COMPUTATIONAL APPROACH FOR SEPARATION BENZENE FROM CYCLOHEXANE

NUR AIMI ATHIRAH BINTI SUHAIMI

CHEMICAL ENGINEERING
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Computational approach for separation benzene from cyclohexane

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Nur Aimi Athirah Binti Suhaimi
15645

Dissertation submitted in partial fulfilment of
the requirement for the
Bachelor of Engineering (Hons)
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Universiti Teknologi PETRONAS,
32610, Bandar Seri Iskandar,
Perak Darul Ridzuan.

CERTIFICATION OF APPROVAL

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Approved by,

_____

(Dr Kiki Adi Kurnia)

UNIVERSITI TEKNOLOGI PETRONAS,

BANDAR SERI ISKANDAR, PERAK

September 2015

CERTIFICATION OF ORIGINALITY

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

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NUR AIMI ATHIRAH BINTI SUHAIMI

ABSTRACT

Hydrocarbons play important role in the petrochemicals industry, such as a primary energy source for current civilization. The predominant use of hydrocarbons is as a combustible fuel source. The majority of hydrocarbons found on earth naturally occur in crude oil. Due to their similar chemical structure and physical properties, the separation and purification of individual component of hydrocarbons are quite challenging. Various methods have been proposed for this particular application, it is, however, most of these methods employ volatile and hazardous chemicals compounds. In recent years, ionic liquids have been proposed as "green" solvent due to their excellent chemical and physical properties. Large numbers of ionic liquids have been proposed as potential solvent for this particular application. However, it should be highlighted that with huge number of potential ionic liquids available, the experiment try-and-error is not practical. A tool to *a priori* predict the best of best ionic liquids for this application is very crucial. Therefore, in this work, the impact of ionic liquids on the separation and purification of benzene and cyclohexane will be carried out using computational study, namely Conductor-like Screening Model for Real Solvent (COSMO-RS). Cyclohexane and benzene are chosen to represent aliphatic and aromatic hydrocarbon, respectively. The ultimate goal is to screen the best ionic liquid for the separation of aromatic from aliphatic hydrocarbon, and subsequently, produce high quality aliphatic hydrocarbon. At the end of this project, it is expected to propose the best ionic liquids for the separation of benzene from cyclohexane

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I also tribute to both of my parents who trust and support me to during my ups and downs. Finally, deepest thanks go to all fellow colleagues and friends. Their support and encouragement will always be a pleasant memory.

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LIST OF ABBREVIATIONS

$[C_4\text{-}4\text{-}C_1py][NTf_2]$	1-butyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide
$[(C_6OC_1)\ 2im][NTf_2]$	1,3-dihexyloxymethylimidazolium bis(trifluoromethylsulfonyl)imide
$[C_4py][NTf_2]$	1-butylpyridinium bis(trifluoromethylsulfonyl)imide
$[C_5py][NTf_2]$	1-pentylpyridinium bis(trifluoromethylsulfonyl)imide
$[COC_2C_1morp][NTf_2]$	4-(2-methoxyethyl)-4-methylmorpholinium bis(trifluoromethylsulfonyl)imide
$[C_5C_1pip][NTf_2]$	1-pentyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide
$[C_6C_1pip][NTf_2]$	1-hexyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide
LLE	Liquid-liquid Extraction
IL	Ionic Liquid
COSMO-RS	Conductor like Screening Model for real solvent

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CHAPTER 1

INTRODUCTION

1.1 Project Background

Hydrocarbons are one of the Earth's most important natural resources. The main source of the world’s electric energy and heat energy is currently from hydrocarbons, such as a primary energy source for current civilization (such as for heating buildings) because they produce large amounts of heat when burned. Also, many hydrocarbons serve as base materials for the synthesis of organic chemicals used in the production of consumer products and industrial materials. In details, hydrocarbons are also raw materials that serve as feedstock for the production of a wide range of organic chemicals, which in turn are used in large production such as pigments, plastics, explosives, pharmaceuticals, and solvents.

For example, in the industry nowadays, cyclohexane demand keeps increasing globally. Simply say, it has been widely used the chemical in the industry. Nevertheless, the high demand of cyclohexane could not be fulfilled due to its challenging separation and purification process. Traditional methods, such as distillation and liquid-liquid extraction, for the separation and purification of cyclohexane and benzene (as impurities in the industrial production of cyclohexane), would only result in 85-98% of pure cyclohexane. The close boiling point of cyclohexane and benzene and their similar physical properties are the main obstacle to producing high-quality cyclohexane. Hence, most of the time, the amount of cyclohexane available could not meet the amount of demand in the market that is currently increasing (Garcia and Mohammadi, 2000).

Production of cyclohexane is mainly done by the process of catalytic hydrogenation of benzene in the presence of hydrogen and catalyst, which occurs only under the extreme condition of a strong catalyst, high temperature, and high pressure. Therefore, it is an extremely important in removing the unreacted and remaining benzene from the reactor's effluent stream. However, the petrochemical industry itself has discovered that separation of benzene and cyclohexane mixtures is one of the toughest tasks because of their 'nearly overlapped' boiling points and formation of an azeotropic mixture (García et al., 2011). Since conventional distillation is not applicable to be used for this separation process, liquid-liquid extractive distillation is the main technology that currently available to separate benzene and cyclohexane mixtures (Garcia and Mohammadi, 2000).

Benzene is a very harmful and hazardous pollutant that its exposure can cause serious health and environmental effects such as leukemia and cancers. According to Gonzalez and co-workers, a current and regular way for the industrial to extract benzene from cyclohexane is by liquid (solvents) extraction. However, Gonzalez and co-workers (2010) also had discovered that the conventional solvents cause the problems as they are flammable, toxic and volatile and as well as causing harm effect to the environment and surrounding. Also, the usage of conventional solvent limits the extraction process by emerging the complexness of the process and high energy consumption due to their low extractive capability, considerable volatility and high mutual solubility between the aromatic hydrocarbon that is benzene and cyclohexane (Garcia and Mohammadi, 2000).

In recent years, ionic liquids have emerged as "green" solvent for numerous chemical reaction and separation process. With their low to negligible vapor pressure, ionic liquids have become a promising alternative and initiatives that comes into attention to replace the conventional solvents. Improving performance and causing less damage to the human health and environment is two (2) reason that been taken into consideration in replacing conventional solvents. Numerous ionic liquids have been studied as potential solvent for the separation and purification of aliphatic from aromatic hydrocarbons, including cyclohexane-benzene systems (Ferreira et. al, 2012). The number of potential ionic liquids for this application keeps increasing and it leads many researchers to question what is the best of the best ionic liquids for this

particular application? With the 10^{18} number of possible combination of cation and anion to form ionic liquids, clearly the choice is not in short supply, even so, this high number of ionic liquids] makes the experimental try-and-error not practical. A tool to screen and select the most suitable and the best ionic liquid to be used in separating benzene from cyclohexane is highly crucial. Therefore, in this project, the screening of the potential ionic liquids will be carried out using COSMO-RS (Conductor like Screening Model for real solvent). COSMO-RS has been proven as reliable computational software for screening of ionic liquids for numerous applications. The screening of the potential ionic liquids would be performed based on the activity coefficient at infinite dilution of cyclohexane and benzene in ionic liquids. By end of this project, it would be possible to identify top 10 ionic liquids with high performance for the separation of benzene from cyclohexane.

1.2 Problem Statement

Ionic liquids have been shown as a promising solvent for the separation and purification of aliphatic from an aromatic hydrocarbon. According to Rogers (2007), it is estimated that there are 1018 numbers of potential ionic liquids. Clearly, this huge numbers of potential ionic liquids make the experimental try-and-error not practical. Therefore, in this work, the screening of the best of the best ionic liquids for the separation and purification of aliphatic from aromatic hydrocarbons will be carried out using computational approach, namely COSMO-RS. As mentioned earlier, the screening of the potential ionic liquids will be performed based on their activity coefficient in ionic liquids, at infinite dilution.

1.3 Objectives

This project embarks on the following objectives:

i. Evaluation of COSMO-RS as a tool to predict activity coefficient for cyclohexane and benzene at infinite dilution.
ii. Determine the capacity and selectivity of ionic liquid for the separation of cyclohexane from benzene.
iii. Identify top ten ionic liquids for the separation of benzene from cyclohexane.
iv. To design the best ionic liquid to separate the mixture of cyclohexane and benzene.

1.4 Scope of Study

i. Aiming at understanding the impact of ionic liquids on the interaction of two hydrocarbons, cyclohexane and benzene will be chosen to represents the aliphatic and aromatic hydrocarbons, respectively.
ii. The ionic liquids – hydrocarbon interaction will be quantified using activity coefficient at infinite dilution.

CHAPTER 2

LITERATURE REVIEW

2.1 Liquid-liquid Extraction (LLE) and Azeotrope Mixture

Extraction is one of separation process and over the centuries, extractions have been widely used by the industry all over the world. In industrial application, separation plays a very important role in order to get an on specification product with high purity. Liquid–liquid or solvent extraction is one of the alternatives or techniques in separation methods under extraction where distillation performs low purity. This specifically applied at azeotropes mixtures or temperature-sensitive components.

Basically, Haslego (2010) stated that there are two main types of azeotrope exist, that is homogeneous azeotrope and heterogeneous azeotrope. For the first type of azeotrope, homogeneous azeotrope, it is where a single liquid phase is in the equilibrium with a vapor phase and the other one. Second type is the heterogeneous azeotrope that occurs when the overall liquid composition which forms two liquid phases is identical to the vapor composition. Haslego (2010) again wrote that there is few other several techniques in separating azeotropic mixtures. An example of the methods mentioned by Haslego (2010) is:

i. Homogeneous azeotropic distillation
ii. Heterogeneous azeotropic distillation
iii. Distillation using ionic salt
iv. Pressure-swing distillation
v. Reactive distillation.

Liquid-liquid extraction is commonly selected as an alternative to extract aromatic compound from aliphatic mixture. The advantages of LLE are LLE is able to separate azeotropes and components with overlapping boiling points, low cost, low to moderate temperature and suitable for recovery of thermally sensitive products.

Based on the figure, organic solvent will mix thoroughly with the aqueous solvent. After the mixing, two separated layers are formed to show a phase separation which is raffinate and extract. In depth, the upper part is called as raffinate (with non-extract solute) and lower part is extract (with extract solutes). After the extraction, raffinate is cyclohexane and the extract is the mixture of benzene and the solvent. Basically, benzene is indicated by the extract solute.

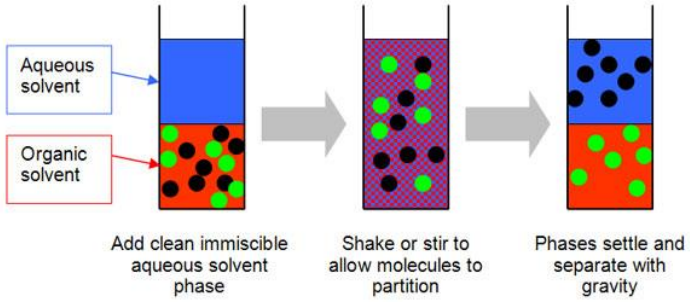

Figure 2.1 Basic principle of liquid-liquid extraction

2.2 Cyclohexane and Benzene

The increasing demand for detergents, plastics, and organic chemicals had to cause the production of benzene increased rapidly since 1950. On the other hand, there are two major factors that pushed for the introduction of new processes of cyclohexane. One was the low purity of product by direct distillation, and the other was the increasing demand for cyclohexane, which could not be met by the amount of natural occurrence of this substance. Cyclohexane demands mainly come from the plastic industry where cyclohexane is used as a feedstock for Nylon 6 and Nylon 6, 6. Presently, virtually all cyclohexane is produced by the hydrogenation of benzene.

Cyclohexane, with the chemical formula C_6H_{12}, is a water-insoluble, non-corrosive and is a non-polar liquid that having a pungent odor. It is less toxic compared to benzene. The most stable chemical structure of cyclohexane, known as ‘chair conformation’. Cyclohexane is used in paints and varnishes, as a solvent in the

plastic industry, particularly for resins used in wire coating, and for the extraction of essential oils. However, the importance of cyclohexane lays mainly in its conversion to the intermediate cyclohexanone, a feedstock for Nylon precursors such as adipic acid, and hexamethylenediamine.

Based on the research done by Garcia and Mohammadi (2000), there are many roots to the production of benzene. Benzene is a simplest aromatic hydrocarbon compound with the chemical formula C_6H_6. It is a non-polar, with a characteristic odor and great thermal stability. Benzene has a stable planar structure with a six-member Kekule ring. The carbon bonds have equal lengths of 1.39 Å and bond angles of 120^o. The principal use of benzene is as a chemical raw material in the synthesis of compounds such as styrene phenolic resins, Nylon, aniline, polyester resins, and detergents. Benzene is also used in the production of drugs, dyes, insecticides, and plastics. Benzene was also used as a solvent, but safer solvents have replaced it in the recent years.

Similarities between benzene and cyclohexane are that, it is a volatile, colorless, flammable and non-polar liquid. Somehow, cyclohexane is having pungent odor. Below is the Chemical structures of benzene (right) and cyclohexane (bottom). Benzene has a planar structure with six equal C–C bonds and bond angles. Cyclohexane possesses a chair conformation.

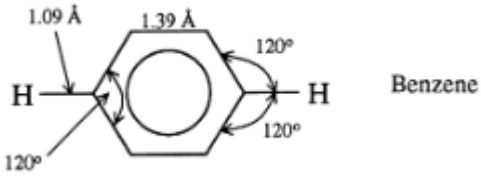

Figure 2.2 Chemical structures of Benzene

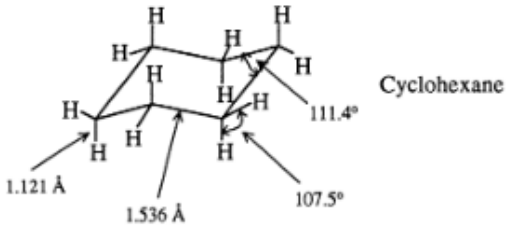

Figure 2.3 Chemical structures of Cyclohexane

Table 2.1 Properties of Cyclohexane and Benzene

PROPERTIES	CYCLOHEXANE	BENZENE
Boiling Point	**80.7°C**	**80.1°C**
Molecular Formula	C_6H_{12}	C_6H_6
Molecular Weight	84.15948 g/mol	78.11184 g/mol
Melting Point	6.47°C	5.56°C
Density at 25°C	0.779 g/mL	0.876 g/mL
Water Solubility	Practically Insoluble	0.18g/100L
Viscosity (absolute) at 20°C	0.977 cP	0.6468 cP
Critical Temperature	281.0 °C	289.45°C

2.3 Ionic Liquids

Extractive distillation was developed in wide area of industrial application. Ionic liquids become one of the alternatives for many purposes in chemical industry. Ionic liquids are salts that are liquid below 100°C which represent a new class of solvents. The application of ionic liquids in biochemistry which is non-volatile nature would improve the performance of separation process instead of volatile molecular liquid. However the selection of suitable ionic liquids depends on several factors that influence the extraction process. Based on extraction study by Zhu et al (2010), the extracted ions concentration, ionic strength of salting out agent and temperature would be the factors of extraction. The strength of the ion, H-bonding, charge distribution on the ions would become the main factors that influence the melting point of ILs.

For the separation and purification of cyclohexane from benzene, it is expected that the ionic liquids will have high benzene capacity and benzene/cyclohexane selectivity. The capacity and selectivity are calculated using the following equations (Anantharaj and Banerjee, 2011):

a) Solvent Capacity, C_{12} at infinite dilution :

$$C_{12}^{\infty} = \frac{1}{\gamma_1^{\infty}} \qquad (1)$$

b) Selectivity of best solvent

$$S_{ij,max} = S_{ij}^{\infty} = \left(\frac{\gamma_2^{\infty}}{\gamma_1^{\infty}}\right) = \left(\frac{\gamma_1^{\infty}}{\gamma_2^{\infty}}\right) \approx \left(\frac{\gamma_2^{\infty}}{\gamma_1^{\infty}}\right) \quad (2)$$

As can be seen, to calculate the solvent capacity and selectivity, the activity coefficient at infinite dilution is required. Thus, in this study, COSMO-RS will be used to estimate the activity coefficient at infinite dilution.

CHAPTER 3

METHODOLOGY

3.1 Project Activities Flow Chart

Figure 4 show the project activities for liquid-liquid extraction process

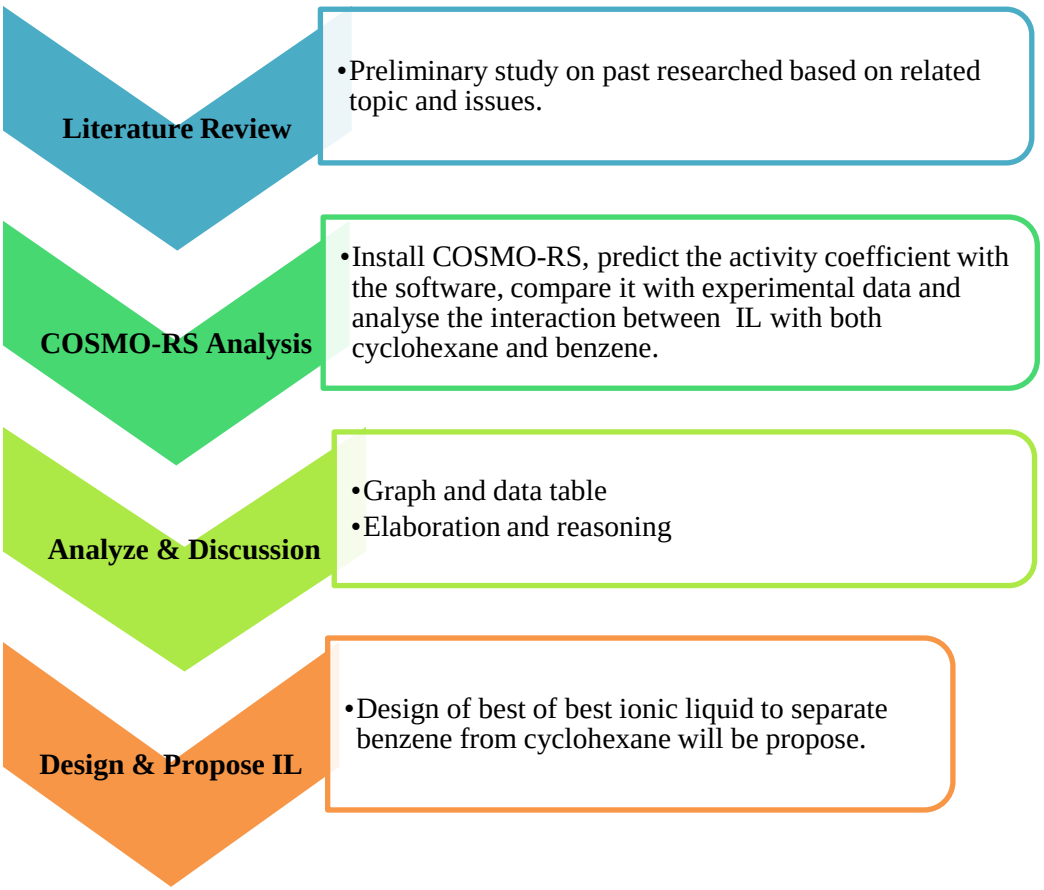

Figure 3.1 Project Activities

3.2 Gantt Chart and Key Milestone

Table 3.1 Planning of Progress

	Selection of project	Week (Semester I)													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of project topics														
2	Preliminary research work														
3	Submission of extended proposal for 1st review														
4	Submission of improved extended proposal														
5	Proposal defense														
6	Report Writing and Project work continue														
7	Submission of interim draft report														
8	Submission of interim final report														
	Selection of project	**Week (Semester II)**													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Project Work Continues														
2	Submission of Progress Report														
3	Project Work Continues														
4	Pre-SEDEX														
5	Submission of Draft Final Report														
6	Submission of Dissertation (soft bound)														
7	Submission of Technical Paper														
8	Viva														
9	Submission of Project Dissertation (Hard Bound)														

Planning and Progress

Key Milestone

3.3 Tools

3.3.1 COSMO-RS

COSMO-RS will provide the activity coefficient of ionic liquids. From activity coefficient predicted by COSMO-RS, the selectivity and capacity of the ILs can be determined.

3.3.2 Microsoft Excel 2010

Graph is plotted by using Microsoft Excel. Desired anions and cations will be selected, and will be plotted.

3.3.3 Matlab

Contour graph for analyzing the best ionic liquid on it solvent capacity and selectivity.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Comparison between Experimental data and COSMO-RS data

Figure 4 and Figure 5 show the comparison between experimental data from literature and predicted activity coefficient at infinite dilution of benzene and cyclohexane, respectively, in ionic liquids. There is a good agreement between literature and predicted activity coefficient at infinite dilution confirming reliability COSMO-RS as screening tool for the separation and purification of cyclohexane from benzene.

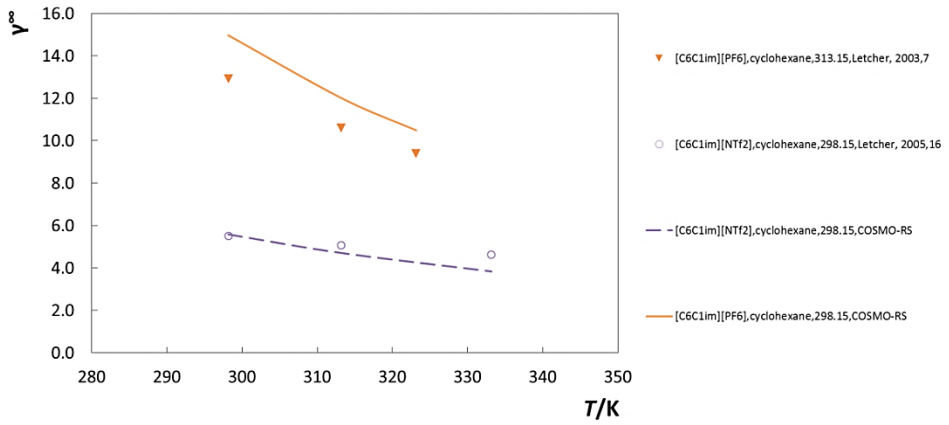

Figure 4.1 COSMO-RS data for interaction between ionic liquid and cyclohexane

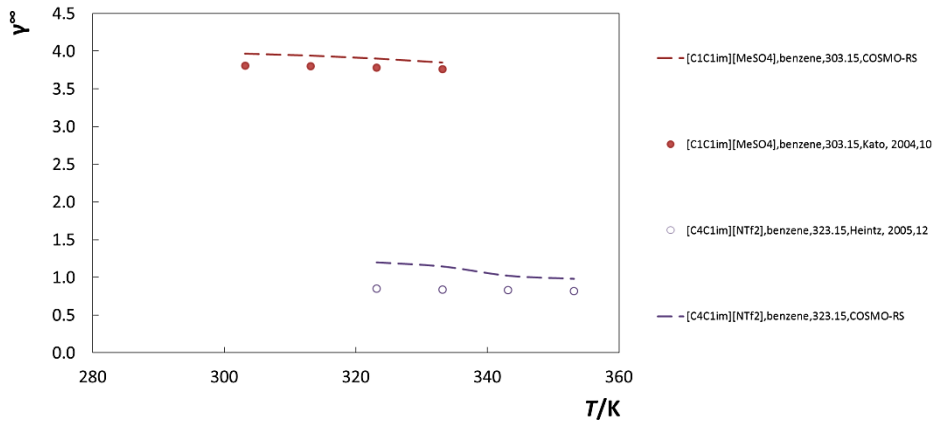

Figure 4.2 COSMO-RS data for interaction between ionic liquid and benzene

4.2 Screening by COSMO-RS

4.2.1 Anion Effect on Cyclohexane and Benzene

By using COSMO-RS, the selected IL is [COC2C1morp][NTf2] as it has highest selectivity. Based on Figure 6, it shows that [(C6OC1)2im][NTf2] has the lowest selectivity, and the highest is [COC2C1morp][NTf2]. Straight line presenting COSMO result, while dotted line presenting literature result. Below is the result for the impact of ionic liquid, anion [NTf2] with different cation , towards Cyclohexane and Benzene.

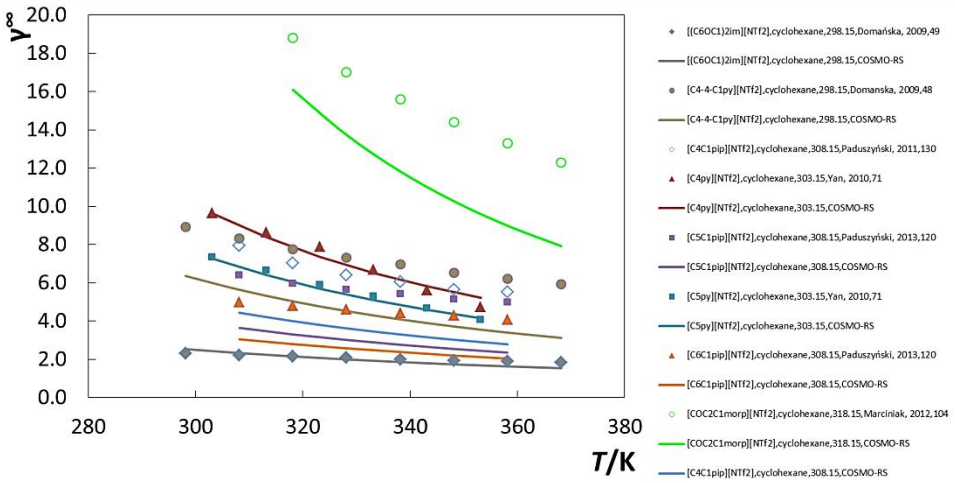

Figure 4.3 Anion Effect on Cyclohexane [Cation][NTf2]

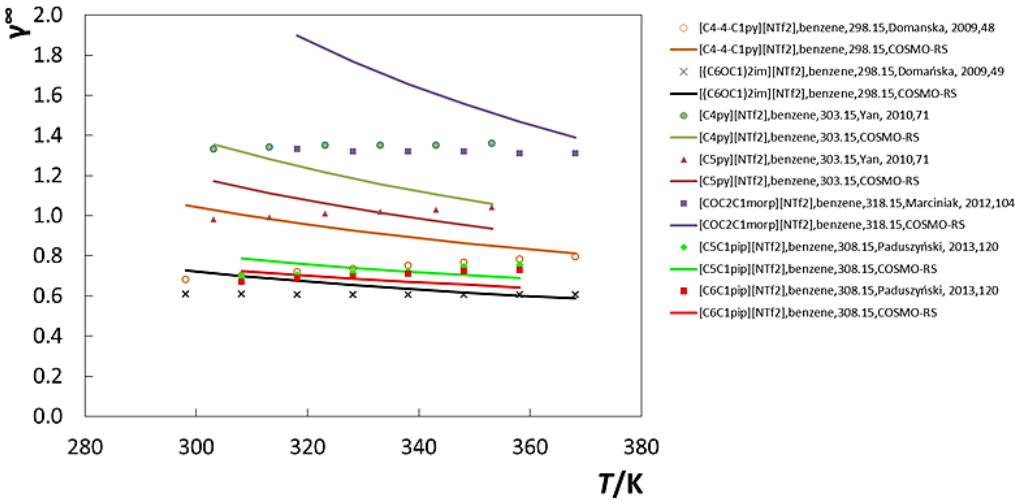

Figure 4.4 Anion Effect on Benzene [Cation][NTf2]

4.3 Solvent Capacity and Selectivity

Based on table 2 below, solvent capacity for the interaction between IL and benzene at 2 different temperature, 298.15K and 368.15K were calculated from the predicted activity coefficient by using formula below,

Solvent Capacity, C_{12} at infinite dilution:

$$C_{12}^{\infty} = \frac{1}{\gamma_2^{\infty}} \qquad (3)$$

Table 2 shows that the solvent capacity at 368.15K is always lower than solvent capacity at 298.15K. Thus, hypothesis that can be made through this is the higher the temperature, the lower the solvent capacity of solvent. Based on the result below, $[COC_2C_1morp][NTf_2]$ exhibits the lowest capacity among all, while $[(C_6OC_1)2im][NTf_2]$ shown the highest capacity

Table 4.1 Solvent Capacity

IONIC LIQUID	ACTIVITY CEFFICIENT, γ		Solvent Capacity, C_{12}	
	@298.15K	@368.15	@298.15K	@368.15
$[C_4\text{-}4\text{-}C_1py][NTf_2]$	0.683	0.795	1.464	1.258
$[(C_6OC_1)2im][NTf_2]$	0.606	0.608	1.650	1.645
$[C_4py][NTf_2]$	1.330	1.360	0.752	0.735
$[C_5py][NTf_2]$	0.980	1.040	1.020	0.962
$[COC_2C_1morp][NTf_2]$	1.310	1.330	0.763	0.752
$[C_5C_1pip][NTf_2]$	0.696	0.753	1.437	1.328
$[C_6C_1pip][NTf_2]$	0.669	0.730	1.495	1.370

4.3.1 Selectivity of Best Solvent

Again, activity coefficient is needed to find the selectivity. Equation below is used find the selectivity of best solvent at infinite dilution.

Selectivity of best solvent at infinite dilution:

$$S_{ij,max} = S_{ij}^{\infty} = \left(\frac{\gamma_2^{\infty}}{\gamma_1^{\infty}}\right) = \left(\frac{\gamma_1^{\infty}}{\gamma_2^{\infty}}\right) \quad (4)$$

Where,

γ1 : Activity coefficients of light component (cyclohexane)

γ2 : Activity coefficients of heavy components (benzene)

It is predicted that the extraction at temperature 298.15K will be higher compared to at temperature 368.15K. This is because, the selectivity of ionic liquid is decreasing with increasing temperature. The predicted result is shown in the Table 3 which that the selectivity at 368.15K is always lower than selectivity at 298.15K. $[COC_2C_1morp][NTf_2]$ shown as the best solvent to extract cyclohexane from benzene as it is the highest selectivity among all, while $[(C_6OC_1)2im][NTf_2]$ shown the lowest selectivity in the graph, and also in the calculation as well.

Table 4.2 Selectivity of Solvent

IONIC LIQUID	**SELECTIVITY**	
	@298.15	**@368.15**
$[C_4\text{-}4\text{-}C_1py][NTf_2]$	13.075	7.459
$[(C_6OC_1)2im][NTf_2]$	3.828	3.010
$[C_4py][NTf_2]$	7.263	3.471
$[C_5py][NTf_2]$	7.500	3.904
$[COC_2C_1morp][NTf_2]$	14.351	9.323
$[C_5C_1pip][NTf_2]$	9.195	6.627
$[C_6C_1pip][NTf_2]$	7.459	5.562

4.4 Contour graph of Selectivity and Solvent Capacity

Cations and anions list for selectivity and solvent capacity study is been referred from International Journal of Chemical and Environmental Engineering entitled COSMO-RS Based Screening Ionic Liquids for Separation of Benzene and Cyclohexane. There are 44 anions and 60 cations at all.

4.4.1 Contour Graph of Selectivity

Activity coefficient for interaction between each anions with each cations is been predicted by using COSMO-RS, and selectivity is been calculated from formula:

$$S_{ij,max} = S_{ij}^{\infty} = \left(\frac{\gamma_2^{\infty}}{\gamma_1^{\infty}}\right) = \left(\frac{\gamma_1^{\infty}}{\gamma_2^{\infty}}\right) \approx \left(\frac{\gamma_2^{\infty}}{\gamma_1^{\infty}}\right) \quad (5)$$

From Figure 4.5 which shown contour graph of selectivity, the reddish the areas, the higher selectivity. From this study, the selectivity for all ionic liquid is in range 0.62-87.56. Ionic liquid with highest selectivity is [ClO_4][MIM] while the lowest selectivity with dark blue coverage area is [Cl][TNAM] which is 0.62.

4.4.2 Contour Graph of Solvent Capacity

8 groups of cations involved in the study of selectivity and solvent capacity, which is imidazolium, pyrridinium, pyrrolidinium, peperidinium, pyrazolium, thiazolium, ammonium, and phosphonium. Imidazolium have low solvent capacity whereas liquids consisting of ammonium cations showed higher capacities. Solvent capacity is also been calculated from the predicted activity coefficient, by using formula:

$$C_{12}^{\infty} = \frac{1}{\gamma_1^{\infty}} \quad (6)$$

From Figure 4.6 which shown contour graph of solvent capacity, it shown that most of the interacted ionic liquid perform low solvent capacity with average solvent capacity 0.82. The highest solvent capacity is [Cl][TNAM] with 81.68 and coming up next is [Cl][TNEAM] with 17.39.

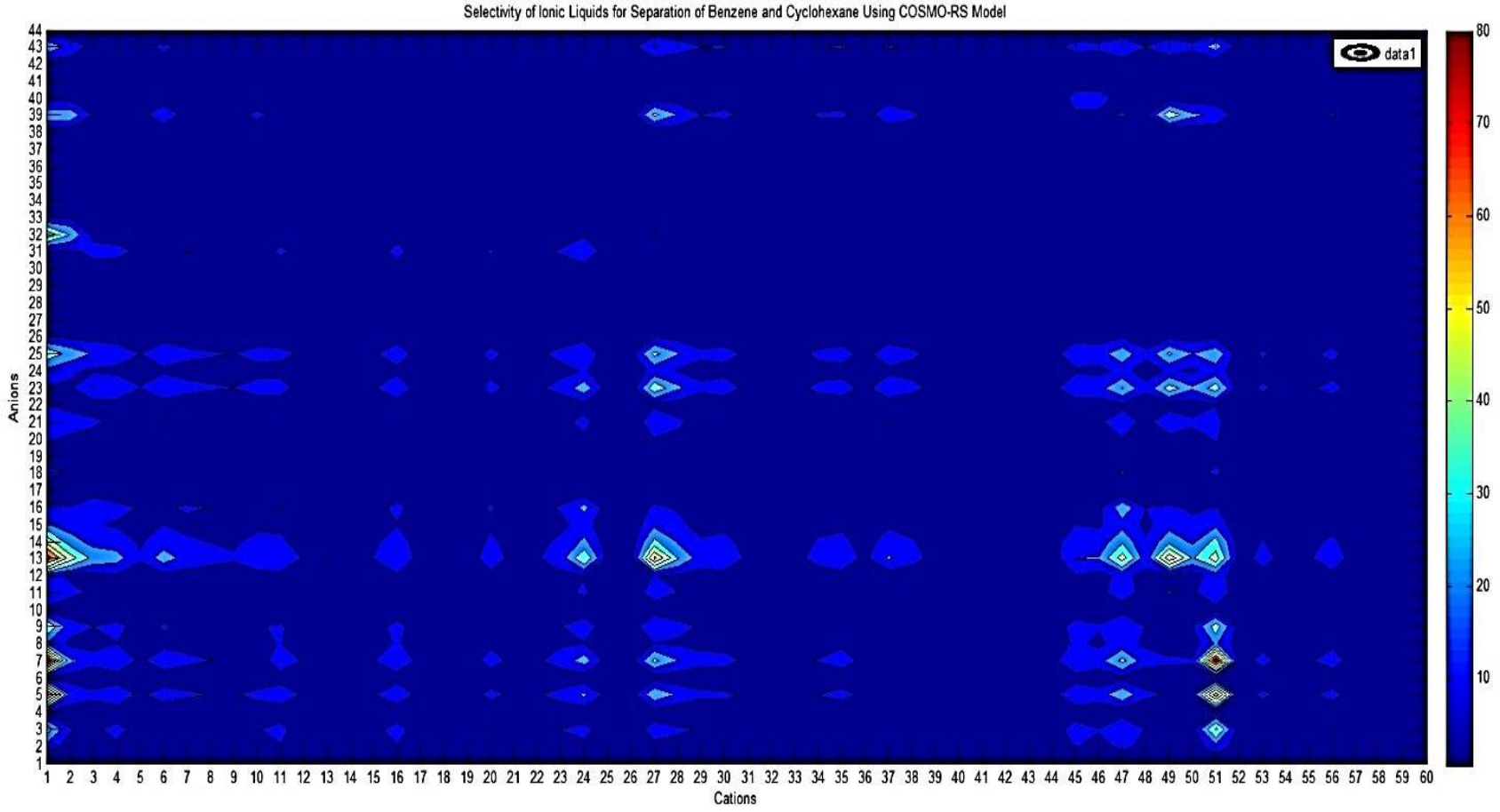

Figure 4.5 Selectivity of ionic liquids at infinite dilution calculated using COSMO-RS model, in MATLAB view. The X and Y-axes represents the cations and anions respectively.

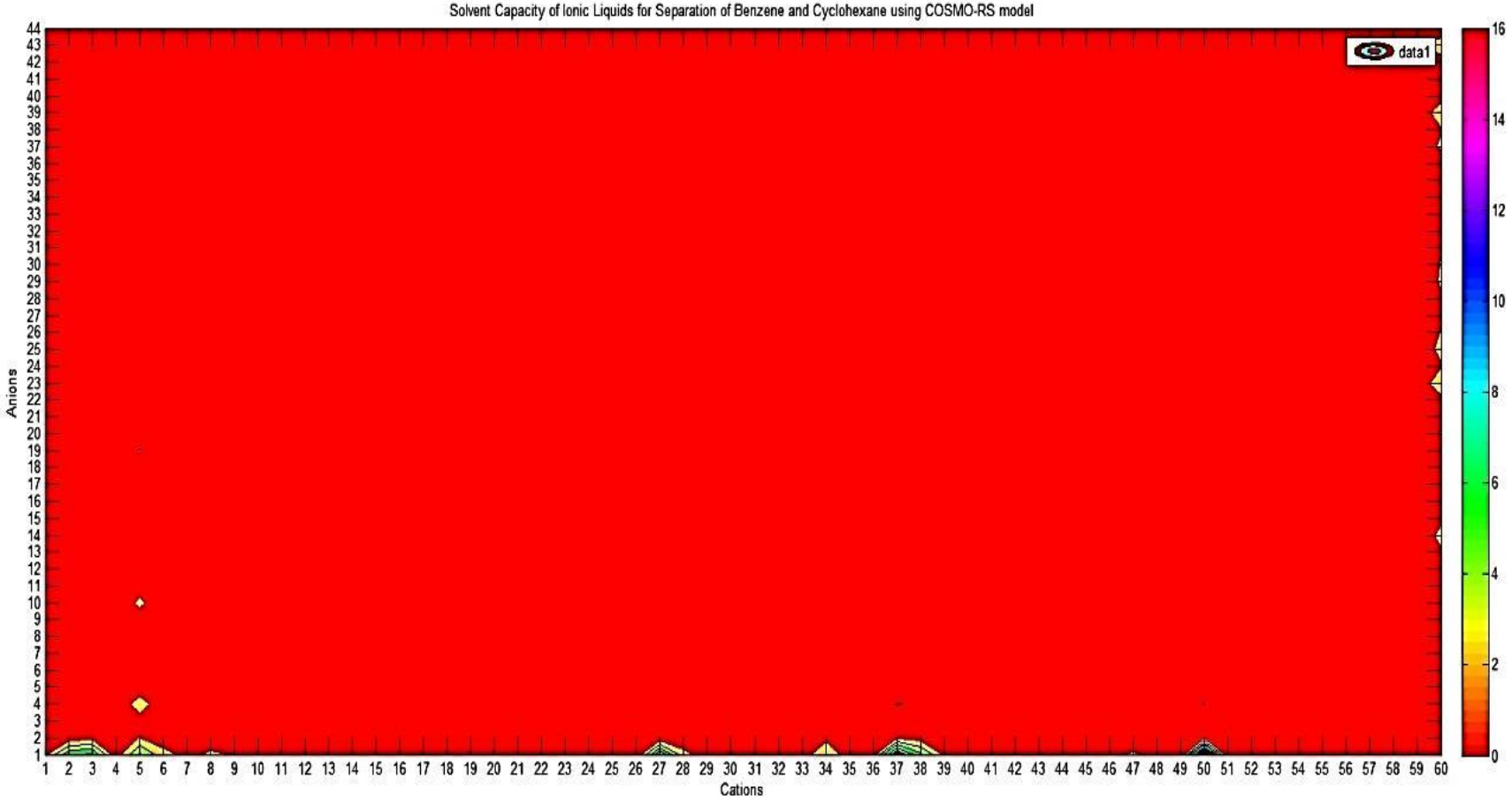

Figure 4.6 Solvent capacity of ionic liquids at infinite dilution calculated using COSMO-RS model, in MATLAB view. The X and Y- axes represents the cations and anions respectively.

4.5 Comparison between Data and Best Ionic Liquid Analysis

From the graph in Figure 4.7, COSMO-RS had predicted the activity coefficient of ionic liquid, and it shown that the result is closed to the experimental data which is presented using straight line, y=x. This can be conclude that predicted data and experimental data are almost close to each other. Thus, the percentage of error is small. Figure 4.8 explained briefly on the selectivity and capacity of ionic liquid that will be propose as best of best ionic liquid to be use in separating benzene from cyclohexane, experimentally.

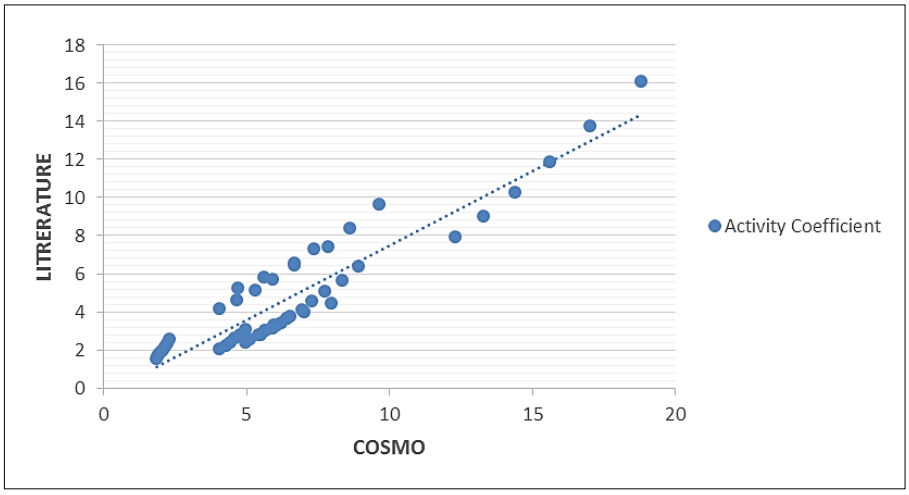

Figure 4.7 Experimental vs prediction of activity coefficient of benzene and cyclohexane in IL using COSMO-RS

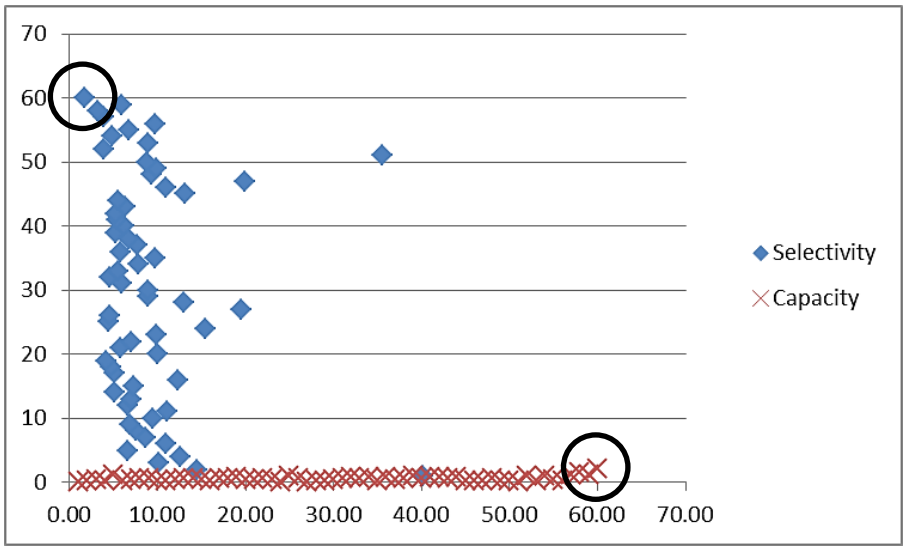

Figure 4.8 Selectivity vs Solvent Capacity

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

A systematic screening of possible cation–anion combinations was done by using COSMO-RS for separation of benzene and cyclohexane. To validate the result, the predicted infinite dilution activity coefficients of benzene and cyclohexane from COSMO-RS were compared with experimental results in literature. For comparison, data points from 298.15K to 368.15K is used. Therefore, the suitable ILs for the separation of benzene and cyclohexane are the one that present higher selectivity and lower capacities.

Solvent capacity is also an important parameter to select solvent for separation process because it determines the amount entrained required which in turn affect the size of the equipment. Generally, solvent with high selectivity have low solvent capacity in separation of non-polar components. However, a few ILs exhibit both a relative high selectivity and good capacity. The selectivity of benzene to cyclohexane increases with a lower temperature. Moreover, [COC2C1morp][NTf2] have selectivity higher and low solvent capacity where as higher capacities were observed for ionic liquids with ionic liquids named [(C6OC1)2im][NTf2] .

In conclusion, and as can be seen, to calculate the solvent capacity and selectivity, the activity coefficient at infinite dilution is required. Thus, in this study, COSMO-RS can be used as a tool to screen and estimate the activity coefficient at infinite dilution, effectively.

5.2 Recommendation

Based on COSMO-RS selectivity and solvent capacity analysis, best ionic liquid that had been designed to separate benzene from cyclohexane is 3-methyl-imidazolium Perchlorate [MIM][ClO_4] and tera-methylammonium chloride [TNAM][Cl].

Thus, the project can be extended by running an experiment on separation benzene from cyclohexane by using these 2 ionic liquid to study its performance in extraction of benzene and cyclohexane.

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APPENDICES

List of anions and cations presented in contour graph.

Table 4. List of Anions

	Anion	Acronym
1	Chloride	**[Cl]-**
2	Nitrate	**[NO_3]**
3	Thiocyanate	**[SCN]**
4	Acetate	**[CH3COO]-**
5	Tetrafluoroborate	**[BF_4]-**
6	Dihydrogen-phosphate	**[$H2PO_4$]-**
7	Perchlorate	**[ClO_4]-**
8	Hydrogensulfate	**[HSO_4]-**
9	Dicyanamide	**[NCN]**
10	Methylsulphonate	**[CH_3SO_3]**
11	Trifluoroacetate	**[CF_3COO]**
12	Methylsulphate	**[$MeSO_4$]**
13	Hexafluorophosphate	**[PF_6]**
14	Tricyanomethane	**[$(CN)_3C$]-**
15	Triflate	**[CF_3SO_3]**
16	Bis(trifluoromethyl)imide	**[$(CH_3SO_2)_2N$]-**
17	Bis(2,4,4-trimethylpenty)phosphinate	**[BTP]-**
18	Ethylsulphate	**[$EtSO_4$]**
19	Dimethyl phosphate	**[DMP]**
20	Methoxyethylsulfate	**[$MDEGSO_4$]-**
21	Imidodiphosphorylfluride	**[$(F_2PO)N$]-**
22	Benzoate	**[ba]-**
23	Tetracyanoborate	**[$B(CN)_4$]**
24	Salicylate	**[Sal]**
25	Bisoxaloborate	**[BOB] -**
26	Butylsulfate	**[$BtSO_4$]-**
27	Heptafluorobutanoate	**[HB]-**
28	Diethyl phosphate	**[DEP]**
29	Ethoxyethylsulfate	**[$EOESO_4$]-**
30	Toluene-4-sulfonate	**[TOS]**

	Anion	Acronym
31	Bismalonatoborate	**[BMB]-**
32	Bis (trifluorosulphonyl) imid	**[Tf_2N]**
33	Bis(trifluoromethylsulfonyl)methane	**[$(C_2F_5SO_2)_2CH$]-**
34	Perfluorobutanesulfonate	**[$F_9C_4SO_3$]-**
35	Decanoate	**[DEC]**
36	Bis-pentafluoroethyl-phosphonate	**[$(C_2F_5)_2PO_2$]-**
37	Octylsulphate	**[$OtSO_4$]**
38	Dibutyl phosphate	**[DBP]**
39	Bissalicylatoborate	**[BSB]-**
40	Bis(pentafluoroethylsulfonyl) imid	**[$(C_2F_5SO_2)_2N$]-**
41	Tris(trifluoromethylsulfonyl)methide	**[$(CF_3SO_2)_3N$]-**
42	Tris(pentafluoroethyl)trifluorophosphate	**[$TPfEPF_3$]**
43	Bisbiphenyldiolatoborate	**[BPB]-**
44	Tris(nonafluorobutyl)triflurophosphate	**[$(C_4F_9)_3PF_3$]-**

Table 5. List of Cations

	Cation	Acronym
1	3-methyl-imidazolium	**MIM**
2	1,3-methyl-imidazolium	**MMIM**
3	1,2,3-trimethylimidazolium	**1,2,3-MIM**
4	2,3,5 trimethylimidazolium	**2,3-5 MIM**
5	1-ethyl-3-methyl-imidazolium	**EMNIM**
6	1-butyl-imidazolium	**BIM**
7	1-butyl-3-ethylimidazolium	**BMIM**
8	dibutylimidazolium	**BBIM**
9	1,2,3,4,5-pentamethylimidazolium	**PMIM**
10	trimethylethylammonium	**TNEAM**
11	hexyltrimethylammonium	**HTNAM**
12	1-methyl-pyridinium	**Mpy**
13	1-ethyl-pyridinium	**Epy**
14	1-butyl-pyridinium	**Bpy**
15	1-ethyl-3-methylpyridinium	**EMPy**
16	1-butyl-3-ethyl-pyridinium	**BEPy**
17	4-methyl-1-octyl-pyridinium	**OtMPy**
18	1-hexyl-3-methyl-pyridinium	**HMPy**
19	1-ethyl-2,6-dimethylpyridinium	**EMMPy**
20	1-ethyl-3-hydroxymethyl-pyridinium	**EHyoMPy**
21	1-butyl-4-(dimethylamino)-pyridinium	**BNAMPY**
22	1,1-dimethyl-pyrrolidinium	**MMP**

	Cation	Acronym
23	1,1-dipropyl-pyrrolidinium	**DPrP**
24	1,3-diethylimidazolium	**EEIM**
25	1,3-diethyl-4-methylimidazolium	**EEM-4-M**
26	1,2-diethyl-3-methylimidazolium	**EEIM-3-M**
27	1-pentyl-3-methyl-imidazolium	**PtMIM**
28	1-butyl-2-3-methyl-imidazolium	**B2-3-MIM**
29	1-butyl-1-ethyl-pyrrolidinium	**BEP**
30	1-butyl-1-methyl-pyrrolidinium	**BMP**
31	1-hexyl-1-methyl-pyrrolidinium	**HMP**
32	bis(2-methoxyethyl)ammonium	**BMeoAM**
33	tributylmethylammonium	**TBMAM**
34	butyl-diethanolammonium	**BDEAM**
35	triethylpentylammonium	**TEPAM**
36	diethanolammonium	**DEAM**
37	tetra-methylammonium	**TNAM**
38	3-butyl-4-methylthiazolium	**BMTHZ**
39	3-ethylthiazolium	**MTHZ**
40	triisobutyl-methyl-phosphonium	**TBMPH**
41	tetrabutyl-phosphonium	**TeBPH**
42	benzyl-triphenyl-phosphonium	**BzTPhPH**
43	trihexyl-tetradecyl-phosphonium	**THeTDePH**
44	1-methyl-2-propylpyrazolium	**MPRPYRZ**
45	1-octyl-3-methyl-imidazolium	**OtMIM**
46	1-methyl-3-nonylimidazolium	**MnonylIM**
47	1-decyl-3-methyl-imidazolium	**DecMIM**
48	1-benzyl-3-methyl-imidazolium	**BzMIM**
49	1,2-dimethyl-3-(phenylmethyl)imidazolium	**1,2-M-3-PhenIM**
50	1-methyl-3-heptoxymethylimidazolium	**M-3-hepoxyMIM**
51	2-methyl-1-(phenylmethyl)-3-propylimidazolium	**MPhMpropylIM**
52	4,5-dichloro-1-ethyl-3-methylimidazolium	**4,5 Cl-1-E-3MIM**
53	1-(2-hydroxyethyl)-3-methylimidazolium	**1-2-hydrocy-3-MIM**
54	1,3-dibutoxy-2-methylimidazolium	**1,3 Butoxy-2MIM**
55	1-butoxymethyl-3-pentoxymethylimidazolium	**Butoxy-3MIM**
56	1-ethyl-1-methyl-pyrrolidinium	**EMP**
57	1-(2-ethoxyethyl)-1-methylpyrrolidinium	**EtoxyMP**
58	1-butyl-1-methylpiperidinium	**BMPIP**
59	1-propyl-3-methyl-imidazolium	**PMIM**
60	1-methyl-2-(phenyl)pyrazolium	**MPHPYRZ**