of temperature.



Figure 10: Graph of viscosity of ionic liquid vs temperature

Table 5 shows the effect of temperature and functionalized anion side chain on nitrile containing imidazole cation with different anion attached as Cl and N(CN)₂. It is observed that the viscosity of the ionic liquid increase in the order of $(C_2CNBim)N(CN)_2 < (C_2CNBim)Cl$. These differences in viscosities might be due to the different electronegativity in each of the ionic liquid. As electronegativity of the anion in the ionic liquid chain increases, the viscosity increases.

The present experimental results on density and refractive index can be represented by the following empirical equation as a function of temperature:

$$\rho/(g \cdot cm - 3) = A0 + A1T$$
 (1)

$$nD = A2 + A3T \tag{2}$$

$$\log \eta(mPa.s) = A4 + A5/T \tag{3}$$

where ρ , n_D and η are the density, refractive index and viscosity respectively. T is the absolute temperature while $A_0, A_1, A_2, A_3, A_4, A_5$ are the correlation coefficient.

Since the density-temperature relationship for ionic liquid is linear, thermal coefficient expansion of the ionic liquid are calculated using density values as a function of temperature together with the calculated correlation coefficient by using the following equation:

$$\alpha/(K-1) = -(1/\rho)(\partial \rho/\partial T) = (A1)/(A0 + A1T)$$
(3)

where α is the thermal expansion coefficient in K⁻¹, ρ is the density, A₀ and A₁ are the fitting parameters of equation 1. Calculated thermal expansion values are as in Table 5 below.

	α(1/K) [10 ⁴]	
T(K)	[C ₂ CN Bim]N(CN) ₂	[C ₂ CN Bim]Cl
	[work]	[4]
298.15	5.30	5.62
303.15	5.32	5.64
308.15	5.33	5.65
313.15	5.34	5.67
318.15	5.36	5.68
323.15	5.37	5.70
328.15	5.39	5.72
333.15	5.40	5.73
338.15	5.42	5.75
343.15	5.43	5.77
348.15	5.45	5.78
353.15	5.46	5.80

 Table 9: Thermal Expansion Coefficient Values of Presented Ionic Liquid as a Function of Temperature.

The thermal expansion coefficient of these series of ionic liquids do not drastically change with temperature for the range from (298.15 to 353.15) K. The study of ionic liquid shows that the thermal expansion coefficient is weakly dependent with temperature, $\alpha = (0.000510 \text{ to } 0.000546)$. From the calculation result, ionic liquids having higher electronegativity offer higher thermal expansion coefficient.

Vapor Liquid Equilibria in Figure 11 below is generated by an azeotropic system of pure benzene and cyclohexane binary mixture. As observed, it is nearly imposible to separate the mixture.



Figure 11: X-Y plot of pure benzene and cyclohexane mixture.

After the introduce of ionic liquid $[C_2CN Bim]N(CN)_2$ as solvent, the azeotrope is broken as shown in Figure 12.



Figure 12: X-Y plot of benzene and cyclohexane mixture with IL.

Then the relative volatility of the benzene and cyclohexane mixture with ionic liquid is calculated by using formula as below:

$$\alpha = \frac{\frac{(y_i)}{x_i}}{\frac{(y_j)}{x_j}} = Ki/Kj$$

where,

 α = the relative volatility of the more volatile component *i* to the less volatile component

 y_i = the vapor-liquid equilibrium concentration of component *i* in the vapor phase x_i = the vapor-liquid equilibrium concentration of component *i* in the liquid phase y_j = the vapor-liquid equilibrium concentration of component *j* in the vapor phase x_j = the vapor-liquid equilibrium concentration of component *j* in the liquid phase

The calculated values of relative volatility of the compound mixture are presented in Figure 13. As potrayed, the relative volatility average value is 1.23 which is higher than 1.05 and this shows that separation of benzene and cyclohexane can simply occur.





CHAPTER 5

CONCLUSION AND RECOMMENDATION

A new functionalize imidazolium-based ionic liquid, namely, 1-propyronitrile-3butyl imidazolium dicyanamide [C2CNBim]N(CN)2 has been synthesized and is characterized by using FTIR, NMR and its thermophysical properties such as density and refractive indices are measured and compared with other ionic liquid's thermophysical properties as [C₂CN Bim]Cl. The effect of different anions in the ionic liquid are studied. The density decreases in order of [C₂CNBim]N(CN)₂< [C₂CNBim]Cl. From this observation, it is clearly shown that as the electronegativity increases, the density increases. The refracvtive indices decreases in order of [C2CN $[C_2 CNBim]Cl.$ From the result, it is clearly potrayed that as Bim]N(CN)₂< electronegativity increases, refractive indices increases. In general, their thermophysical properties of density and refractive indices decrease by increasing temperature. The coefficient of thermal expansion is considered to be independent of temperature in the range of (298.15 to 353.15) K as no appreciable change is observed with an increase of temperature. For extractive distillation part, based on the x-y diagram, it can be seen that aftar the present of ionic liquid of 1propyronitrile-3-butyl imidazolium dicyanamide [C₂CNBim]N(CN)₂ as solvent, the azeotrope phase is broken and the calculated relative volatility is greater than 1. As a result, the separation of benzene and cyclohexane can take place. For future work, it is recommended that solvent of ionic liquid relative volatility need to be compared with other solvent relative volatility with the same solvent to feed ratio and the separation efficiency can be compared to get the most ideal ionic liquid solvent. In addition, the cost of different ionic liquids for the industrial application is to be studied for the separation of benzene and cyclohexane.

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APPENDICES



Figure 14: Schematic diagram of industrial extractive distillation process.

Stream	Description	
27	Solvent stream	
47	Feed stream	
28	Product stream (cyclohexane)	
29	Benzene-Solvent stream	
30	Product stream (benzene)	
31	Solvent stream (recycle)	