Extraction of β–carotene from Hexane phase using Ionic Liquids: Screening suitable Ionic Liquids

by

Nurfahzalina Abul'as Binti Nazlan

16258

Dissertation submitted in partial fulfilment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

JANUARY 2015

Universiti Teknologi PETRONAS

32610 Bandar Seri Iskandar

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

(Dr. Muhammad Moniruzzaman)

UNIVERSITI TEKNOLOGI PETRONAS

BANDAR SERI ISKANDAR, PERAK

January 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.

NURFAHZALINA ABUL'AS BINTI NAZLAN

ABSTRACT

β-carotene is one of the biologically active compounds in plants and it contribute major coloring in fruits and vegetables. Carrots, oil palm fruit, sweet potato and other edible plants are currently the main sources of β-carotene. The benefits of β-carotene were antioxidant activity, inhibiting growth of colon cancer, food additives and high added-value product for cosmetics and pharmaceutical. In addition, the applications of β-carotene are mainly in food, cosmetic and pharmaceutical industries. Typically, the current extraction process of β-carotene had done through supercritical fluid extraction, ultrasound assisted extraction and conventional extraction using organic solvent. However, this process needs special equipment and very expensive. Therefore, to overcome these problems, Ionic liquids will be alternatives process to extract β-carotene from hexane using Ionic Liquids. For this research, the main objective was to extract β-carotene from hexane using Ionic Liquids and the specific objectives were to find suitable Ionic Liquids that can extract β-carotene selectively and to optimize the extraction parameters. The focus of this study was screening suitable Ionic Liquids using COSMO-RS Software and validation through experiment laboratory work. From COSMO-RS findings, 1-ethyl-3-methylimidazolium acetate [EMIM] was suitable Ionic Liquids while from experiment laboratory work findings, 8 hours was identified as optimum extraction time and 1:1 ionic liquids to standard solution ratio was identified as optimum ratio. Besides, 100 rpm was the highest extraction rate. As conclusion, this study would help the development of Ionic Liquids in extraction of β-carotene from hexane.

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Last but not least, thank you to my family and also friends in UTP for their support and encouragement which enable me to do my best for this project. I have undergoes a lot of hardship and challenges in completing this project. Their support had given me the driving force to give my best for this project and complete it within the time allocated.

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CHAPTER 1

INTRODUCTION

1.1 Background

The sources of β –carotene from vegetables is derived from solvent extraction of carrots, oil of palm fruit, sweet potato and other edible plants with subsequent purification. The solvents used for the extraction include hexane, acetone, ethyl acetate, ethanol and ethyl lactate (Ribeiro, 2011). The main coloring principle are α and β –carotenes of which β– carotene accounts for the major part. Besides the color pigments, these substances may contain oils, fats and waxes naturally occurring in the source material. β –carotenes can also be used as a nutrient ingredient to replace vitamin A lost in processing or as an added nutrient that may be lacking in the diet (FDA Website, Types of Food Ingredients, 2010). It may be added in flour, breads, cereals, rice, macaroni, margarine, salt, milk, fruit beverages, energy bars and instant breakfast drinks.

Other than that, β –carotene can be found in oil palm biomass. The biomass from oil palm residue includes oil palm trunks, fronds, kernel shell, empty fruit bunches, presses fruit fiber and palm oil mill effluent. According to MPOB statistics in 2005, 11.9 million tonnes of palm-pressed mesocarp fiber was produced in Malaysia and it constitutes about 15.7% of solid biomass of fresh fruit bunch. Oil palm biomass was enriched with biologically active compounds such as cellulose, hemicellulose, lignin, pectin, pigments, β-carotene, vitamin E, sterols and co-enzymes. The benefits of β-carotene were antioxidant activity, inhibiting growth of colon cancer cells and food additives. Other than that, β-carotene can be transformed into high added-value products such as bio actives for food, additives for cosmetics and pharmaceutical industries.

Supercritical fluid extraction (SFE) was the typically methods that use for pressed palm fiber that provides an oil rich in carotene. The important parameters for this extraction were temperature and pressure. Supercritical carbon dioxide (SC-CO_2) was also used as extracting solvent. For this extraction, SFE unit need such as a cooling bath, a pneumatic pump, an electric oven, two extraction vessels and a compressor. All these equipment are difficult to find in laboratory scale and consideration of time constrains for this projects.

Besides, Ultrasound assisted extraction (UAE) was extraction technique for the extraction of lipids, proteins, flavonoids, carotenoids, hemicelluloses, triterpenoids and aromatic compounds. These extraction techniques need various parameters such as extraction time, solvent type, biomass to solvent ratio, temperature, electrical acoustic intensity, length of the probe tip dipped into the solvent, duty cycle and pretreatment.

Other typical extraction was solvent extraction process. Organic solvent such as hexane, diethyl ether and heptane was used as extracting solvent. This typical extraction would have the residue level and heavy metals content that comes from solvent itself. By using conventional extraction, it has several disadvantages such as immiscibility with water, low boiling point and flash point. Ionic Liquids (ILs) was introduced as a new green solvent in extraction process to replace the conventional due to its properties.

Ionic liquids (ILs) are organic salts with a melting point less than 100˚C and are considered as “green solvents” due to their negligible vapor pressure, non-flammability, non-explosiveness, electrochemical and thermal stability, high conductive characters and can easily recycled (Earle & Seddon, 2000). ILs can emit no volatile organic compounds, attracted and as media for green synthesis. ILs was made up of at least two components which can be anion and cation. ILs can be categories into two categories which are simple salts that made up of one single anion and cation and binary ionic liquids. The properties of ionic liquids are melting point, viscosity, density and hydrophobicity and its can changes their properties due to the changes of structure of the ions. The examples of ILs are 1,3-dialkylimidazolium chloride ,1-alkyl-3-methylimidazolium tetrafluoroborates, 1-butyl-3-methylimidazolium chloride,1-ethyl-3-methylimidazolium acetate and 1-butyl-3-methylimidazolium hexafluorophosphate.

1.2 Problem Statement

Nowadays, extraction process of β-carotene have been developed in different processes such as supercritical fluid extraction, ultrasound assisted extraction and conventional extraction using organic solvents. Supercritical fluid extraction (SFE) is conducted with high temperature and pressure using special equipment, whereas ultrasound assisted extraction uses cavitation bubbles into high shear stress for allowing solvent to penetrate compound (Leighton,1994). In addition, through ultrasound assisted extraction it needed high energy, special equipment and very expensive. To overcome these limitations, Ionic Liquids (ILs) will be alternative process to extract and selecting β–carotene. ILs was chosen because green solvent, easier for selecting and required simple extraction process. For this research, ILs was chosen based on screening process using COSMO-RS Software to identify suitable ILs for extraction of β-carotene. The challenges are not all suitable ILs is available in PETRONAS Ionic Liquids Center. Therefore, for this study 1-ethyl-3-methylimidazolium acetate [emim] was selected and conducted the study of extraction of β-carotene from hexane using Ionic Liquids (ILs).

1.3 Objectives

The main objective of this project is to extract β-carotene from hexane using Ionic Liquids (ILs). The specific objectives include:

i. To find the suitable Ionic Liquids (ILs) that can extract β- carotene selectively.
ii. To optimize the extraction parameters such as ratio of standard solution with ionic liquids, mixing time and mixing rate.

1.4 Scope of study

As this project was involved experiment laboratory work, the study will focus to extract β-carotene by using Ionic Liquids (ILs). ILs was used as designer solvent for this project due to its properties that can be adjusted to suit the requirement of extraction process. β- carotene were selected to extract due to its contribution to environment friendly and proper management of oil palm biomass.

In order to achieve the main objective of this research, COSMO-RS Software was used to find the suitable ILs that can extract β-carotene selectivity. This software would be a new approach for undergraduate student but not post graduates student. COSMO-RS Software was screening software to identify suitable ILs. Activity Coefficient was the parameter to study in COSMO-RS. Then, proceed with manual calculation to identify selectivity based on activity coefficient of β-carotene and hexane. As the activity coefficient is lower the interaction of ionic liquids with β-carotene is higher. 1-ethyl-3-methylimidazolium acetate [emim] was identified as the suitable ILs for this study. Physical chemistry subject were applied for this software.

To achieve the objective, to extract β-carotene from hexane using ILs, the sample of standard solution was analyzed using UV-VIS before adding with ILs. After mixing with ILs, the sample was analyzed again using UV-VIS and compare the absorption rate. Standard curve was using as references to identify the extraction of β-carotene from hexane using ILs. General chemistry, organic chemistry, analytical chemistry and separation process studies were applied. In addition, to study and optimize the extraction parameters, the standard solution sample was mix with ILs with ratio 1:1 to study the effects of ratio of standard solution and ILs. For the mixing time of solution parameter was set at different time. Last but not least, the mixing rate for solution was set to be constant at 200 rpm.

CHAPTER 2

LITERATURE REVIEW

2.1 β -carotene

Figure 2.1(a): β-carotene in powder form

Based on Malaysian Palm Oil Board (MPOB), the fact is that Malaysia's oil palm area until 2011 are 5Mha. Malaysia as a tropical country that has hot and wet weather throughout the year would make Malaysia's a major global oil palm biomass producer compare to other countries. Despite the large amount of palm oil production, 100 million tons of biomass are produced in the oil palm industry in Malaysia (Norzita, 2014). The oil contributes to less than 25% by weight of the palm fruit bunch (FAO, 2011). For every kg of palm oil produced, approximately four kg of dry biomass is produced, excluding palm oil mill effluent (POME). In 2010, 88.74 Mt of Fresh Fruit Bunch (FEB) of oil palm was processed (GGS, 2011). In addition, the total crop of fresh fruit bunch is more than 30 million tons per year, which generate more than 10 million tons of EFB (Norzita, 2014). Empty fruit bunches fiber are mostly natural fibers primarily consist of cellulose about 65 to 70% of plant.

β-carotene was the highest molecular weight (536g/mol) among other minor components in palm pressed fiber oil. The benefits of β-carotene were antioxidant activity, inhibiting growth of colon cancer cells and food additives. Other than that, β-carotene can be transformed into high added-value products such as bio actives for food, additives for cosmetics and pharmaceutical industries. β –carotene was use as a food colorant in food in order to enhance its visual appeal and to match consumer expectations. Carotenoids are natural pigments, which are synthesized by plants and are responsible for the bright colors of various fruits and vegetables. Figure 2.1 (b) shows chemical structure of β –carotene. β –carotene is the most common carotenoid consisting of a highly branched, unsaturated chain containing identical substituted ring structures at each end.

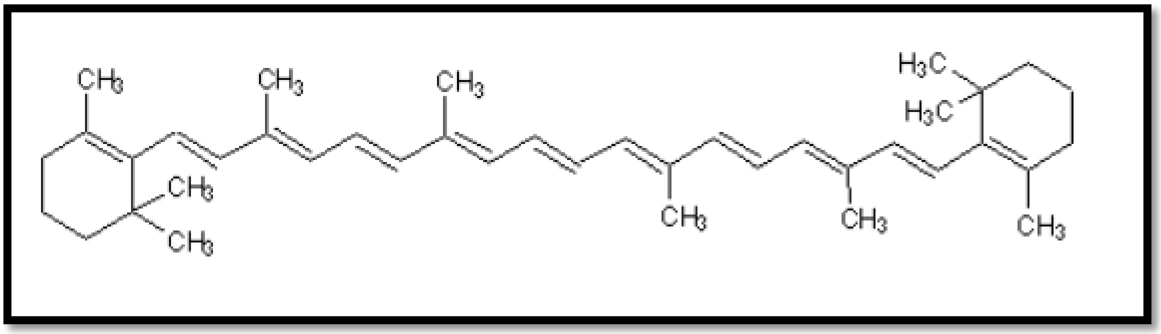


Figure 1.1 (b): β-carotene chemical structure

In plants, β –carotene occur almost always together structure with chlorophyll (Merck Index, 2006). It is the major coloring principle in carrot and as well palm oil seed extracts. In addition, β –carotene is found in cantaloupe, apricots, sweet potatoes, pumpkin, winter squash, mangos, collard greens, spinach, kale, broccoli and others. Other sources, β –carotenes can be produced from *Dunalilla salina* which is a unique species of alga that has a high content of natural carotenoids. This algal species has served and still as the major source for the extraction of β- carotene for commercial applications (Bosma and Wijffels, 2003). Carotenoids act as secondary pigments in photosynthetic organisms and as antioxidants and pro vitamin factors for non-photosynthetic organisms.

The properties of the β –carotene is insoluble in water, acids and alkali but it is soluble in carbon disulfide and chloroform. β –carotene is practically insoluble in methanol and ethanol and soluble in ether, hexane and oils. It absorbs oxygen from the air giving rise to inactive, colorless oxidation products (Merck Index, 2006). In other words, β –carotene changes in color from a fairly deep reddish-orange to the oxidized product which is a light, yellowish gray. (Furia, 1972). β –carotene melts between 176°C and 182 °C and its molecular weight is 536.87g/mol.

2.2 Extraction process

Supercritical fluid extraction (SFE) is one of the extraction processes for sustainable utilization of biomass. The unique about this process it need supercritical fluids which are duality between pure gas and liquids. The common solvent use was supercritical carbon dioxide (SC-CO_2) in extraction process of β-carotene, vitamin E, sterols, squalene from palm-pressed fiber and palm leaves (Birtigh, Johannsen, Brunner & Nair, 1995). Supercritical fluids properties can allow achieving high diffusion coefficient, high solvation power, high degree of selectivity and easy solvent separation (Kruse, 2010). These extraction process required special equipment such as cooling bath, a pneumatic pump, an electric oven, two extraction vessels, compressor and flow totalizer. Furthermore, several studies have demonstrated that supercritical fluid extraction (SFE) is more effective than conventional techniques for the extraction of compounds (Franca & Meireles, 1997)

Many researchers have done Ultrasound Assisted Extraction (UAE) uses acoustic cavitation for producing cavitation bubbles which implodes resulting into high shear forces (Leighton,1994). This helps in disrupting the cell wall allowing the solvent to penetrate into the plant material and increases the contact surface area between the solvent and compound of interest (Vinatoru, 1997). Many applications of UAE have done to extract lipids, proteins, flavonoids, carotenoids, hemicelluloses, triterpenoids and aromatic compounds. Soumen & Virendra, have done ultrasound assisted extraction of β-carotene from Spirulina platensis to study the effect of electrical acoustic intensity, extraction time biomass to solvent ratio and duty cycle. All this parameters study are required special equipment and very expensive.

ILs was introduced as a new green solvent in extraction process to replace the conventional due to its properties. The studied have done by Young et al, the ability of 1-ethyl-3-methylimidazolium methyl sulfate ([EMIM][CH_3SO_4]) to extract lipids from biomass samples. In their research, a mixture of ([EMIM][CH_3SO_4]) with polar covalent molecule was used for extracting lipids from microalgae biomass. The extraction of lipids by using ILs is higher compared to conventional solvents due to its properties. Other research have done, to extract cellulose from empty fruit bunch fiber by using ILs and followed by alkaline method. The properties of untreated and cellulose fiber were investigated using Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD) and Thermogravimetric (TG) analysis. By using ILs, the large amount of cellulose was removed (Norzita, 2014). For β – carotene content was analyzed using UV-VIS spectrometer after it had been extract by using ionic liquids.

2.3 Ionic liquids (ILs)

Ionic liquids (ILs) are organic salts that are composed by cations and anions with low melting temperatures, negligible vapor pressure and exceptional thermal and chemical stability. ILs are label as “designer solvent” due to its inimitable characteristic that offer a combination of different types of anion and cation that will eventually results in a wide range of solvent properties (Rogers, R.D. et.al. 2003). The selection of the most suitable ionic liquids for certain applications must require knowledge on the characteristic and properties of the solvent.

Ionic liquids had attracted many industrial personnel for the usage of ionic liquids as a solvent in their processes such as catalytic reactions. Ionic liquids had also being called as “green solvents” as it is eco-friendly and sustainable. However, the challenge that must be face is due to lack of information of this new solvent (Wilkes, J.S 2003). Until now, researches on application of ionic liquids are still being carried out to boost up its involvement in the industry.

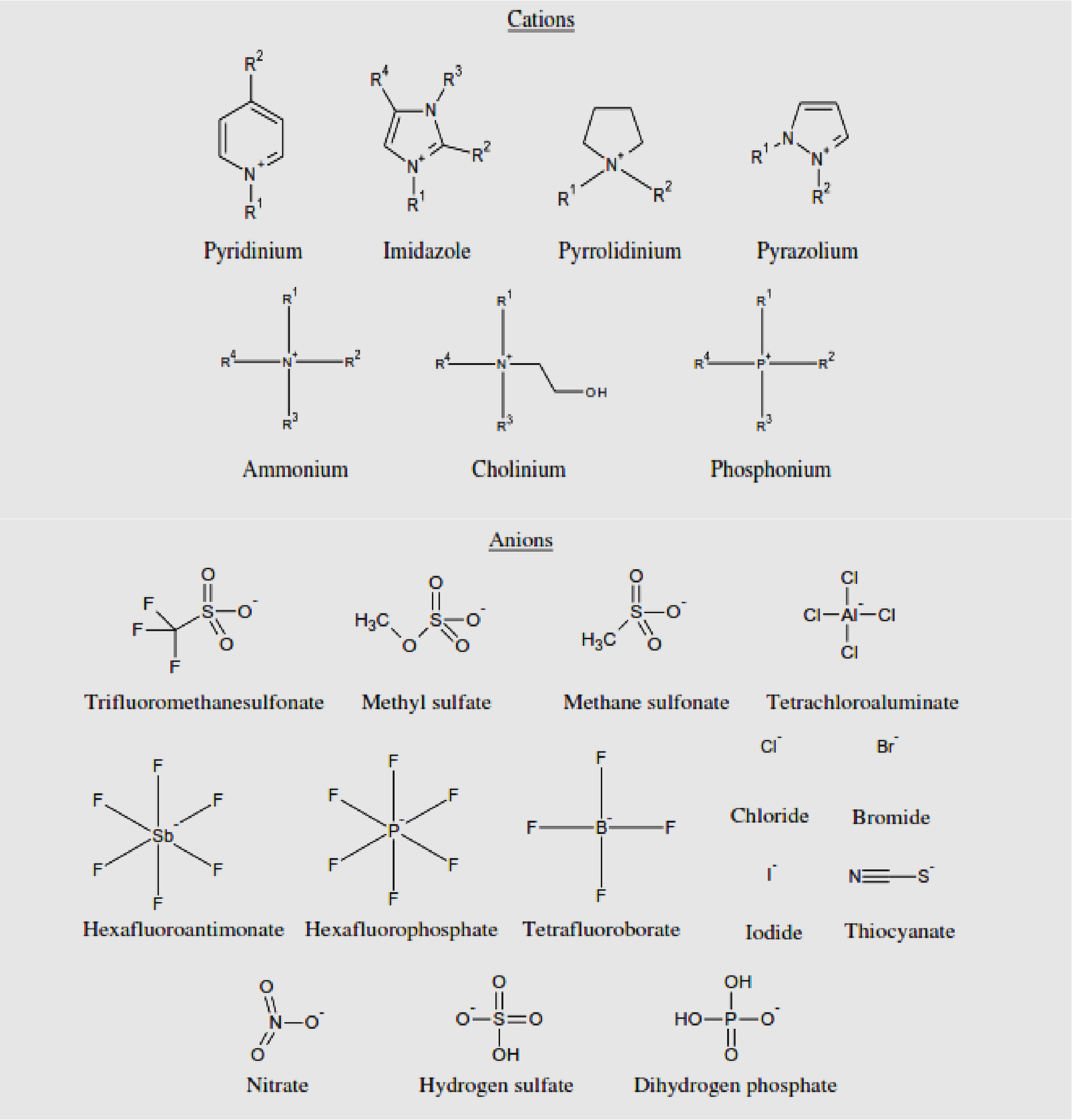


Figure 2.2: The commonly structure of anion and cation in ILs

The figure 2.3 shows the typical structure of cations and anions that are usually used in synthesizing ionic liquids. Ionic liquid consists of a cation which is normally a bulk of organic structure with low symmetry. While the anions of ionic liquids may be either be organic or inorganic.

Besides, the combination of the cation and anion will determine the melting point value of the ILs. The melting point of ILs can be correlated with the composition and structure of ILs. Combination of different anion and cation will result in different melting value (Singh. G, et.al., 2008). The symmetry of the ILs cation affects the melting point value. The cation with high symmetry will have higher melting point compared to the one with lower symmetry. This is among the uniqueness of ILs where its properties can be designed through combination of anion and cation.

The densities of ILs it highly depended on the bulkiness of the organic cation and the choices of the anion. The magnitude of ILs density depends on the constituent of its cation and anion. But generally ILs is denser than water with the range of 1.05 to 1.36g/cm^3 at ambient temperature. On the other hand, different ILs possesses different viscosity value. It is a fact that a high viscosity solvent is not suitable to be used as a solvent media. Some ionic liquids have high viscosity and it must be alert that these type of ILs are not suitable to be used as a solvent. It will affect the progress of the chemical reaction.

The properties of ILs are negligible vapor pressure it suitable to conduct organic synthesis and evaporate at high temperature for conducting synthesis in chemical application (Hafiidz & Aishah, 2012). Due to their properties negligible vapor pressure, ILs does not evaporate easily unless at very high temperature. ILs also can operate over a large temperature range. No vapor pressure means non-volatile solvent and no loss of solvent to the atmosphere can be beneficial in environment sustainability. The research have done by Qiao and Deng (2003), the cyclization of 1-dodecene to cyclododecane using 1-butyl-3-methylimidazolium chloride removed more volatile component which is ethanol by heating the product at 80-90°C without loss of ILs.

Ionic liquids (ILs) also manage to maintain its stability even at high temperatures. Most of it are still stable until 400°C. For thermal stability of ILs, anion itself will determine the thermal stability of an ILs rather than cation. Besides, before choosing an ILs as a solvent, it is very important for us to know its diffusivity and conductivity value. The influenced of ILs are based on size and pairing of ions. Van Valkenburg, have done studied about ILs have high thermal stability. They used 1-methyl-3-ethylimidazolium tetrafluoroborate, 1-methyl-3-butylimidazolium tetrafluoroborate and 1,2-dimethyl-3-propylimidazolium bis(trifluorosulfonyl)imide to determine the thermal decomposition temperature samples. They discovered all ILs have thermal decomposition above 400˚C.

2.4 COSMO-RS Software

Conductor-like Screening Model for Real Solvents (COSMO-RS) is a fully predictive model because it only requires universal parameters and element-specific parameters. Eckert & Klamt (2002) have found, based on COSMO-RS calculations is a fast and simple tool for predicting thermophysical and chemical properties of fluids and liquid mixtures. In a standard COSMO-RS prediction, COSMO files that containing all the molecular information is needed. Nowadays, the available COSMO database already covers COSMO files of thousands of conventional chemicals and most of the reported IL cations and anions. It has been proven that COSMO-RS can make relatively accurate predictions of activity coefficients of different solutes in ILs without re-parameterization or even parameter adjustment (Diedenhofen et.al., 2003). For these reasons, COSMO-RS is widely accepted as a fast ILs screening tool for various separation problems.

The residual contribution to the activity coefficient was determined by using the model COSMO-RS with parameter BP_TZVP. In general, ILs might either be modeled by different conformers with respect to the relative arrangement of their ions in the COSMO calculation or simple as two independent, equimolar, ionic species, whose COSMO files can be combined freely (Kahlen et. al., 2010) Within COSMO-RS the thermodynamic properties of a substance are directly correlated to the histogram of its surface charge distribution called the σ-profile. COSMO calculations within COSMO were performed using the BP-RI-DFT method and the TZVP basis set. The resulting monomeric conformers are weighted automatically by COSMOtherm according to their chemical potential in a given solution. For this purpose, the total free energy of each confirmation in the mixture is calculated as a sum of its DFT/COSMO energy in the conductor reference state and its individual pseudo chemical potential as obtained from COSMO-RS model.

CHAPTER 3

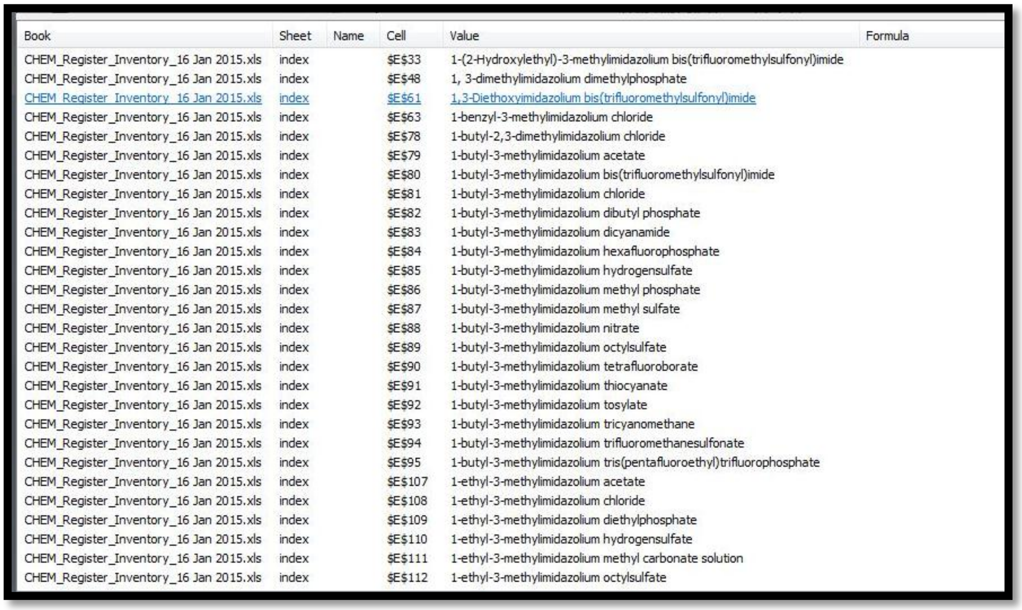
METHODOLOGY

3.1 COSMO-RS Software

COSMO software is a program allows the prediction of many properties of pure fluids, fluid mixtures and solutions. This software also a screening model for realistic solvents based. This software is used for this study to find suitable Ionic Liquids (ILs) by calculating the activity coefficient of ILs that can extract β-carotene selectively. By using this software, the best ILs will select based on interactions of ILs with solvent and ILs with extract. The screening method consists of two steps. The first step is the COSMO-RS based thermodynamics prediction. COSMO-RS was used to evaluate the effect of different cations and anions on the selectivity of IL. The most suitable cation and anion combination is subsequently suggested. The second step is the experiment validation. It involves simple experiment to study and confirm the selected IL.

3.1.1 List of cations

The list of cations was getting from chemical inventory at PETRONAS Ionic Liquids Centre, Universiti Teknologi PETRONAS.



Book	Sheet	Name	Cell	Value	Formula
CHEM_Register_Inventory_16 Jan 2015.xls	index		E33	1-(2-Hydroxylethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	
CHEM_Register_Inventory_16 Jan 2015.xls	index		E48	1, 3-dimethylimidazolium dimethylphosphate	
CHEM_Register_Inventory_16 Jan 2015.xls	index		E61	1,3-Diethoxyimidazolium bis(trifluoromethylsulfonyl)imide	
CHEM_Register_Inventory_16 Jan 2015.xls	index		E63	1-benzyl-3-methylimidazolium chloride	
CHEM_Register_Inventory_16 Jan 2015.xls	index		E78	1-butyl-2,3-dimethylimidazolium chloride	
CHEM_Register_Inventory_16 Jan 2015.xls	index		E79	1-butyl-3-methylimidazolium acetate	
CHEM_Register_Inventory_16 Jan 2015.xls	index		E80	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	
CHEM_Register_Inventory_16 Jan 2015.xls	index		E81	1-butyl-3-methylimidazolium chloride	
CHEM_Register_Inventory_16 Jan 2015.xls	index		E82	1-butyl-3-methylimidazolium dibutyl phosphate	
CHEM_Register_Inventory_16 Jan 2015.xls	index		E83	1-butyl-3-methylimidazolium dicyanamide	
CHEM_Register_Inventory_16 Jan 2015.xls	index		E84	1-butyl-3-methylimidazolium hexafluorophosphate	
CHEM_Register_Inventory_16 Jan 2015.xls	index		E85	1-butyl-3-methylimidazolium hydrogensulfate	
CHEM_Register_Inventory_16 Jan 2015.xls	index		E86	1-butyl-3-methylimidazolium methyl phosphate	
CHEM_Register_Inventory_16 Jan 2015.xls	index		E87	1-butyl-3-methylimidazolium methyl sulfate	
CHEM_Register_Inventory_16 Jan 2015.xls	index		E88	1-butyl-3-methylimidazolium nitrate	
CHEM_Register_Inventory_16 Jan 2015.xls	index		E89	1-butyl-3-methylimidazolium octylsulfate	
CHEM_Register_Inventory_16 Jan 2015.xls	index		E90	1-butyl-3-methylimidazolium tetrafluoroborate	
CHEM_Register_Inventory_16 Jan 2015.xls	index		E91	1-butyl-3-methylimidazolium thiocyanate	
CHEM_Register_Inventory_16 Jan 2015.xls	index		E92	1-butyl-3-methylimidazolium tosylate	
CHEM_Register_Inventory_16 Jan 2015.xls	index		E93	1-butyl-3-methylimidazolium tricyanomethane	
CHEM_Register_Inventory_16 Jan 2015.xls	index		E94	1-butyl-3-methylimidazolium trifluoromethanesulfonate	
CHEM_Register_Inventory_16 Jan 2015.xls	index		E95	1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate	
CHEM_Register_Inventory_16 Jan 2015.xls	index		E107	1-ethyl-3-methylimidazolium acetate	
CHEM_Register_Inventory_16 Jan 2015.xls	index		E108	1-ethyl-3-methylimidazolium chloride	
CHEM_Register_Inventory_16 Jan 2015.xls	index		E109	1-ethyl-3-methylimidazolium diethylphosphate	
CHEM_Register_Inventory_16 Jan 2015.xls	index		E110	1-ethyl-3-methylimidazolium hydrogensulfate	
CHEM_Register_Inventory_16 Jan 2015.xls	index		E111	1-ethyl-3-methylimidazolium methyl carbonate solution	
CHEM_Register_Inventory_16 Jan 2015.xls	index		E112	1-ethyl-3-methylimidazolium octylsulfate	

Figure 3.1.1: List of ILs in chemical inventory

There are seven groups of cations which are pyrrolidinium, imidazolium, ammonium, pyridinium, sulphonium, phosphonium, pyrazolium and cholinium**.** Figure 3.1.1 shows the list of ILs from chemical inventory. Some ILs was stable and some mixtures with water.

3.1.2 Drawing structure

After getting the list name of ILs, their structure was draw using Chem-Draw software. The group of cations are found and arranged in a serial relation. Then, anions were selected before run with COSMO-RS.

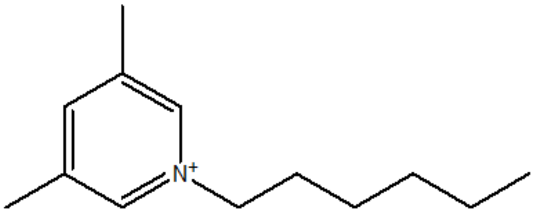
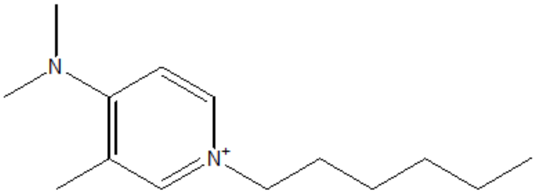
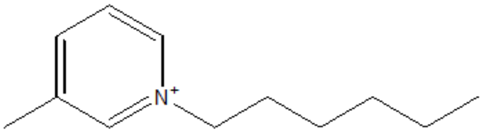
1-hexyl-3,5-dimethylpyridinium	 1-hexyl-3,5-dimethylpyridinium_cation
1-hexyl-3-methyl-4-(dimethylamino)pyridinium	 1-hexyl-3-methyl-4-(dimethylamino)pyridinium_cation
1-hexyl-3-methyl-pyridinium	 1-hexyl-3-methyl-pyridinium_cation

Figure 3.1.2(a): List name of pyridinium group and their structures

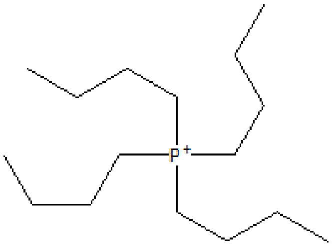
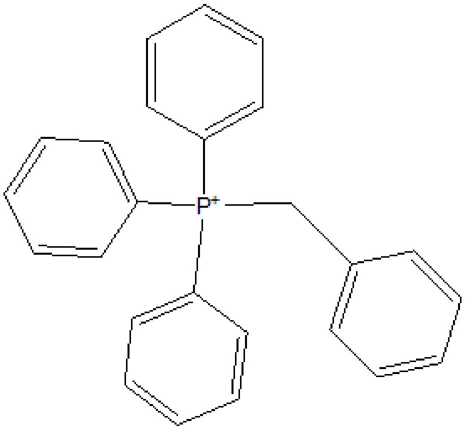
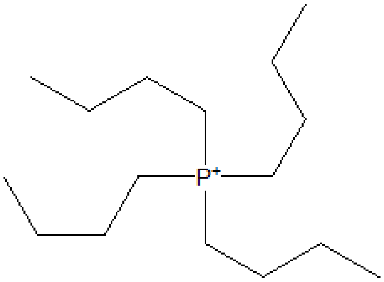
Name	Structure
tetra-n-butylphosphonium	 tetra-n-butylphosphonium
benzyl-triphenyl-phosphonium	 benzyl-triphenyl-phosphonium_cation
tetrabutyl-phosphonium	 tetrabutyl-phosphonium_cation

Figure 3.1.2(b): List name of phosphonium group and their structures

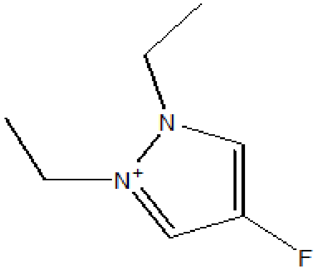
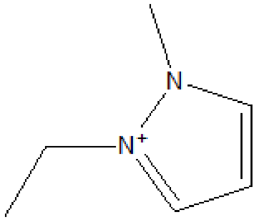
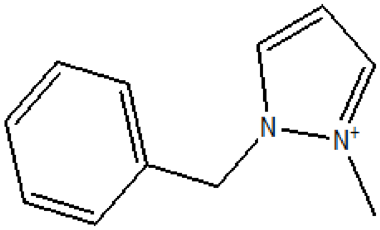
Name	Structure
1,2-diethyl-4-fluoropyrazolium	 1,2-diethyl-4-fluoropyrazolium_cation
1-ethyl-2-methylpyrazolium	 1-ethyl-2-methylpyrazolium_cation
1-methyl-2-(phenylmethyl)pyrazolium	 1-methyl-2-(phenylmethyl)pyrazolium_cation

Figure 3.1.2(c): List of pyrazolium group and their structures

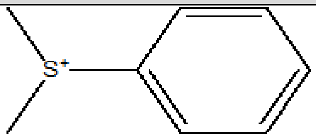
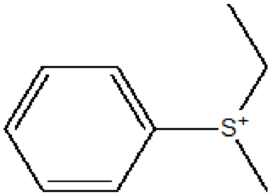
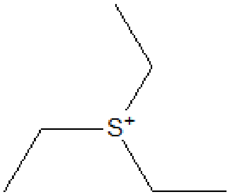
Name	Structure
Dimethyl-phenylsulfonium	 dimethyl-phenylsulfonium_cation
Ethyl-phenyl-methylsulfonium	 ethyl-phenyl-methylsulfonium_cation
Triethylsulfonium	 triethylsulfonium_cation

Figure 3.1.2 (d): List of sulfonium group and their structures

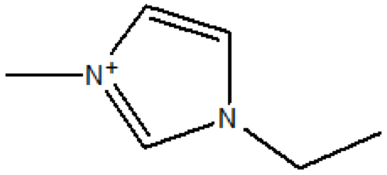
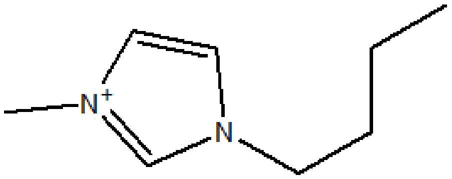
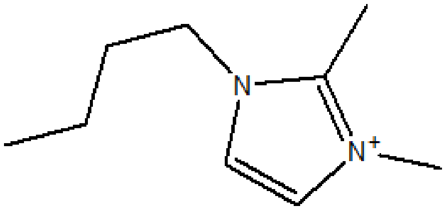
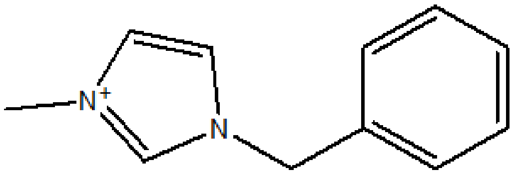
Name	Structure
1-ethyl-3-methylimidazolium	 1-ethyl-3-methylimidazolium
1-butyl-3-methylimidazolium	 1-butyl-3-methylimidazolium
1-butyl-2,3-dimethylimidazolium	 1-butyl-2,3-dimethylimidazolium
1-benzyl-3-methylimidazolium	 1-benzyl-3-methylimidazolium

Figure 3.1.2 (e): List of imidazolium group and their structures

3.1.3 COSMO-RS based thermodynamics predictions

The capability of COSMO-RS to calculate the chemical potential of an arbitrary solute *i* in any pure or mixed solvent enables the prediction of thermodynamics properties such as the activity coefficient and solubility. The activity coefficient at any concentration can be predicted by

$$\ln(\Upsilon i) = (\mu_{i}^{sol} - \mu_{i}^{p}) / RT \tag{1}$$

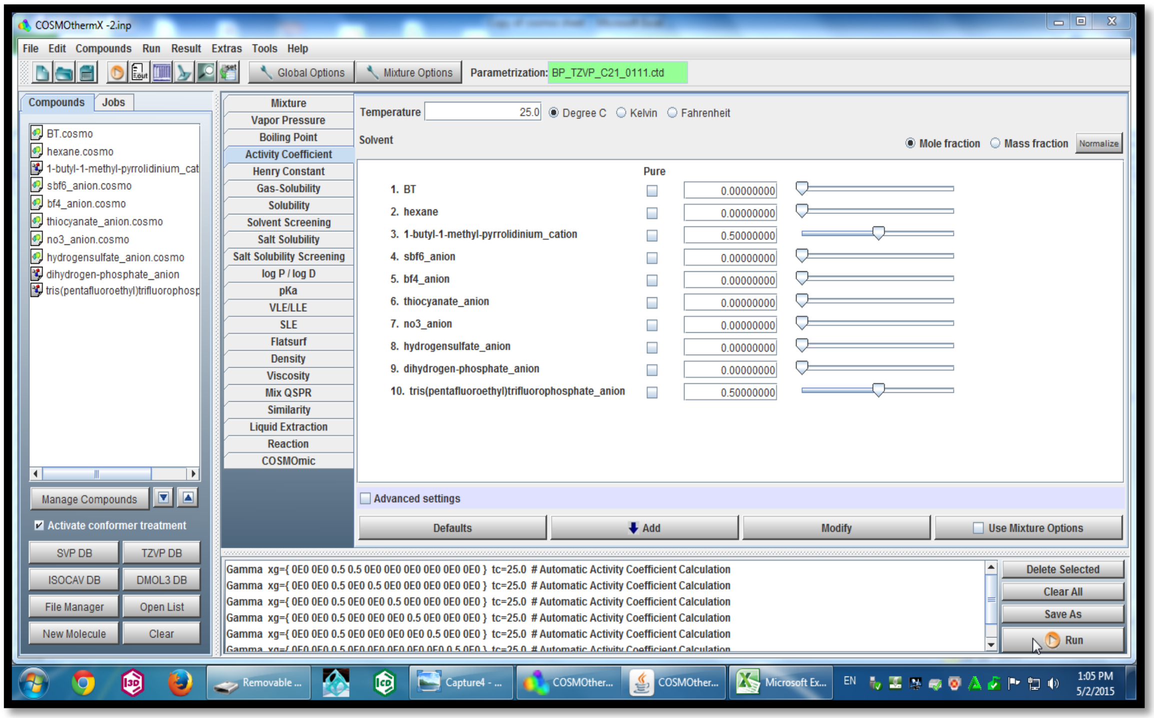
In Eq. 1, μ_{i}^{sol} and μ_{i}^{p} represent the chemical potential of the solute *i* in the solvent and in the pure solute, respectively. The extraction capacity ($C^{\epsilon\infty}$) and selectivity (S^{∞}) at infinite dilution, can be determined from the COSMO-RS calculated infinite dilution activity coefficient. These two parameters are widely used to evaluate the separation ability of a solvent for a specific task. (Jork et al., 2005; Kumar and Banerjee, 2009; Wilfred et al., 2013)

$$C^{\infty} = (1/\Upsilon\frac{\infty}{i})^{\text{IL}} \tag{2}$$

$$S^{\infty} = (\Upsilon_{j}^{\infty}/\Upsilon_{i}^{\infty})^{\text{IL}} \tag{3}$$

Where Υ_{i}^{∞} and Υ_{j}^{∞} refer to the infinite dilution activity coefficient of solute i and j in the IL phase, respectively.

The effect of cations and anions were start to investigate by chosen File manager menu to insert β-carotene data into COSMO database. The TZVP-DB menu were chosen to insert hexane, cation and anion. The cations were added in serial relation but the anion were select one by one and followed by hexane. Activity coefficient was chosen as a parameter. Normalize button were used to make sure the charges of cations and anions are balanced and equal to 1. Then, run button were click to run the model. After certain time, the modeling result will obtained. The result obtained was the value of ln ϒ which is activity coefficient. Proceed with manual calculation to calculate the selectivity.



Parametrization: BP_TZVP_C21_0111.ctd

Temperature 25.0 ● Degree C ○ Kelvin ○ Fahrenheit

Solvent ● Mole fraction ○ Mass fraction Normalize

	Pure	
1. BT	☐	0.00000000
2. hexane	☐	0.00000000
3. 1-butyl-1-methyl-pyrrolidinium_cation	☐	0.50000000
4. sbf6_anion	☐	0.00000000
5. bf4_anion	☐	0.00000000
6. thiocyanate_anion	☐	0.00000000
7. no3_anion	☐	0.00000000
8. hydrogensulfate_anion	☐	0.00000000
9. dihydrogen-phosphate_anion	☐	0.00000000
10. tris(pentafluoroethyl)trifluorophosphate_anion	☐	0.50000000

```
Gamma  xg={ 0E0 0E0 0.5 0.5 0E0 0E0 0E0 0E0 0E0 0E0 }  tc=25.0  # Automatic Activity Coefficient Calculation
Gamma  xg={ 0E0 0E0 0.5 0E0 0.5 0E0 0E0 0E0 0E0 0E0 }  tc=25.0  # Automatic Activity Coefficient Calculation
Gamma  xg={ 0E0 0E0 0.5 0E0 0E0 0.5 0E0 0E0 0E0 0E0 }  tc=25.0  # Automatic Activity Coefficient Calculation
Gamma  xg={ 0E0 0E0 0.5 0E0 0E0 0E0 0.5 0E0 0E0 0E0 }  tc=25.0  # Automatic Activity Coefficient Calculation
Gamma  xg={ 0E0 0E0 0.5 0E0 0E0 0E0 0E0 0.5 0E0 0E0 }  tc=25.0  # Automatic Activity Coefficient Calculation
Gamma  xg={ 0E0 0E0 0.5 0E0 0E0 0E0 0E0 0E0 0.5 0E0 }  tc=25.0  # Automatic Activity Coefficient Calculation
```

Figure 3.1.3: Print screen of COSMO-RS software

3.2 Standard Curve

Preparation of stock solution

Figure 3.2(a): B-carotene

Figure 3.2 (a) shows the commercial of β –carotene. β –carotene were soluble in hexane about 0.1g/L. (Wikipedia). These values approximately equal to 100 ppm. The standard solutions were prepared in series start from 10 ppm until 100 ppm. 2 mg of β–carotene were weighing out from the β-carotene sample bottle.

Figure 3(b): Hexane as solvent

To dissolves β- carotene, hexane was used as a solvent. Figure 3.2 (b) shows the sample of hexane. For stock solution, 20 ml of hexane have been measured and took out.β–carotene was dissolves in hexane by using magnetic stirrer at room temperature.

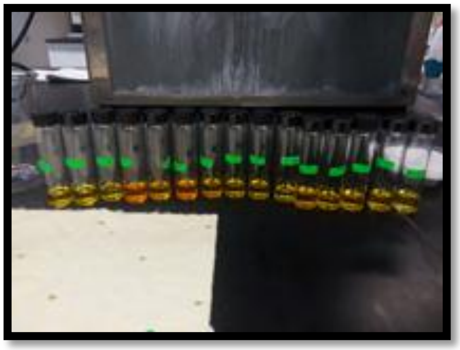


Figure 4.2 (c): The sample mixtures of b-carotene and *hexane*

After that, the mixtures must undergo dilution with pure hexane for the calibration solutions. Figure 3.2 (c) shows the sample mixtures of β-carotene with hexane. Every sample should have the amount which is 6ml based on concentration 100ppm. By using the formula:

$$C_1V_1 = C_2V_2 \qquad (4)$$

C_1 = Original concentration of the solution, before it diluted

C_2= final concentration of the solution, after dilution

V_1= volume about to be diluted

V_2= final volume after dilution

Here are preparations of calibration solution,

Table 3.2: Preparation of calibration solution

Concentration (ppm)	Stock solution (ml)	Dilution of hexane required (ml)
100	6	0
90	5.4	0.6
80	4.8	1.2
70	4.2	1.8
60	3.6	2.4
50	3.0	3.0
40	2.4	3.6
30	1.8	4.2
20	1.2	4.8
10	0.6	5.4

The sample was tested using UV-VIS Spectrometry to analyze the intensity of β-carotene in the samples solution. The standard curve was obtained through this analysis. This standard curve would be the references for this research to study the extract of β-carotene using Ionic Liquids. The standard curve experiment was done and the result will discuss in next chapter.

3.3 Experiment Laboratory work

Preparation for the study of extraction time

The sample of β-carotene and hexane were prepared as the same as standard solution sample. These two samples were dissolved in beaker and stirred until β-carotene turns yellowish gray as shown in figure 3.3 (a).

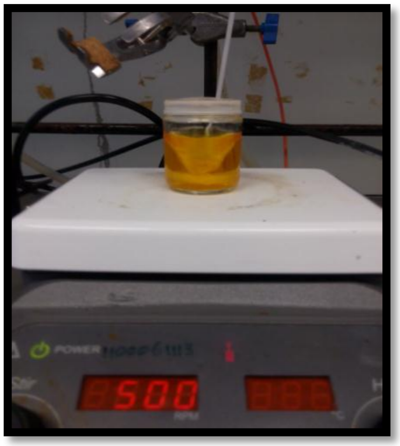


Figure 3.3(a): The mixture of B-carotene and hexane on the hot plate

After the sample turns yellowish gray, took out 2ml and added into 1-ethyl-3-methylimidazolium acetate [emim] about 2ml. The ratio of solution to the ratio of ILs is 1:1.Then, the sample was continued stir about 200rpm and left for 24 hours. The step was repeated for sample 18 hours, 8 hours, 5 hours and 2 hours without changes the mixing rate and ratios.

Table 3.3(a): Preparation of samples with different extraction time

No.	Extraction time (hours)	Ionic liquids to standard solution ratio (ml/ml)	Extraction rate (rpm)
1.	2	1 :1	200
2.	5	1 :1	200
3.	8	1 :1	200
4.	18	1 :1	200
5.	24	1 :1	200

Figure 3.3(b): 1-ethyl-3-methylimidazolium acetate [emim] as ILs

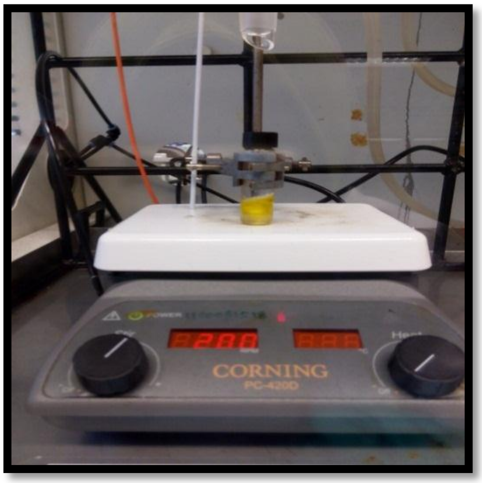


Figure 3.3 (c): The sample stirred at 200 rpm for 24 hours

After certain time, the stirrer was stopped and waited until the mixtures were separated into two phases. Simple liquid-liquid extraction method was applied to separate the mixture of hexane with β-carotene and the mixture of ILs with β-carotene.

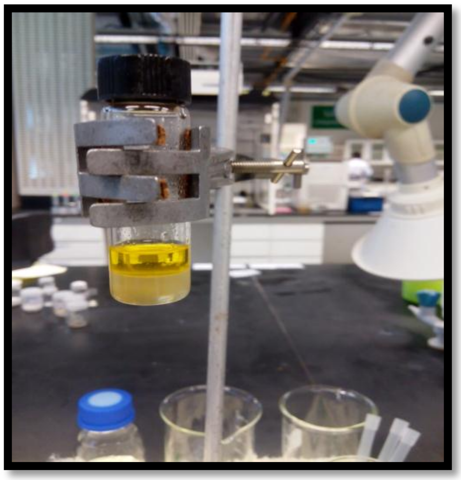


Figure 3.3(d): The mixtures were separated into two phases

Figure 3.3 (d) shows the mixtures of two phases. The top part was extract phase and the bottom part was Ionic Liquids with some β-carotene. The extract phase must undergoes dilution again before analyzed using UV-VIS Spectrometer. The result obtained was referred and compare with standard curves.

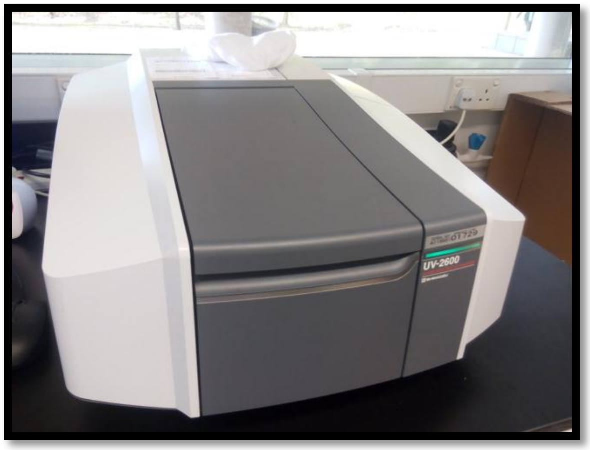


Figure 3.3 (e): UV-VIS Spectrometer

Same steps were repeated for the preparation of sample for different ionic liquids to standard solution ratio and extraction rate. Table 3.3 (b) and table 3.3 (c) shows the different of ionic liquids to standard solution ratio and different extraction rate.

Preparation for the study of different ionic liquids to standard solution ratio

Table 3.3 (b): Preparation of samples with different Ionic Liquids to standard solution ratio

No.	Extraction time (hours)	Ionic liquids to standard solution ratio (ml/ml)	Extraction rate (rpm)
1.	8	1 :0.8	200
2.	8	1 : 1	200
3.	8	1 : 2	200
4.	8	1 : 3	200
5.	8	1 : 4	200
6.	8	1 : 5	200

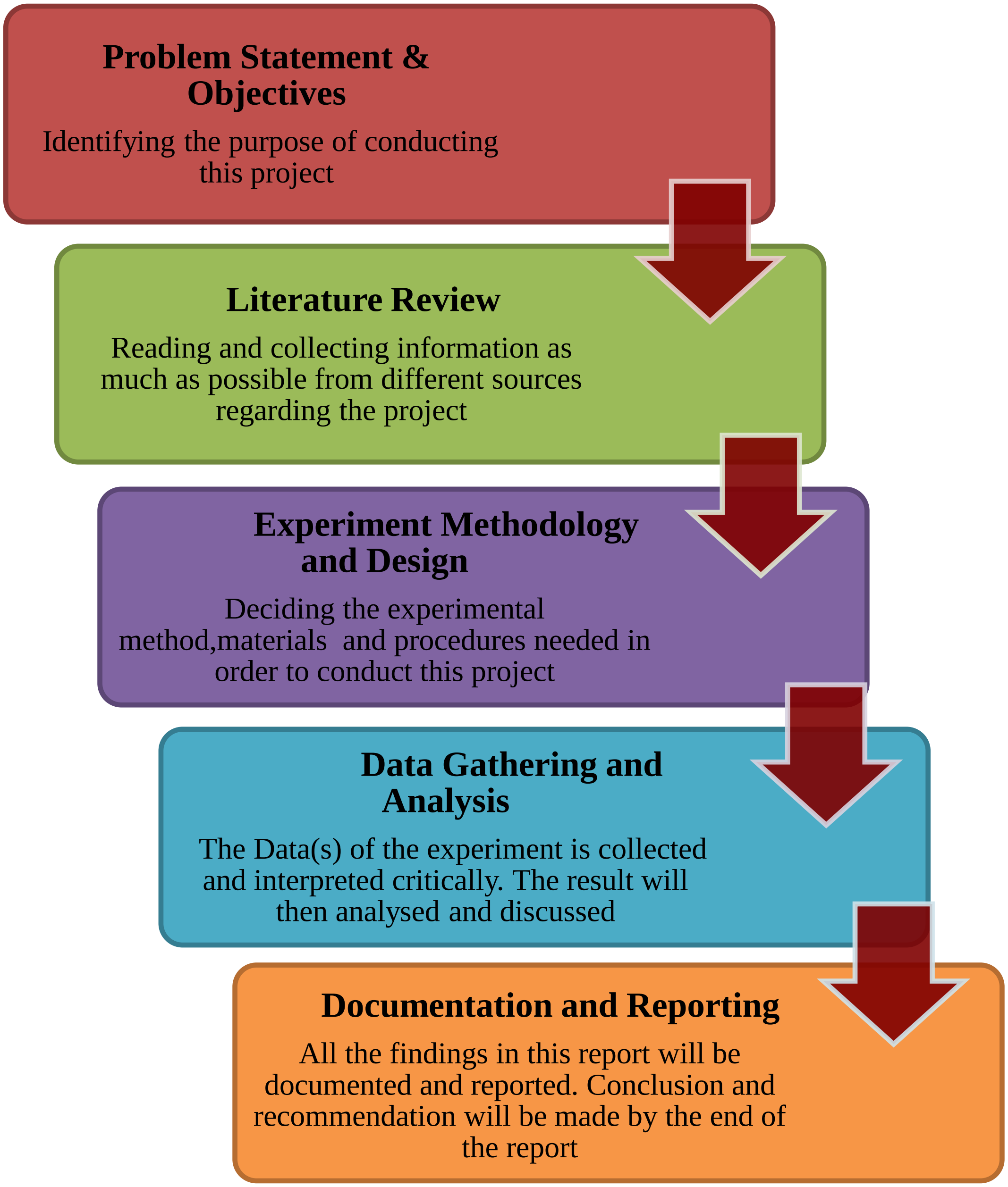
Preparation for the study of different extraction rate

Table 3.3 (c): Preparation of sample with different extraction rate

No.	Extraction time (hours)	Ionic liquids to standard solution ratio (ml/ml)	Extraction rate (rpm)
1.	8	1 : 1	100
2.	8	1 : 1	200
3.	8	1 : 1	300
4.	8	1 : 1	400
5.	8	1 : 1	500

3.4 Project Process Flow

This is the process flow for the project activity that must be followed in order to achieve the objective of the study:



Problem Statement & Objectives

Identifying the purpose of conducting this project

Literature Review

Reading and collecting information as much as possible from different sources regarding the project

Experiment Methodology and Design

Deciding the experimental method,materials and procedures needed in order to conduct this project

Data Gathering and Analysis

The Data(s) of the experiment is collected and interpreted critically. The result will then analysed and discussed

Documentation and Reporting

All the findings in this report will be documented and reported. Conclusion and recommendation will be made by the end of the report

Figure 3.4: Process Flow of the project

3.5 Gantt chart and Key milestone

Table 5 and 6 show the gantt chart and key milestone of the project that need to be followed during this study:

🟥 Gantt chart 🟨 Key milestone

Table 3.5 (a): Gantt Chart & Key Milestone (FYP 1)

No.	Detail / week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1.	**Selection of Project Topic**	🟥	🟥												
2.	**Preliminary Research Work**		🟥	🟥	🟥	🟥	🟥								
3.	**Submission of extended proposal**							🟨							
4.	**Proposal Defense**								🟨						
5.	**Project work continues**								🟥	🟥	🟥	🟥	🟥	🟥	🟥
6.	**Submission of interim draft report**												🟨		
7.	**Submission of interim report**													🟨	

🟥 Gantt chart 🟨 Key milestone

Table 3.5 (b): Gantt chart & Key Milestone (FYP 2)

No.	Detail / week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1.	Project activities	🟥	🟥	🟥	🟥	🟥	🟥	🟥								
2.	Submission of progress report								🟨							
3.	Project work continues								🟥	🟥	🟥	🟥	🟥			
4.	Pre-Sedex											🟨				
5.	Submission of draft final report												🟨			
6.	Project work continues												🟥	🟥	🟥	🟥
7.	Submission of softbound													🟨		
8.	Submission of tech paper														🟨	
9.	Viva															🟨
10.	Submission of hardbound															🟨

CHAPTER 4

RESULTS AND DISCUSSION

In this section, the author will discuss on the result for two sections which are the modeling using COSMO-RS and experimental laboratory result for validation purposes. For COSMO-RS, the author had identified a few groups of cations that suitable for this research. The suitable groups are sulfonium, ammonium and imidazolium. From this groups, the suitable ILs have been identified such as triethylsulfonium acetate, triethylsulfonium chloride, triethylsulfonium bromide, tetrabutyl ammonium hydroxide, tributylmethyl ammonium hydroxide, 1-ethyl-3-methylimidazolium acetate [emim] and 1-ethyl-3-methylimidazolium chloride. However, the author also had done others groups of cations and the result do not shows the potential of suitable ionic liquids for this project. The details of the result might be referred in the appendices.

Here are the result and findings from COSMO-RS prediction:

Table 4.0(a): Triethylsulfonium with acetate, chloride and bromide anions

Triethylsulfonium	**ln (ϒ)**	**ϒ @ ternary system**	**ϒ @ binary system**	**K**	**S**	**PI**
Acetate						
Beta-carotene	1.58625713	4.885429139	2.44271457	0.409380618	0.990	0.405
Hexane	1.59612541	4.933878585	2.466939293			
Chloride						
Beta-carotene	-4.02709136	0.017826104	0.008913052	112.1950125	0.018	2.042
Hexane	-0.02057204	0.979638121	0.48981906			
Bromide						
Beta-carotene	-1.41416588	0.243128327	0.121564164	8.226108508	0.117	0.963
Hexane	0.73084951	2.076844158	1.038422079			

Table 4.0(b): Tetrabutyl ammonium with hydroxide anions

tetrabutyl ammonium	**ln (ϒ)**	**ϒ @ ternary system**	**ϒ @ binary system**	**K**	**S**	**PI**
Hydroxide						
Beta-carotene	0.4718785	1.60300267	0.801501	1.2476585	0.9589214	1.196406
hexane	0.5138246	1.67167251	0.835836			

Table 4.0(c): Tributylmethyl ammonium with hydroxide anions

Tributylmethyl ammonium	**ln (ϒ)**	**ϒ @ ternary system**	**ϒ @ binary system**	**K**	**S**	**PI**
Hydroxide						
Beta-carotene	-0.15538782	0.856083107	0.428041553	2.33622178	0.565	1.319
Hexane	0.41640886	1.516505781	0.75825289			

Table 4.0(d): 1-ethyl-3-methylimidazolium with acetate and chloride anions

1-ethyl-3-methylimidazolium	**ln (ϒ)**	**ϒ @ ternary system**	**ϒ @ binary system**	**K**	**S**	**PI**
Acetate						
Beta-carotene	3.52357177	33.90531443	16.95265722	0.058987803	3.781	0.223
Hexane	2.19357484	8.967212234	4.483606117			
Chloride						
Beta-carotene	-2.71946902	0.065909742	0.032954871	30.34452728	0.045	1.370
Hexane	0.37835412	1.459879824	0.729939912			

Activity coefficient (ϒ) is the result of the effects of interactions between ion or molecule and its surroundings. Activity coefficient (ϒ) very hard to define, it is usually measured with reference to an ideal state. The activity coefficient (ϒ) is defined as the limit of the equation derived for activity and has no units. For this project, the activity coefficient (ϒ) can be calculated in terms of mole fractions for liquids and solid mixtures in terms of molalities for dilute solutions. Based on the table above, the value of activity coefficient (ϒ) directly getting from COSMO-RS. By using that value, it can proceed to identify solvent capacity (K), selectivity (S) and performance index (PI). The selectivity provides a useful index for selection of suitable ILs which defined as

$$S_{12} = \Upsilon 1/\Upsilon 2 \qquad (5)$$

Where ϒ1= activity coefficient of β-carotene and ϒ2 = activity coefficient of hexane in ILs respectively.

But at the same time solvent capacity (K) is also an important index and should be considered. Solvent capacity is defined as

$$K = \frac{1}{\Upsilon 1} \qquad (6)$$

Therefore, a suitable ILs should possess both a high selectivity and a high solvent capacity for the components to be separated. However, for this research the selectivity which is lower than 1 should be chosen. This is because the lower the selectivity the higher the interaction of β-carotene-IL compare to interaction of hexane-IL. Due to the limitations, 1-ethyl-3-methylimidazolium acetate [emim] was chosen as the best ILs for this project.

Here are the results from experimental laboratory work:

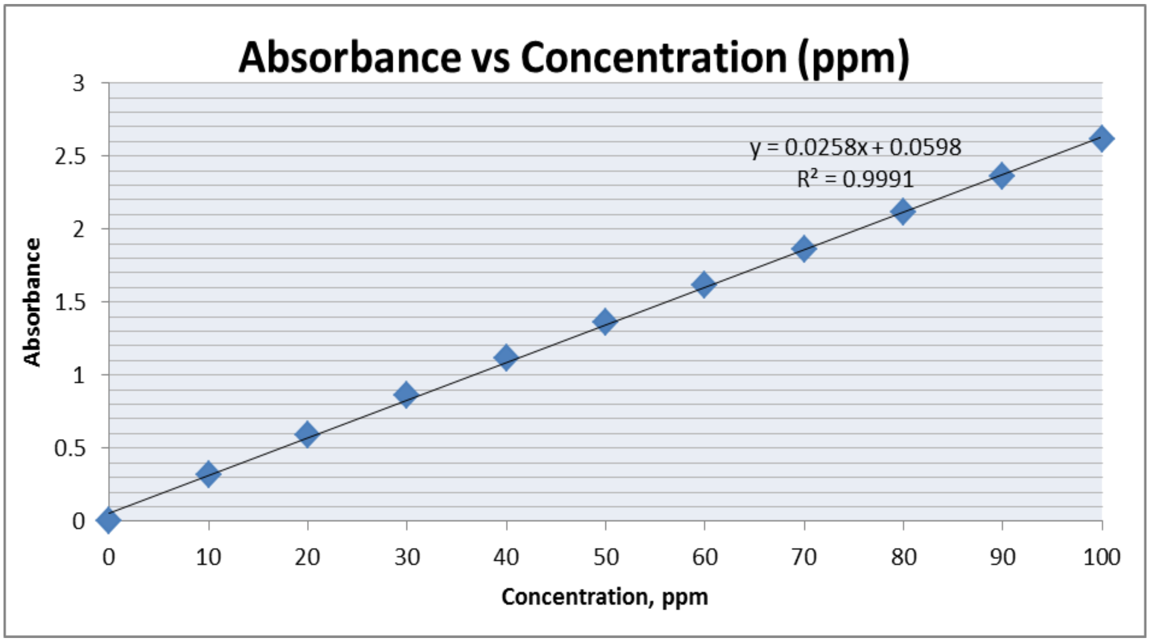


Figure 4.0: Absorbance against concentration

Figure 4.0 shows, the standard curve for absorbance against concentration. The concentration was the mixtures of β-carotene and hexane solution whereas the absorbance was after done analyzing the sample using UV-VIS. As seen in the graph, the curve was linear as the concentration increases the absorbance also increases. These curves were prepared earlier and important for the experiment as the references for this research to study the extract of β-carotene using ILs.

These researches have three objectives need to be achieved at the end of this experiment. One of the objectives is to optimize the extraction parameter such as extraction time, extraction rate and ionic liquids to standard solution ratio.

4.1 Result for extraction time:

Table 4.1: Effect of extraction time towards extraction efficiency

Run	Extraction time (hr)	Extraction rate (rpm)	Ratio	Volume of extract (V_2')	Absorbance (y)	Volume after dilution (V_2)	C_2' (x)	C1 (ppm)	C2 (ppm)	Efficiency (%)
1	2	200	1	1.2	1.877	4	70.43	100	21.13	78.87
2	5	200	1	1.4	1.185	4	43.61	100	15.26	84.74
3	8	200	1	1.6	1.019	4	37.18	100	14.87	85.128
4	18	200	1	1.6	1.416	4	52.57	100	21.03	78.97
5	24	200	1	1.8	1.075	4	39.35	100	17.71	82.29

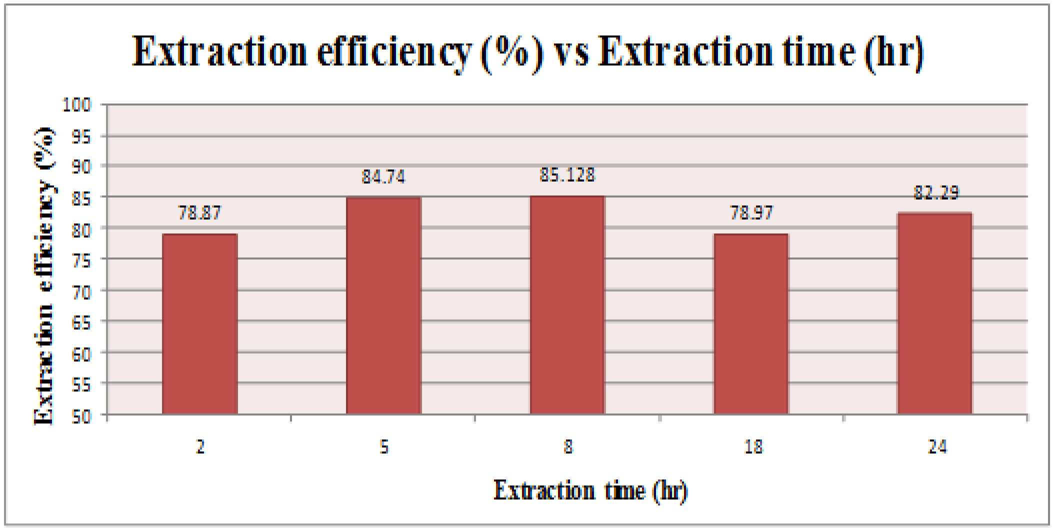


Figure 4.1: Extraction efficiency (%) against extraction time (hours)

Effect of extraction time:

Table 11 shows the effect of extraction time towards extraction efficiency. The values of absorbance (y) getting from UV-VIS are substitutes into standard curve equation **y= 0.0258x + 0.0598.** For the extraction efficiency (%) equation (7) was used.

$$C_2'V_2' = C_2V_2 \qquad (7)$$

The details of the calculation might be referred in appendices.

Figure 21 shows the extraction efficiency of Ionic Liquids to extract β-carotene from hexane at different extraction time. It has been observed that the extraction gradually increases from 2 hours, 4 hours and 8 hours. Then, at 18 hours, the extraction decreases and becomes increases again at 24 hours extraction time. At 8 hours was the highest efficiency about 85.128%. This is because the concentration gradient achieves the optimum rate whereas as increases in the extraction time, the concentration gradient decreased as well as the extraction become difficult. As shown at 24 hours, the continuous of extraction increase again about 82.29%. This is because it release of product of interest due to extraction, the solvent become saturated with product.

4.2 Result for Ionic Liquids to standard solution ratio:

Table 4.2: Effect of extraction ratio towards extraction efficiency

Run	mixing time (hr)	mixing rate (rpm)	Ratio (IL/Solution)	absorbance (y)	C1 (ppm)	C2 (ppm)	Efficiency (%)
1	8	200	1.25	0.604	100	21.09	79.98
2	8	200	1	1.272	100	18.79	81.12
3	8	200	0.5	2.615	100	84.18	15.82
4	8	200	0.33	2.615	100	99.04	0.96
5	8	200	0.25	2.615	100	99.04	0.96
6	8	200	0.2	2.615	100	99.04	0.96

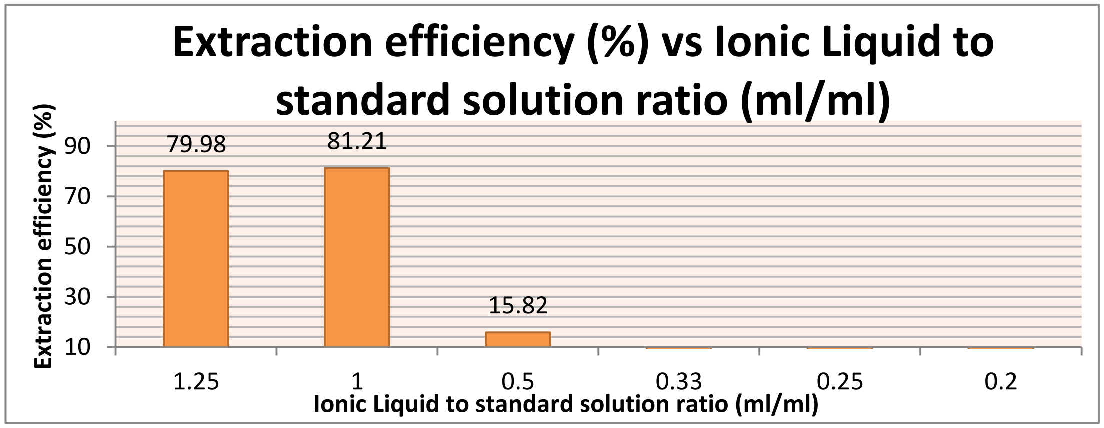


Figure 4.2: Extraction efficiency (%) against Ionic liquids to standard solution ratio (ml/ml)

Effect of ionic liquids to standard solution ratio:

For the result regarding ratio, the initial concentration are out of the standard curve range. For this study, the author have to proceed to calculate the extraction efficiency by directly getting the absorbance values from initial sample after analyze using UV-VIS and absorbance values of extract phase. The details of the calculation might be referred in appendices.

Figure 22 shows the extraction efficiency of Ionic Liquids to extract β-carotene from hexane at different extraction ratio. Ionic liquids to standard solution ratio are one of the most important parameters to be optimized in extraction process. Thus, the extraction ratio was measured at different ratios ranging from 1.25 (ml/ml) to 0.2 (ml/ml) and the results as shown in the figure 22. It has been observed that the extraction gradually increases from 1.25 (ml/ml) to 1.0 (ml/ml) and then decreases gradually as increases the ratios. The highest extraction efficiency was at 1.0 (ml/ml) about 81.21%. This is because the solvent volume was high and the concentration of β-carotene to be extracted was low. As ratio increases, the solvent slowly become saturated and non-complete interaction of solvent and β-carotene.

4.3 Result for extraction rate:

Table 4.1: Effect of extraction rate towards extraction efficiency

Run	Extraction time (hr)	Extraction rate (rpm)	Ratio	Volume of extract (V_2')	Absorbance (y)	volume after dilution (V_2)	C_2' (x)	C1 (ppm)	C2 (ppm)	Efficiency (%)
1	8	100	1	1.4	0.554	4	19.16	100	6.706	93.29
2	8	200	1	1.6	0.631	4	40.98	100	16.39	83.61
3	8	300	1	1.4	0.611	4	21.36	100	7.48	92.52
4	8	400	1	1.6	0.641	4	22.53	100	9.012	90.99
5	8	500	1	1.6	0.588	4	20.47	100	8.188	91.81

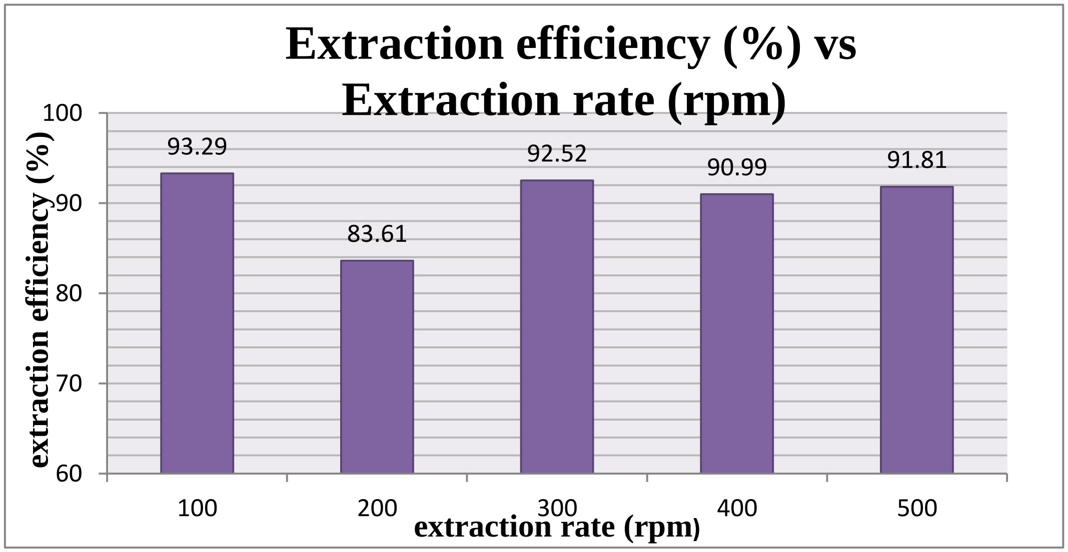


Figure 4.3: Extraction efficiency (%) against extraction rate (rpm)

Effect of extraction rate

Table 13 shows the effect of extraction time towards extraction efficiency. The values of absorbance (y) getting from UV-VIS are substitutes into standard curve equation **y= 0.0258x + 0.0598.** For the extraction efficiency (%) equation (8) was used.

$$\mathbf{C_2'V_2' = C_2V_2} \qquad (8)$$

The details of the calculation might be referred in appendices.

Figure 23 shows the extraction efficiency of Ionic Liquids to extract β-carotene from hexane at different extraction rate. The extraction rate of β-carotene is influenced by the stirrer speed. Theoretically, the extraction rate increases at a higher stirrer speed. However, the optimum extraction rate for the extraction of β-carotene would be around 100 rpm to 170 rpm. At 100 rpm, β-carotene was undergoes highest extraction rate about 93.29% and then decreases gradually at 200 rpm about 83.61%. Hejazi (2003) have said, the effectiveness of extraction with respect to power input is comparable for all the applied mixing rates.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion and Recommendations

As a conclusion, the specific objectives to find suitable ILs have done by using COSMO-RS which is 1-ethyl-3-methylimidazolium acetate [EMIM] as suitable ILs. For the second specific objectives which is to optimize the extraction parameter, 8 hours was the optimum extraction time, 1:1 ionic liquids to standard solution ratio was the optimum extraction ratio and 100 rpm was the highest extraction rate. Hopefully this project would give many contributions to the society and industry. With the blessings, hopefully this project would help many researchers out there carry on researches on application of ionic liquids and boost up its involvement in the industry.

As recommended, the organic solvent for this project was hexane and it easily to vaporize, safety precaution and experiment must be handled with great care by using bottle sample with cap to avoid vaporized. The sample should be placed in refrigerator with 4°C before testing with UV-VIS. Next, the limitations of ionic liquids in UTP, synthesis activities should be done and plans one semester earlier to have a variety of ionic liquids. However, the continuity of this project should be done by other student by focusing on the optimum parameter only. Therefore, this project is feasible by taking into account the time constraint and the capability of final year student to finish their project on time with the assist from the supervisor and post graduate student.

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APPENDICES

Appendix 1: Findings from COSMO-RS predictions

Table 6.0 (a): 1-hexyl-4-methyl-pyridinium with different anions

(1-hexyl-4-methyl-pyridinium)	**ln (ϒ)**	**ϒ @ ternary system**	**ϒ @ binary system**	**K(1/ϒ BT)**	**S (ϒ BT/ϒ Hex)**	**PI**
acetate						
beta-carotene	5.0709059	159.3185887	79.65929435	0.0125535	15.28206166	0.191842795
hexane	2.3442262	10.42520258	5.212601292			
TF2N						
beta-carotene	4.25587402	70.51842478	35.25921239	0.0283614	7.097815708	0.201303864
hexane	2.29608693	9.935229044	4.967614522			
chloride						
beta-carotene	4.61381764	100.8684951	50.43424756	0.0198278	10.29187419	0.204065188
hexane	2.28246297	9.800789758	4.900394879			
Trifluoromethanesulfonate						
beta-carotene	5.91114814	369.1297248	184.5648624	0.0054181	19.34546703	0.104816631
hexane	2.94869001	19.08094151	9.540470753			
methyl sulfate						
beta-carotene	6.35095136	573.0376148	286.5188074	0.0034902	26.49897651	0.092485993
hexane	3.07384525	21.62489614	10.81244807			
methane sulfonate						
beta-carotene	5.82620053	339.0679501	169.533975	0.0058985	21.5269341	0.126977109
hexane	2.75689563	15.75087044	7.875435222			
hexafluoroantimonate						
beta-carotene	4.63840706	103.379539	51.68976948	0.0193462	5.683409519	0.109952309
hexane	2.90085574	18.18970437	9.094852184			

Table 6.0 (b): 1-hexyl-4-methyl-pyridinium with different anions

(1-hexyl-4-methyl-pyridinium)	**ln (ϒ)**	**ϒ @ ternary system**	**ϒ @ binary system**	**K(1/ϒ BT)**	**S (ϒ BT/ϒ Hex)**	**PI**
tetrafluoroborate						
beta-carotene	6.97181618	1066.157327	533.0786634	0.0018759	30.24000268	0.056727093
hexane	3.56265054	35.25652223	17.62826112			
iodide						
beta-carotene	6.6320641	759.0473043	379.5236522	0.0026349	33.6517594	0.088668412
hexane	3.11599876	22.55594708	11.27797354			
bromide						
beta-carotene	5.95499566	385.6752368	192.8376184	0.0051857	26.31810381	0.136478059
hexane	2.6847386	14.65437023	7.327185114			
thiocyanate						
beta-carotene	7.62648997	2051.835362	1025.917681	0.0009747	64.64932149	0.063016091
hexane	3.45751236	31.7379257	15.86896285			
nitrate						
beta-carotene	6.77199526	873.0521233	436.5260616	0.0022908	34.67312704	0.079429684
hexane	3.22603031	25.17950349	12.58975175			
hydrogen sulfate						
beta-carotene	8.95498804	7746.435182	3873.217591	0.0002582	175.936413	0.045423839
hexane	3.7848654	44.02974376	22.01487188			
dihydrogen phosphate						
beta-carotene	8.60338642	5450.084652	2725.042326	0.000367	187.0131827	0.068627625
hexane	3.37220731	29.14278327	14.57139164			

Table 2: Triethylsulfonium with different anions

(Triethylsulfonium)	**ln (ϒ)**	**ϒ @ ternary system**	**ϒ @ binary system**	**K(1/ϒ BT)**	**S (ϒ BT/ϒ Hex)**	**PI**
TF2N						
beta-carotene	6.96600493	1059.979588	529.9897938	0.001886829	35.78446498	0.067519159
hexane	3.38849107	29.62122218	14.81061109			
Trifluoromethanesulfonate						
beta-carotene	8.47422606	4789.714379	2394.857189	0.000417561	84.48496166	0.035277662
hexane	4.03765251	56.69309999	28.34654999			
methyl sulfate						
beta-carotene	5.6920652	296.5053316	148.2526658	0.006745241	13.50979989	0.09112686
hexane	3.08864986	21.94742587	10.97371293			
methane sulfonate						
beta-carotene	2.71930946	15.16984324	7.584921622	0.131840519	2.003336078	0.264120867
hexane	2.02449563	7.572290745	3.786145373			
hexafluoroantimonate						
beta-carotene	9.89868892	19904.25725	9952.128625	0.000100481	151.9820908	0.015271315
hexane	4.87492623	130.9644916	65.4822458			
tetrafluoroborate						
beta-carotene	8.64272601	5668.761882	2834.380941	0.000352811	77.84168308	0.027463381
hexane	4.28804895	72.82424606	36.41212303			
iodide						
beta-carotene	2.04219934	7.707542077	3.853771039	0.259486096	1.116494527	0.289714805
hexane	1.93200545	6.903340673	3.451670337			
thiocyanate						
beta-carotene	7.22931171	1379.272838	689.6364188	0.001450039	38.78810626	0.056244284
hexane	3.57119805	35.55916931	17.77958465			

Table 6.0(d): Ammonium with different anions

(Ammonium)	**ln (ϒ)**	**ϒ @ ternary system**	**ϒ @ binary system**	**K(1/ϒ BT)**	**S (ϒ BT/ϒ Hex)**	**PI**
acetate						
b-carotene	53.750269	2.20519E+23	1.10259E+23	9.06953E-24	3.32108E+16	3.01206E-07
hexane	15.70861733	6639965.529	3319982.764			
chloride						
b-carotene	-216.24737951	1.21606E-94	6.08032E-95	1.64465E+94	1.50248E-71	2.47105E+23
hexane	-53.17095462	8.09371E-24	4.04686E-24			
hydroxide						
b-carotene	-345.7606488	6.8874E-151	3.4437E-151	2.9038E+150	7.6205E-114	2.21285E+37
hexane	-85.29678376	9.03811E-38	4.51905E-38			
thiocyanate						
b-carotene	-40.99101791	1.57698E-18	7.88492E-19	1.26824E+18	7.82431E-15	9923.1375
hexane	-8.50947725	0.000201549	0.000100775			

Table 6.0 (e): 1-hexyl-3-methylimidazolium with different anions

(1-hexyl-3-methylimidazolium)	**ln (ϒ)**	**ϒ @ ternary system**	**ϒ @ binary system**	**K(1/ϒ BT)**	**S (ϒ BT/ϒ Hex)**	**PI**
bis(trifluoromethylsulfonyl)imide						
b-carotene	5.25018014	190.6006002	95.30030008	0.010493146	13.69303282	0.143683
hexane	2.63329299	13.91953139	6.959765696			
chloride						
b-carotene	5.50449163	245.7934699	122.8967349	0.008136913	18.91070568	0.15387476
hexane	2.56476343	12.99758317	6.498791584			
hexafluorophosphate						
b-carotene	7.34323966	1545.711591	772.8557955	0.001293902	33.18806522	0.04294212
hexane	3.84104933	46.57432064	23.28716032			
tetrafluoroborate						
b-carotene	8.97955673	7939.112165	3969.556083	0.000251917	118.6990561	0.02990235
hexane	4.20296538	66.88437485	33.44218742			
trifluoromethanesulfonate						
b-carotene	7.38941609	1618.760626	809.3803132	0.001235513	53.02522639	0.06551336
hexane	3.41864832	30.52812287	15.26406143			

Appendix 2: Calculation

***This calculation applied for all extraction parameters.**

For example,

Absorbance, $Y= 0.631$ (from UV-VIS)

Applied in standard curve equation:

$$\mathbf{y= 0.0258x + 0.0598}$$

$x= 22.14$

C_2' is concentration of extract before dilution

$x = C_2'$ values that need to be used in dilution equations.

$$\mathbf{C_2'V_2' = C_2V_2}$$

$V_2'= 1.6$ ml

$V_2 = 4.0$ ml

Dilution factors

By substitute this values, final concentration after dilution, C_2 will obtained.

To calculate extraction efficiency, this formula should apply:

$$\mathbf{(C_1- C_2)/ C_2 \times 100\%}$$

C_1 is initial concentration at 100 ppm

$$(100-16.39)/100 \times 100\%$$

$$= 83.61\%$$