

**NOVEL DEEP EUTECTIC SOLVENTS AND
THEIR APPLICATION IN THE LIQUID-LIQUID EXTRACTION
OF AROMATIC COMPOUNDS**

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LIQUID-LIQUID EXTRACTION OF AROMATIC COMPOUNDS**

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ABSTRACT

The thermal cracking of naphtha is a major source of ethylene. It supplies more than half of the demand on ethylene to the industry. Naphtha contains in some cases high concentrations of aromatic hydrocarbons. They were found to be cracking-resistant and thus their existence in naphtha imposes negative effects on the overall process of ethylene production. Their removal from naphtha was achieved by liquid-liquid extraction using sulfolane as extractant. The extraction by sulfolane is not efficient at low concentrations of aromatics. Additionally, sulfolane is applied at high temperatures. Ionic liquids were proposed by different researches to replace sulfolane as extractants to achieve decent extraction for low concentrations of aromatics. However, their application is still limited at elevated temperatures only. Deep eutectic solvents (DESs) are a new group of ionic liquids which have added advantages. In this work, DESs are proposed as extractants for the above mentioned process. They are synthesized using different salts and hydrogen bond donors. Some DESs have viscosities of less than 0.0686 Pa.s at room temperature which allows them to be easily handled. Sixteen DESs out of twenty one synthesized in this work were applied in the extraction. Different systems of aromatics + aliphatics + DESs were studied at various operating conditions. For a ternary system of benzene + hexane + (methyltriphenylphosphonium bromide:ethylene glycol), a high distribution coefficient of more than 2 was achieved in one extraction experiments, with selectivity as high as 98.3 in another experiment. Other ternary systems studied were toluene + heptane + (tetrabutylphosphonium bromide:ethylene glycol), toluene + heptane + (tetrabutylphosphonium bromide:sulfolane), toluene + heptane + (ethyltriphenylphosphonium iodide:ethylene glycol) and toluene + heptane + (ethyltriphenylphosphonium iodide:sulfolane). The distribution coefficients ranged generally between 0.02 and 0.95 while selectivities ranged generally between 1.5 and 65.8. The experimental results were ascertained by

two different correlations methods. The regression coefficients were more than 0.9 for many cases. The non-random two liquids (NRTL) activity coefficients model was applied to correlate the experimental data and to estimate the activity coefficients. Calculated and experimental data show very good agreement and the error criterion is less than 10^{-4} . This work shows that DESs have the advantage over conventional extraction solvents for separation of aromatic hydrocarbons due to their ease of synthesis, tunable physical properties and high selectivities in extraction experiments.

PELARUT “DEEP EUTECTIC” BARU DAN APLIKASINYA DALAM
PENGASINGAN FASA-FASA CECAIR SEBATIAN AROMATIK

ABSTRAK

Pemecahan termal nafta adalah sumber utama etilen. Ia menyumbang lebih daripada separuh permintaan dari industry. Di dalam sesetengah kes, nafta mengandungi kepekatan hidrokarbon aromatik yang tinggi. Ia dilaporkan tahan retakan dan dengan itu kehadirannya didalam nafta memberi kesan negative terhadap proses pengeluaran etilen secara keseluruhannya. Pengekstrakan mereka dari nafta boleh dicapai melalui pengesktrakan cecair-cecair dengan menggunakan *sulfolane* sebagai pengekstrak. Pengekstrakan oleh *sulfolane* tidak efisien pada kepekatan hidrokarbon yang rendah. Tambahan lagi, *sulfolane* digunakan pada suhu tinggi. Cecair ionik telah dicadangkan oleh beberapa kajian berasingan untuk menggantikan *sulfolane* sebagai pengekstrak untuk mencapai pengekstrakan sesuai pada kepekatan hidrokarbon yang rendah. Namun, kegunaan mereka masih terbatas pada suhu tinggi sahaja. Pelarut-pelarut eutektik dalam (Deep eutectic solvents-DESs) adalah kumpulan baharu cecair ionik yang mempunyai kelebihan tambahan. Di dalam kerja ini, DESs telah dicadangkan sebagai pengekstrak untuk proses yang telah disebutkan di atas. Mereka telah disintesis menggunakan garam dan penderma ikatan hidrogen yang berbeza-beza. Sesetengah DES memiliki kelikatan kurang daripada 0.0686 Pa.s pada suhu bilik dan ini membuatkan mereka mudah untuk dikendalikan. Sepuluh daripada 21 DES yang disintesis telah digunakan sebagai medium pengekstrakan dalam pengekstrakan cecair-cecair hidrokarbon aromatik daripada campuran pelbagai hidrokarbon. Keseimbangan fasa untuk pelbagai sistem yang terdiri daripada aromatik + alifatik + DES telah dikaji. Untuk sistem ternari (tiga fasa) yang terdiri daripada benzena + heksana + (C₁₉H₁₈P.Br:C₂H₆O₂), pekali taburan (distribution coefficient) yang tinggi iaitu lebih daripada 2 telah diperolehi dalam sesetengah eksperimen keseimbangan fasa, dengan

pemilihan (selectivity) terhadap aromatik yang berada di kedudukan maksima 98.2662 dalam sebuah eksperimen yang lain. Sistem ternari lain yang dikaji termasuklah toluena + heptana + (C₁₆H₃₆P.Br:C₂H₆O₂), toluena + heptana + (C₁₆H₃₆P.Br:C₄H₈O₂S), toluena + heptana + (C₂₀H₂₀IP:C₂H₆O₂) dan toluena + heptana + (C₂₀H₂₀IP:C₄H₈O₂S). Pekali taburan yang diperolehi berada dalam julat antara 0.02 hingga 0.95 sementara pemilihan aromatik berada dalam julat antara 1.5 hingga 65.8. Konsistensi untuk keputusan eksperimen dalam sesetengah kes disahkan menggunakan korelasi Othmer-Tobias dan Hand. Pekali regresi adalah sentiasa lebih daripada 0.99 untuk sebahagian sistem ternari, kecuali dalam kes toluena + heptana + (C₁₆H₃₆P.Br: C₂H₆O₂) di mana nisbah molar DES ialah 1:2, pekali regresi ialah 0.9613. Bagi tujuan mengkorelasi data eksperimen dan membuat anggaran untuk pekali aktiviti (activity coefficient), model “non-random two-liquid” (NRTL) telah digunakan ke atas sistem ternari toluena + heptana + (C₁₆H₃₆P.Br:C₂H₆O₂), toluena + heptana + (C₁₆H₃₆P.Br:C₄H₈O₂S), toluena + heptana + (C₂₀H₂₀IP:C₂H₆O₂) dan toluena + heptana + (C₂₀H₂₀IP:C₄H₈O₂S). Perbandingan antara data yang dikira menggunakan model dan data yang diperoleh daripada eksperimen menunjukkan kepersisan yang baik dan kriteria ralat adalah kurang daripada 10⁻⁴. Kajian ini membuktikan bahawa DES memiliki kelebihan jika dibandingkan dengan pelarut konvensional untuk proses pengekstrakan bagi tujuan pengasingan hidrokarbon aromatik kerana DES mudah untuk disintesis, sifat-sifat fizikal yang boleh diubahsuai mengikut keperluan, dan pemilihan aromatik yang tinggi dalam keseimbangan fasa.

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LIST OF ABBREVIATIONS

Deep Eutectic Solvents	DESs
Gas Chromatography	GC
Hydrogen Bond Donor	HBD
Ionic Liquids	ILs
Liquid-Liquid Equilibrium	LLE
Room Temperature Ionic Liquids	RTILs
Volatile Organic Compounds	VOCs
Choline Chloride	ChCl

NOMENCLATURE

β_{aro}	Distribution coefficient of aromatic compound in ternary system
β_{ali}	Distribution coefficient of aliphatic compound in ternary system
S	Selectivity of the solvent used in liquid-liquid extraction toward aromatic compound
η	Efficiency of separation
w_{Tol}^I	Mass fraction of toluene in top layer
w_{Hep}^I	Mass fraction of heptane in top layer
w_{Tol}^{II}	Mass fraction of toluene in bottom layer
w_{DES}^{II}	Mass fraction of DES in bottom layer
a	Fitting parameters of Othmer–Tobias correlation
b	Fitting parameters of Othmer–Tobias correlation
c	Fitting parameters of Hand correlation
d	Fitting parameters of Hand correlation
ω	Liquid-liquid splitting ratio
x_i	Composition of component i in ternary mixture
x_i^I	Composition of component i in the liquid phase I
x_i^{II}	Composition of component i in the liquid phase II
γ_i^I	Activity coefficient of component i in the liquid phase I
γ_i^{II}	Activity coefficient of component i in the liquid phase II
N_C	Number of constituents
S_{ijk}^{exp}	Solubility expressed in mole fraction. Superscripts exp and cal represent experimental and calculated. Subscripts i , j , and k

designate the component, phase, and the tie lines

μ	Viscosity (Pa.s)
μ_o	Viscosity constant (Pa.s)
E_μ	Activation energy of viscosity (Pa.L.mol ⁻¹)
R	Ideal gas constant (kPa.L.mol ⁻¹ .K ⁻¹)
K	Electrical conductivity (mS.cm ⁻¹)
K_o	Electrical conductivity constant (mS.cm ⁻¹)
E_K	Activation energy of electrical conductivity (Pa.L.mol ⁻¹)
ρ	Density (gm.cm ⁻³)
n_D	Refractive index

CHAPTER I

INTRODUCTION

1.1 Introduction

Ethylene ($\text{H}_2\text{C}=\text{CH}_2$) is the intermediate chemical in the manufacture of other chemicals, especially plastics. It is widely used in the polymer industry to produce mainly polyethylenes, the world's most widely-used plastics. Polyethylenes use more than half of the world's ethylene supply and they are utilized in the production of films used in packaging, carrier bags and trash liners. Linear alpha-olefins, produced by oligomerization (formation of short polymers) are used as precursors, detergents, plasticisers, synthetic lubricants, additives, and also as co-monomers in the production of polyethylenes (Kissin, 1989). It is also possible to chlorinate ethylene to make ethylene dichloride, which is a precursor to the polyvinyl chloride. It can be combined with benzene to produce ethylbenzene, a raw material in the manufacture of polystyrene, another important plastic. Ethylene oxide, ethanol, and polyvinyl acetate are also produced from ethylene by oxidation.

Ethylene is produced from natural gas or naphtha by thermal cracking. Possible feedstocks for ethylene production are butane, propane, ethane, refinery gas, natural gas, and light or heavy naphtha. Most naphthas contain 10 – 25% of aromatic components. A typical naphtha composition was given by Melpolder et al. (1952). It was shown that the aromatic composition in total naphtha is about 24% by volume. Due to their ring-shape structure, the aromatic compounds are not converted to olefins by heating in the cracking furnace. Small amounts of aromatics were found to be formed during the cracking process in the cracker furnaces (Zimmermann and Walzl, 2005). Thus, they

occupy a large part of the capacity of cracking furnaces. Moreover, they make an extra load on the separation section of the C_5^+ aliphatic compounds (Meindersma, 2005).

For these reasons, it is beneficial to remove the aromatic hydrocarbons from naphtha or lessen their concentration prior to the thermal cracking. Many benefits could be achieved in this way, like higher capacity, higher thermal efficiency, less fouling, increasing economic efficiency, long life for the heat exchangers and lower environmental impact. Typical separation processes are distillation and extraction.

It was found that the liquid-liquid extraction is possible to separate the aromatic hydrocarbons from naphtha utilizing different solvents. Sulfolane, N-methyl pyrrolidone, N-formyl morpholine, ethylene glycol, propylene carbonate and furfural are commercially used solvents for aromatics extraction (Chen et al., 2000, Krishna et al., 1987, Yorulmaz and Karpuzcu, 1985, Wang et al., 1998, Al-Sahhaf and Kapetanovic, 1996 and Ali et al., 2003, Meindersma, 2005). Aqueous solutions of cyclodextrins were also investigated for aromatics separation (Uemasu and Kushiyama, 2004). However, sulfolane was the solvent of choice by industry as it possessed high aromatics distribution coefficients and high selectivities toward aromatics.

The aromatics extraction process utilizing sulfolane as solvent is widely used to recover benzene, toluene, xylene, and C_9^+ aromatics from aromatic-rich streams (Cho et al., 1999). This process has drawbacks such as the reported low distribution coefficients and selectivities, the high application temperature, and the high melting temperature of sulfolane that limits its application at low temperatures (Meindersma et al., 2005)

Recently, non-conventional solvents were identified as possible replacements for common and conventional solvents. Ionic liquids (ILs) and deep eutectic solvents (DESs) are examples of these non-conventional solvents. Many research works were conducted on various aspects related to ILs and DESs and are available in the literature. Brief introductions to ILs and DESs are presented in the following Sections. One of the

important topics in regard to naphtha purification is the use of ILs as solvents in the liquid-liquid extraction of aromatics from naphtha.

1.2 Ionic liquids and their importance

The late 1990s witnessed a significant increase in ILs research. From synthesis and characterization to their possible applications, research on ILs was very versatile. Currently there are numerous publications available covering the latest advances on ILs.

A room temperature IL, or molten salt, is defined as a material containing only ionic species without any neutral molecules and having a melting point of lower than 25°C (Hagiwara and Ito, 2000). A dramatic increase in activity in this area was afforded by the discovery of 1-ethyl-3-methylimidazolium chloroaluminates (Wilkes et al., 1982). This IL has a wide liquid range and electrochemical window of more than 3 V, and has been of great interest for both electrochemical and synthetic purposes. However, the applications have been limited due to the chemical instability, mainly against moisture. Since the discovery of water stable 1-ethyl-3-methylimidazolium tetrafluoroborate (Wilkes and Zaworotko, 1992), several combinations of alkylimidazolium cations and inorganic and organic anions have been investigated.

ILs are promising compounds for chemical applications and the literature is rich of examples of their potential applications. Electrochemistry, extraction and chromatography are examples of these applications. They were used in the separation of aromatic hydrocarbons from naphtha mixtures (Arce et al., 2007, Cassol et al., 2007, Meindersma et al., 2004). They were also used as liquid membranes (Gan et al., 2006), as media for biological reactions and as mobile phase for HPLC (Polyakova et al., 2006). Furthermore, scientists believe that ILs can be further applied in more complicated processes such as the treatment of highly radio-active waste because ILs are not affected by ionizing radiation. ILs can also be used as absorbents for carbon

dioxide (Ahmady et al., 2011), which opens the opportunity for them to be used for the purification of gases in submarines and spaceships.

To date, most chemical reactions have been carried out in molecular solvents. Most of the understanding of chemistry is based upon the behaviour of molecules in the solution phase in molecular solvents. ILs as solvents have many fascinating properties which make them of fundamental interest to the chemical industry since both the thermodynamics and kinetics of reactions carried out in ILs are different to those in conventional molecular solvents. The chemistry is different and unpredictable at our current state of knowledge. In addition to the important properties ILs possess, they have no measurable vapor pressure which means they can emit no volatile organic compounds (VOCs) (Earle and Seddon, 2000).

1.3 Introduction to deep eutectic solvents

ILs analogues, known as deep eutectic solvents (DESs), have been recognized as an alternative to traditional solvents and ILs (Hou et al., 2008). An individual DES is composed of a combination of a salt and a hydrogen-bond donor (HBD) whereby a new compound is formed, usually possessing a lower melting point than the components of the combination. The reason of the eutectic mixture formation is that the HBD shares a hydrogen bond with the anion of the salt to create an interaction between them that changes their physical behavior, including their freezing temperature.

The first generation of DESs was formed by mixtures of quaternary ammonium salts with amines and carboxylic acids as HBDs. The first work to describe the deep eutectic phenomenon was that of Andrew Abbott and colleagues (Abbott et al., 2004). In that work, a mixture of choline chloride (ChCl), a quaternary ammonium salt, and urea, as HBD, with a salt:HBD molar ratio of 1:2 was utilized to synthesize a DES.

Melting point of ChCl is $302\text{ }^{\circ}\text{C}$ and that of urea is $133\text{ }^{\circ}\text{C}$ while their eutectic mixture, i.e. their DES, melts as low as $12\text{ }^{\circ}\text{C}$.

DESs are favorable in comparison to ILs due to their ease of preparation in the laboratory as well as their low cost (Zhang et al., 2012). Also, their components are biodegradable and they could be low in toxicity. Moreover, most DESs are non-reactive with water (Chen et al., 2010). Like ILs, DESs have numerous potential applications in the chemical industry, including electrochemical applications, electroless applications and separation and purification processes.

To date, a large number of research papers have been published concerning the various possible applications of DESs. In Chapter Two, a comprehensive literature review on ILs and DESs is presented.

1.4 Problem statement

As mentioned earlier, ethylene is the largest-volume petrochemical produced worldwide. It has no direct end uses (Zimmermann and Linde, 2011). It has been recovered from coke-oven gas and other sources in Europe since 1930. Ethylene is considered as a large-volume intermediate in the 1940s. The oil and chemical companies in the United States began separating it from refinery waste gas and producing it from ethane obtained from refinery byproduct streams and from natural gas. Since then, ethylene has almost completely replaced acetylene for many syntheses.

Global production and consumption of ethylene in 2010 were both approximately 123 million metric tons according to World Petrochemical report. In comparison to 3916 million metric tons of total refined products of crude oil, which contains many products, it can be seen that the ethylene consumption is relatively high (Meindersma, 2005).

It was shown in the work of Meindersma (2005) that the aromatic compounds present in concentrations varying between 10 – 25 % by weight in the feed streams of the thermal cracking units for ethylene production. Table 1.1 shows a typical composition of naphtha which is one source of ethylene production, as was presented in the mentioned work.

Table 1.1: Typical naphtha composition (Meindersma, 2005).

Component	wt%	Component	wt%	Component	wt%
N-Butane	1.5	Cyclohexane	2.8	2,6-dimethyl-	1.9
I-Pentane	4.2	2-Methyl-hexane	2.8	heptane	2.0
N-Pentane	10.3	3-Methyl-hexane	3.8	Ethylbenzene	1.9
Cyclopentane	1.5	N-Heptane	4.4	P-xylene	2.7
2,3-dimethyl-butane	0.8	Methyl-cyclohexane	4.8	3-methyl-octane	1.0
2-methyl-pentane	6.0	Toluene	3.0	O-xylene	2.6
3-methyl-pentane	4.0	2-Methyl-heptane	2.4	N- nonane	3.0
N-Hexane	8.6	1,3-dimecyclohexane	7.0	N-decane	4.0
Me-cyclopentane	4.1	N-octane	5.4	I-decane	
Benzene	1.8	Ethyl-cyclohexane	2.0	Total	100

It was described in Section 1.1 that the presence of the aromatic compounds inside the thermal cracking unit imposes negative drawbacks to the process, such as excessive heat consumption and fouling of the radiation sections. For this reason, the concentrations of aromatic compounds must be reduced to the minimum to achieve the financial and environmental benefits mentioned earlier in this Chapter.

The work elaborated in this thesis is an attempt to overcome the shortcomings detailed in Section 1.1 regarding the application of various solvents as extractants for the aromatic hydrocarbons. Hence, the main objective of this project is the development of a new and efficient liquid-liquid extraction solvent for the removal of aromatic hydrocarbons before the naphtha enters the cracking unit.

As ILs have been investigated as possible solvents for the process mentioned above (Meindersma et al., 2006a and 2006b, Domańska et al., 2007, García et al., 2010a,

2010b and 2010c), the present work focuses on DESs as replacement for ILs. This work deals with only DESs synthesized from phosphonium salts.

1.5 Research objectives

DESs are novel and relatively new in the literature. Up to the year 2009, there were only a few research articles available in the literature on their utilization in various applications. There were no works on the characterization of their physical properties available in the literature, though these properties are essential in the process design. Thus, a characterization of DESs is an obvious need to enrich the knowledge about these solvents. The characterization of DESs for their important physical properties forms one objective for this work. Following the characterization, the application of these solvents in the liquid-liquid extraction of aromatic compounds from aromatic/aliphatic mixtures forms another objective.

For reasons of simplicity, benzene/hexane and toluene/heptane mixtures were used as a model to represent the naphtha in the extraction experiments.

The objectives of this research are summarized as follows:

1. Synthesis of new DESs in the laboratory.
2. Measuring the physical properties for some of these solvents.
3. Studying the liquid-liquid phase equilibria of selected solvents attaining high separation factor for the extraction of different aromatic hydrocarbons.
4. Applying thermodynamic models to correlate the experimental data.

1.6 Research methodology

The methodology of this work is listed in the following steps:

1. Synthesis of DESs.
2. Characterization of physical properties of these solvents using various equipment.

3. Preparation of hydrocarbon mixtures at different aromatic concentrations.
4. Liquid-liquid equilibrium (LLE) experiments.
5. Sampling of the extraction mixtures.
6. Analysis by gas chromatography.
7. Calculation of concentrations after the LLE to find experimental compositions.
8. Applying validation models such as Othmer – Tobias and/or Hand correlations to ascertain the experimental compositions profiles.
9. Applying the non-random two liquid (NRTL) model for activity coefficients to correlate the experimental results.

1.7 Thesis outline

This thesis comprises five chapters and the bibliography section. Chapter I presents a brief introduction about this research is given. Chapter II is where the literature is reviewed and summaries are given. Chapter III presents in details the research methodology of this work. Chapter IV is where the experimental results are presented and discussed thoroughly. Lastly, Chapter V presents the conclusions drawn over the obtained results and their analysis.

CHAPTER II

LITERATURE REVIEW

2.1 Ethylene

Ethylene is the lowest alkene hydrocarbon with two carbon atoms. It is a colourless gas with acute sweet odor.

It is used in the manufacture of numerous chemicals, plastics in particular. Through polymerization process, it is polymerized directly to produce polyethylene in its two types, the high density and low density. Polyvinyl chloride, polystyrene, ethylene oxide, ethanol, and polyvinyl acetate are all chemicals produced from ethylene as the starting material. Ethylene is also used as plants-growing hormone. It is produced in all higher plants and is usually associated with fruit ripening and the tripple response (Mauseth, 1991, Arteca, 1996).

Ethylene is one components forming the natural gas which is extracted from underground reservoirs. However, it is also produced from various sources. One of these sources is the thermal cracking of naphtha. In the thermal cracking process, the long-chain hydrocarbons, such as butane; propane and ethane, are converted to ethylene. In addition, other feedstocks for ethylene production are refinery gas, natural gas and light or heavy naphtha. Figure 2.1 shows a simplified ethylene production process flow diagram.

The feedstock is fed into the furnace and heated to 750 – 900 °C for a short period of 1 second. At this temperature and short residence time, the long-chain molecules will split into smaller hydrocarbons. The cracking process is then followed by rapid quenching to minimize side reactions. The effluent gases from the cracker are cooled to

30 °C by direct contact with water. The process then advances to numerous steps to produce ethylene gas by distillation of the effluent gases from the cracking furnace (Kniel et al., 1980).

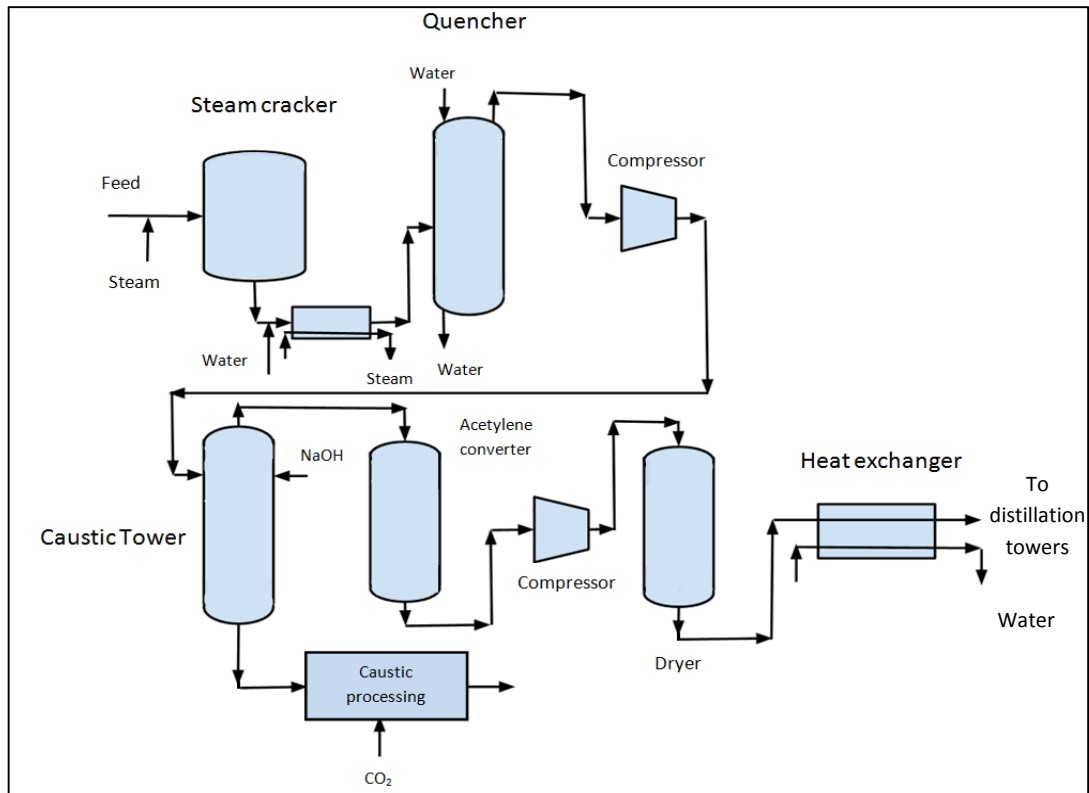


Figure 2.1: Simplified process flow diagram for ethylene production adopted from Toyo Engineering Corporation, Japan.

2.1.1 Aromatics presence in naphtha

Most naphtha cracker feeds contain 10 – 25% of aromatic components. A typical naphtha composition was given by Melpolder et al. (1952). It was shown that the aromatic composition in total naphtha is about 24% by volume. Table 2.1 shows these aromatic hydrocarbons and their estimated volume percentages.

Due to their ring-shape structure, the aromatic compounds are not converted to olefins by heating in the cracking furnace. They absorb the heat supplied and remain in their shape. Small amounts of aromatics were found to be formed during the cracking process in the cracker furnaces (Zimmermann and Walzl, 2005). Thus, they occupy a large part of the capacity of cracking furnaces. Moreover, they contribute to an extra load on the separation section of the C_5^+ aliphatic compounds (Meindersma, 2005).

Table 2.1: Aromatics composition in total naphtha (Melpolder et al., 1952).

Aromatic	Vol. % of naphtha
Benzene	0.21
Toluene	2.32
Ethylbenzene	1.07
o-Xylene	1.20
m-Xylene	2.30
p-Xylene	0.84
Isopropylbenzene	0.18
n-Propylbenzene	0.16
Methylethylbenzenes	0.96
Trimethylbenzenes	4.98
$C_6H_5-C_4H_9$	3.90
$C_6H_5-C_5H_{11}$	1.78
$C_6H_5-C_6H_{13}$	0.56
$C_6H_5-C_7H_{15}$	0.052
$C_6H_5-C_3H_5$	0.27
$C_6H_5-C_4H_7$	0.66
$C_6H_5-C_5H_9$	0.92
$C_6H_5-C_6H_{11}$	0.30
$C_6H_5-C_7H_{13}$	0.027
Dicyclic aromatics	1.30
Total	23.989

2.1.2 Removal of aromatics from naphtha

It was shown in Chapter I that the removal or reduction in concentration of aromatic compounds is necessary in the process of ethylene production. This is due to the negative effects that the aromatic hydrocarbons impose on ethylene production process. Numerous benefits could be achieved in this way, such as higher capacity, higher thermal efficiency, less fouling, increasing economic efficiency, long life for the heat exchangers and lower environmental impact. Typical separation processes are

distillation and extraction. As it is known, distillation is possible when the components of the feed have a big difference in their boiling points and these components do not form azeotropes. These conditions are not applicable for naphtha, and thus it is not possible to separate the aromatics from naphtha with distillation.

2.1.3 Liquid-liquid extraction of aromatics

Extraction is another solution for the removal of aromatics from naphtha. The liquid-liquid extraction is a process whereby two miscible components or more in a mixture can be separated by adding a third component, which is immiscible with some of them, serving as a liquid-liquid extraction solvent. This solvent should be able to dissolve one or more component of the mixture in high capacity when mixed with the mixture. Phase separation is the next step to separate the two immiscible phases. Usually, the denser phase is the solvent phase which is now carrying solute in it. The initial separation is achieved now and solvent recovery is usually done to recycle it for further use (Treybal, 1951).

The solvent that can be used for extraction must be of special characteristics to be favorable for use. The solute should show a high distribution coefficient, i.e. a measure of solubility between the two phases, when a good solvent is used. A high selectivity which means a measure for the tendency of the solvent to dissolve the solute more than the other solvent is also required for a solvent to be used. It is also important that the solvent is recyclable as many times as possible and thermally stable at the operating conditions. Most important is that the solvent should show the minimum possible loss to the raffinate phase.

It was found that this extraction is possible to separate the aromatic hydrocarbons from naphtha utilizing different solvents. Sulfolane, N-methyl pyrrolidone, N-formyl morpholine, ethylene glycol, propylene carbonate and furfural are commercially used

solvents for aromatics extraction (Chen et al., 2000, Krishna et al., 1987, Yorulmaz and Karpuzcu, 1985, Wang et al., 1998, Al-Sahhaf and Kapetanovic, 1996 and Ali et al., 2003).

The aromatics extraction process utilizing sulfolane as solvent is widely used to recover benzene, toluene, xylene, and C₉⁺ aromatics from aromatic-rich streams (Cho et al., 1999). Sulfolane has a good selectivity to aromatics and it has a high boiling point. The extraction process consists of numerous units such as extraction unit, distillation units and other related units, such as strippers and settlers. Figure 2.2 shows a process flow diagram of aromatics extraction process.

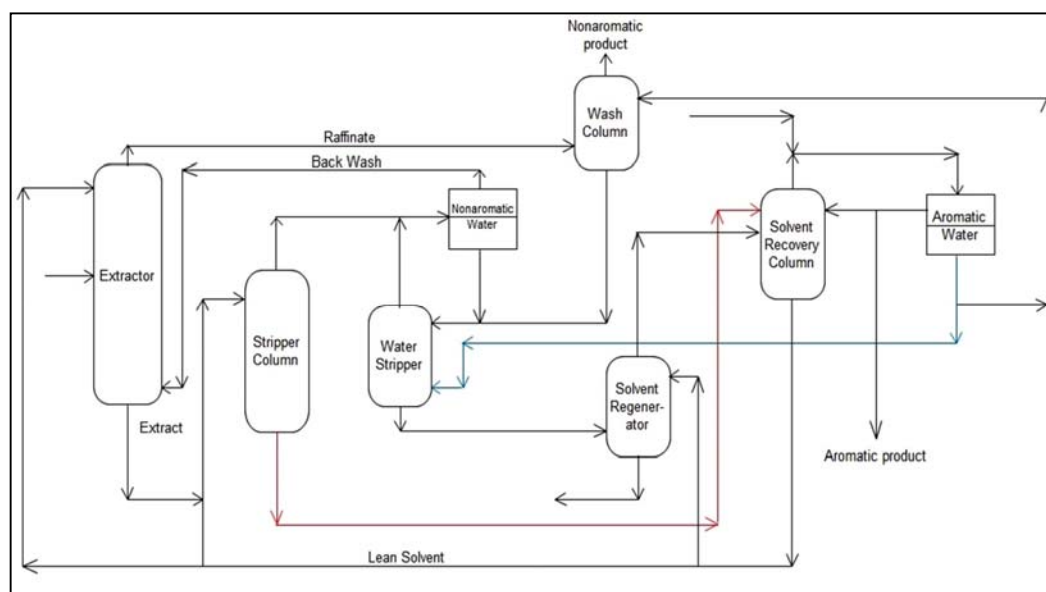


Figure 2.2: Process flow diagram of the aromatics extraction adopted from Sinopec Corporation, China.

It was reported that the sulfolane extraction process is possible for feedstocks containing aromatics concentrations of about 20% to 65% (Meindersma, 2005). This concentration is much higher than the typical concentration of aromatics reported in Table 2.1. Thus, it is necessary to replace sulfolane with a solvent which is able to extract aromatics at low concentrations. This proposed solvent must attain high selectivities for aromatics at low concentrations. The aromatics must also possess high

distribution coefficients using this solvent. Numerous solvents were proposed as potential replacements for sulfolane, such as cyclodextrines, 3-methoxypropionitrile, ethylene glycol, dimethylsulfoxide, phenol and nitrobenzene (Hamid and Ali, 1996 and Uemasu and Kushiya, 2004).

In recent years, researchers identified non-conventional solvents as possible replacements for common and conventional solvents. ILs and deep eutectic solvents (DESS) are examples of these non-conventional solvents. Numerous research papers appeared in the literature from year 2000 and research findings related to these non-conventional solvents in various applications continue to be vigorously published. One of these applications is the liquid-liquid extraction of aromatics from naphtha. In the following sections the synthesis, characterization and applications of ILs and DESS are presented.

2.2 Introduction to ionic liquids

ILs are chemical materials which contain organic cations and inorganic anions with unique and favorable properties, such as low melting point ($< 100^{\circ}\text{C}$), high thermal stability, non-flammability, wide liquid phase range and very low vapor pressure (Hu et al., 2004 and Sun et al., 1998). They are also immiscible with numerous organic solvents, and this provides a non-aqueous polar alternative for two-phase systems (Welton, 1999). To melt in a temperature which is less than 100°C , requires that the melting point of the IL be close to a temperature that is not very far from the glass temperature (McKenna and Angell, 1991).

The increasing interest of ILs in regards to green chemistry and engineering is largely a result of their non-measurable vapor pressure, which means they do not emit organic vapors such as volatile organic compounds (VOCs) (Renner, 2001 and Visser et al., 2002). For this characteristic, they can be used in high vacuum systems (Harris,

2008). However, replacing VOCs is just one of the advantages. In fact, ILs are becoming popular materials and they enjoy a variety of applications in various domains of physical sciences, ranging from electrochemistry to extraction and chromatography. ILs have been used in the separation of aromatic hydrocarbons from naphtha mixtures (Arce et al., 2007, Cassol et al., 2007, and Meindersma et al., 2004). They were also used as liquid membranes (Gan et al., 2006), as media for biological reactions, and as mobile phase for HPLC (Polyakova et al., 2006). Furthermore, scientists believe that ILs can be applied in more complicated processes, such as the treatment of highly radio-active waste because ILs are not affected by ionizing radiation. The solubility of carbon dioxide (CO₂) in ILs was studied by many researchers (Brennecke and Gurkan, 2010). Thus, they can be used for the purification of gases in submarines and spaceships.

ILs were introduced for the first time at 1914 when Paul Walden (1863–1957), a Latvian-German chemist known for his work in stereochemistry and history of chemistry, synthesized the first room-temperature ionic liquid (RTIL), ethylammonium nitrate (Koel, 2008 and Letcher, 2004). However, interest in them remained at low level till the discovery of binary ILs made of mixtures of aluminum(III) chloride and N-alkylpyridinium (Chun, 1975) or 1,3-dialkylimidazolium chloride (Wilkes, 1982).

ILs can be classified into two main categories, simple salts (single anion and cation) and binary ILs (salts where equilibrium is involved). For instance, [EtNH₃][NO₃] is a simple salt whereby mixtures of aluminum(III) chloride and 1,3-dialkylimidazolium chlorides (a binary ionic liquid system) contain several different ionic species, and their melting point and properties depend upon the mole fractions of the aluminum(III) chloride and 1,3-dialkylimidazolium chloride present (Earle and Seddon, 2000).

As these ILs are combinations of cations and anions, it is possible to design them in a way that the required physical properties of the product can be controlled (Marsh et al., 2004). The ions in ILs are found to be large and bulky with the cationic component having a low degree of symmetry. By considering these components, it is possible to prepare ILs that are liquid around and below room temperature (Welton, 1999, Ohno, 2005, and Wasserscheid and Keim, 2000).

Due to this possibility, ILs can be implemented in unit operations for use as reaction media or as separation tools with higher efficiency, more reliability, and less operation time than conventional chemical compounds (Zhao, 2006). Physical properties, such as freezing point, viscosity, density and hydrophobicity can be controlled by simple changes to the structure of the ions. For example, the freezing points of 1-alkyl-3-methylimidazolium tetrafluoroborates and hexafluorophosphates are functions of the length of the 1-alkyl group, and they form liquid crystalline phases for alkyl chain lengths over 12 carbon atoms (Holbrey and Seddon, 1999, Gordon et al., 1998, and Earle and Seddon, 2000).

Another important property that changes with structure is the miscibility of water in these ILs. For example, 1-alkyl-3-methylimidazolium tetrafluoroborate salts are miscible with water at 25 °C where the alkyl chain length is less than 6, but at or above 6 carbon atoms, they form a separate phase when mixed with water. This behavior can be of substantial benefit when carrying out solvent extractions or product separations as the relative solubilities of the ionic and extraction phase can be adjusted to make the separation as easy as possible.

While useful in the fine chemical industry, applications of ILs in the food and pharmaceutical industries have been very limited; due to the issues of high costs, toxicity and purity (Morrison et al., 2009).

2.2.1 Synthesis of ionic liquids

As mentioned in section 2.2, the first reported IL synthesized was ethylammonium nitrate in 1914. This IL was synthesized by adding concentrated nitric acid to ethylamine, followed by distillation to remove the water (Wasserscheid and Wleton, 2008).

The synthesis of ILs usually begins with the quaternisation of an imidazole, an amine or phosphine to produce the cationic component (Wilkes et al., 1982, and Wasserscheid and Keim, 2000). The cations in Figure 2.3 below are the most common in the literature.

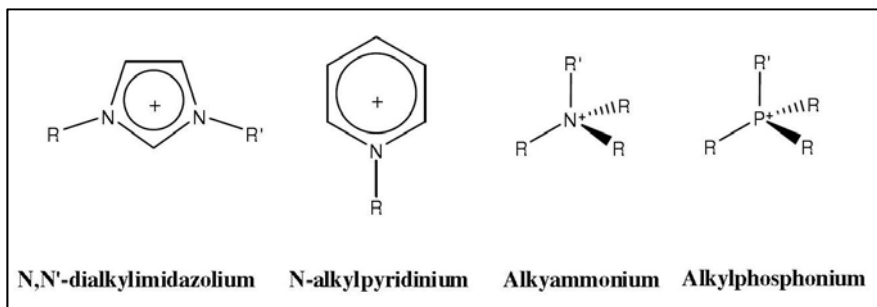


Figure 2.3: Common cations used for IL synthesis.

Quaternisation is done by using an alkylating agent which is usually a halogeno-alkane. It is possible to produce salts that melt below 100 °C by this process (Welton, 1999 and Wasserscheid and Keim, 2000). Examples of ILs that can be formed by direct quaternisation are [BMIM]Cl and [EMIM]CF₃SO₃ (Wasserscheid and Keim, 2000).

There is another method for synthesizing ILs, and this is known as the anion-exchange reaction. It can be further divided into two categories: direct reaction of halide salts with Lewis acids, and the formation of ILs by anion metathesis. Numerous researches have described and reviewed the synthesis of ILs comprehensively (Wasserscheid and Wleton, 2008).

2.2.2 Physical properties of ionic liquids

As it is possible to vary the structure of ILs, consequently it is also possible to tune their physical properties as required. This facilitates designing an ionic solvent for a specific process.

ILs have lower melting or freezing points than those of classical inorganic salts. Inorganic salts generally have very high melting points, for instance NaCl melts at 808 °C. This is due to the strong electrostatic interactions between the ions and the correspondingly high lattice energy of the salt. When the sodium ion (Na^+) was replaced with an organic species such as $[\text{EMIM}]^+$ or $[\text{BMIM}]^+$, the melting point was reduced largely to 87 °C and 65 °C respectively (Wilkes et al., 1982). Studies on the effect of varying the chemical structure of ILs on their freezing point are common in the literature. KCl is another salt which melts around 770 °C. Lidel (1992) reported that if the cation (K^+) in KCl was replaced by the same previous organic cations, its melting point decrease to 65 °C. It is also found that the anion itself affects the melting point as well. For $[\text{EMIM}]\text{Cl}$, if the chloride atom is replaced by NO_3 , it further reduces the freezing point to 38 °C (Wilkes et al., 1982).

The solubility of metal salts in the halometalate ILs is generally high. This could be due to the high halide concentration. Conversely, ILs containing discrete anions generally have relatively weak coordinating properties. They possess small solvation energy that is incapable of breaking the electrostatic interactions between ions in metal salts (Barron, 2009).

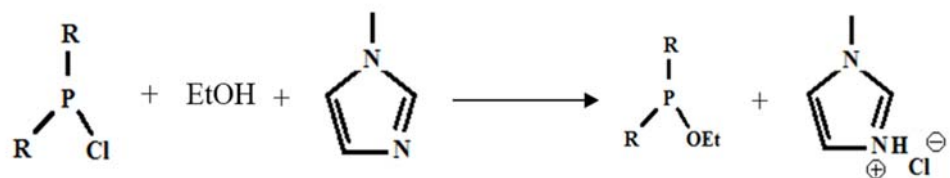
ILs are known for their dense form. Generally, their densities range from 1 – 1.6 g/cm^3 . There is one reported IL with a density less than the density of water (Galinski et al., 2006 and Jacquemin et al., 2008).

It was shown that the viscosity of ILs is inversely proportional to conductivity. The range of viscosities was estimated to be between 10 to 500 mPa.s⁻¹ at 25 °C (Endres and El Abedin, 2006). Some researches explained the high viscosities and low conductivities of ILs, and related them to the low mobility of the species in the liquid. A theory has been proposed to explain the low conductivity of ILs is based upon the availability of holes (Abbott, 2005). In this theory, it is assumed that as solid melts, voids of various sizes are formed. The probability of an ion moving through a liquid is therefore dependent upon the presence of an adjacent suitably sized hole (Barron, 2009). Calculations have shown that the average hole size in ILs is smaller than in aqueous electrolytes whereas the average ion size is larger. Thus, the ion's movement is reduced, leading to decreased ion conductivity and increased viscosity. The major factors contributing to the viscosity of an IL are the strong interaction of Van derWaals bonds and the tendency to form hydrogen bonds (Bonhote et al., 1996). Thus, it was found that hydrogen bonding plays a large part in the viscosity of the chloroaluminate systems (Harris, 2008).

2.2.3 Applications of ionic liquids

A very comprehensive review on ILs published in the Chemical Society Reviews (Plechko and Seddon, 2008), had summarized many commercial and lab-scale applications for ILs as well as the uses of ILs in industry and research up to that date. A summary of some of significant applications is introduced in the present review.

The BASIL™ process was the first and most successful industrial process using a IL technology. BASIL stands for *Biphasic Acid Scavenging utilizing Ionic Liquids*. In this process, a generic photoinitiator precursor alkoxyphenylphosphines is produced according to the following reaction:



Previously, triethylamine was used to scavenge the acid that was formed in the course of the reaction. This act made the reaction mixture difficult to handle as the waste by-product, triethylammonium chloride formed a dense insoluble paste.

Replacing triethylamine with 1-methylimidazole resulted in the formation of 1-methylimidazolium chloride, which is an IL that separates out of the reaction mixture as a discrete phase. This alteration to the process required a much smaller reactor than the initial process. In addition, the space-time yield is increased from 8 kg m⁻³ h⁻¹ to 690,000 kg m⁻³ h⁻¹, and the yield increased from 50% to 98%. 1-methylimidazole is recycled by base decomposition of 1-H-3-methylimidazolium chloride in a proprietary process.

Extractive distillation is the most widely utilized technology used to separate azeotropes and other mixtures that have key components with a relative volatility below 1.1 over a range of concentration (Lei et al., 2005, Lei et al., 2003, Li J. et al., 2005). The application of ILs as entrainers for extractive distillation was proposed firstly by Arlt and colleagues (Arlt et al., 2001a, Arlt et al., 2001b, Seiler et al., 2004, Lei et al., 2006, Lei et al., 2007, Jork et al., 2004). ILs were used to break common azeotropes like water–ethanol, water–tetrahydrofuran and ethyl acetate–ethanol (Li Q. et al., 2009).

Cellulose is an abundant biorenewable material, which is technologically well-established. Products derived from cellulose have many important applications in the fiber, paper, membrane, polymer and paints industries. Cellulose consists of polydispersed linear glucose polymer chains which form hydrogen-bonded

supramolecular structures. It is insoluble in water and in most common organic liquids. Many of the technologies currently used in cellulose processing are decidedly non-green (Swatloski et al., 2002). The application of ILs as green solvents to dissolve cellulose has the benefits of increased solution efficiency and reduction or elimination of undesirable solvents. Some ILs showed a good dissolution capability for cellulose, and this has been mentioned in the work of Swatloski and colleagues.

ILs were also implemented in electrochemistry. The electroless plating of aluminum in an IL electrolyte solution was presented by Koura et al. (2008). AlCl_3 -1-ethyl-3-methylimidazolium chloride was used as the candidate IL. Results showed that the plated film consisted of aluminum only with no impurity phases such as C, Li, and H. This electroless plating was further discussed by Shitanda et al. (2009). The same IL used by Koura and colleagues was used by Shitanda and colleagues, but diisobutyl aluminum hydride was added to this IL to serve as a reducing agent. It was found that the results of this new study are similar to the previous one; however, the addition of the reducing agent made it easier to prepare the plating bath and to control the temperature of this bath.

ILs as reaction media were implemented in nickel-catalysed dimerisation reactions. The dimersol process consists of the dimerisation of alkenes like propene and butene to convert them to the more valuable branched hexenes and octenes (Chauvin et al., 1974). It is an important industrial process, with many plants in operation worldwide producing between 20,000 and 90,000 tonnes per year of dimer (Chauvin, 2006). The dimerisation reaction is catalysed by a cationic nickel complex of the general form $[\text{LNiCH}_2\text{R}^+][\text{AlCl}_4^-]$ where $\text{L} = \text{PR}_3$, and it is commonly operated without the use of solvent. It was found that the catalyst shows greater activity when it is dissolved in undesirable aromatic or halogenated hydrocarbons. The reaction can be performed as a

biphasic system, in a temperature range between -15°C and 5°C , as the products form a second layer that can be easily separated and the catalysts remains selectively dissolved in the IL phase (Plechkova and Seddon, 2007). Eichmann et al. (2009) reported the implementation of 1-ethyl-3-methylimidazolium chloride in the nickel-catalyzed dimerisation of propene. It was found that the activity of the catalyst is much higher when the IL is implemented than in both solvent-free and conventional solvent systems, and the selectivity for desirable dimers is enhanced.

Other reported applications of ILs are in their use as paint additives, electrolytes for lithium-ion batteries, separation of aromatic hydrocarbons by liquid-liquid extraction and more. Figure 2.4 adopted from Plechkova and Seddon (2007) shows a hypothetical sketch for the potential applications of ILs that could come to reality in the future. Some of these applications are already undergoing research.

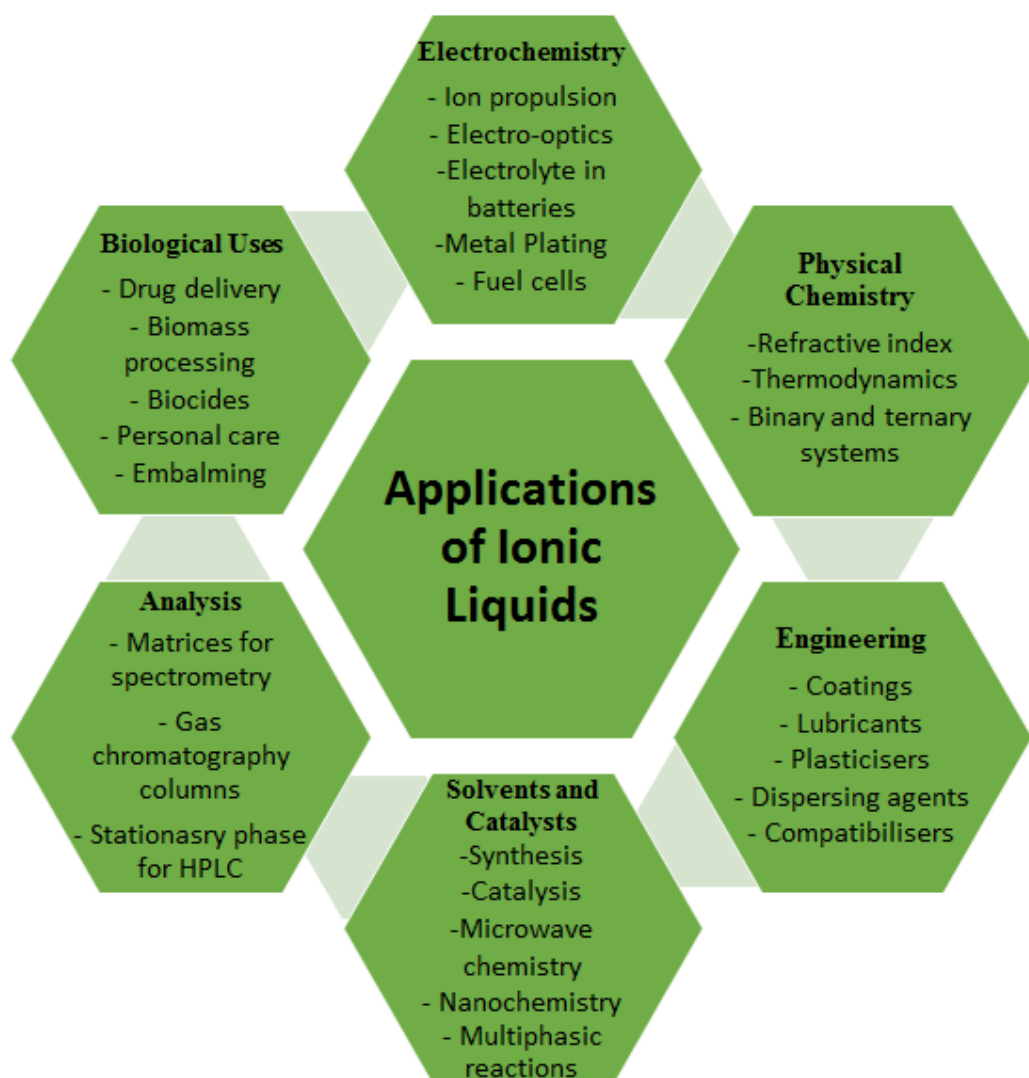


Figure 2.4: Possible applications of ILs.

2.3 Deep eutectic solvents

While useful in the fine chemical industry, applications of ILs in the pharmaceutical industry and food industry have been very limited due to issues of toxicity, purity, and high costs (Morrison et al., 2009). Thus, they are not easily applicable in laboratory experiments and pilot plants. As a matter of fact, these ILs cannot be prepared in the laboratory with one step synthesis. Therefore, researchers have to buy them from commercial manufacturers. Due to the multi-stage purification processes required to purify the ILs after their synthesis, their price is considerably

expensive. In certain cases, the price is as high as \$ 7/g for 1-butyl-1-methylpyrrolidinium trifluoroacetate (quoted by Merck Chemicals). Even worse, there are other ILs that are as expensive as \$ 53/g such as 3-(triphenylphosphonio)propane-1-sulfonic acid tosylate and some are even more than \$ 80/g such as methyltrioctylammonium thiosalicylate (quoted by Sigma Aldrich).

DESs were introduced as novel solvents in the last decade. The advantage of these solvents is the ease of their preparation. Each DES is a combination of a salt and a hydrogen-bond donor (HBD) or a complexing agent in which a new compound is formed. The resulting DES usually has lower melting point than the constituting components. DESs are basically molten salts that interact by the formation of hydrogen bonds or metal halide bonds through the anion of a salt, as opposed to relying purely on electrostatic forces between anion and cation, as in the case of ILs (Harris, 2008).

The first generation of DESs was based on mixtures of quaternary ammonium salts with hydrogen donors such as amines and carboxylic acids. The deep eutectic phenomenon was first described for a mixture of choline chloride (ChCl) as salt and urea as a HBD with a salt:HBD molar ratio of 1:2. ChCl has a melting point of 302 °C and that of urea is 133 °C while the eutectic mixture melts as low as 12 °C (Abbott et al., 2003a). Abbott et al. (2003a) showed that eutectic mixtures of salts were utilized to decrease the temperature for molten salt applications. To illustrate this, he reported that ambient temperature molten salts can be formed by mixing, for instant, quaternary ammonium salts with metal salts, and called the resultant compound as IL analogue or deep eutectic mixture. This eutectic is a result of the formation of complex anions, such as $Al_2Cl_7^-$ and $Zn_2Cl_5^-$, thus decreasing the lattice energy and decreasing the freezing point of the system.

The preparation of eutectic solvents in a pure state can be accomplished more easily than that of ILs without the need of post-synthesis purification because the purity of the resulting DES depends on the purity of its individual components (Carriazo et al., 2012). These components are able to share a hydrogen bond between them to form a complex known as eutectic mixture. They can be selected from cheap, renewable, biodegradable, water-stable chemicals (Chen et al., 2010). In comparison to ordinary solvents, eutectic solvents also have a very low volatility and are non-flammable.

DESs cannot be considered as ILs for many reasons, such as a) DESs are not entirely composed of ionic species and b) DESs can also be obtained from non-ionic species. However, DESs are attractive since they exhibit similar physico-chemical properties to traditional imidazolium-based ILs and can thus advantageously replace them in numerous applications. Hou et al. (2008) recognized them as possible replacements for ILs.

The two components of a DES are categorized as a salt and a hydrogen bond donor (HBD). Since research on DESs have appeared in the literature, numerous combinations of salts and HBDs or complexing agents were reported to produce DESs successfully. Examples of salts are ChCl (Abbott et al., 2009), methyltriphenylphosphonium bromide (Kareem et al., 2010, Kareem et al. 2012a, Shahbaz et al., 2010) and tetrabutylphosphonium bromide (Kareem et al., 2012b), while for HBDs or complexing agents, the literature lists numerous examples such as urea, thiourea, 1-methyl urea, 1,3-dimethyl urea, 1,1-dimethyl urea, acetamide, benzamide (Abbott et al., 2003), ethylene glycol, glycerol, 2,2,2-trifluoroacetamide (Kareem et al., 2010) and d-fructose (Hayyan et al., 2012).

ChCl ($C_3H_{14}ClNO$) is one of the first cited salts to be used as a starting material for DES synthesis (Abbott et al., 2003). Nowadays, it is considered as one of the most

widespread salts used for the formation of DESs (Zhang et al., 2012). It has many benefits as it is a cheap, biodegradable, non-toxic and it can be either extracted from biomass or readily synthesized from fossil reserves. The reason for its popularity is the ease of using it to form a DES with different HBDs such as oxalic, citric, succinic or amino acids, glycerol or carbohydrates. As compared to the traditional ILs, DESs derived from ChCl share many advantages such as low price, water-stable and ease of preparation. Most of them are biodegradable, biocompatible and non-toxic, making them truly green solvents.

Most of the research laboratories around the world which are dealing with DESs are focusing on quaternary ammonium salts, mostly ChCl, to prepare their DESs (Abbott et al., 2003, Abbott et al., 2004, Abbott et al., 2006a, Abbott et al., 2006b, Abbott et al., 2006c, Abbott et al., 2007a, Abbott et al., 2007b, Abbott et al., 2008, Aidoudi et al., 2011, D'Agostino et al., 2011, Gutiérrez et al., 2011, Steichen et al., 2011, Shamsuri and Abdullah, 2011, etc.). However, the author's research group (Kareem et al., 2010, Kareem et al., 2012a, Kareem et al., 2012b, Hayyan et al., 2012, Shahbaz et al., 2011a, Shahbaz et al., 2011b, Shahbaz et al., 2011c, Shahbaz et al., 2012a, Shahbaz et al., 2012b) has dealt with quaternary phosphonium salts-based DESs. The salts under investigation are methyltriphenylphosphonium bromide, benzyltriphenylphosphonium chloride, tetrabutylphosphonium bromide and ethyltriphenylphosphonium iodide. If ChCl has its own advantages, phosphonium salts for use in DESs' synthesis have their own advantages too. In a review by Fraser and McFarlane (2009), it was reported that phosphonium salts are of numerous favorable characteristics. They are available widely and cost less in comparison to ammonium salts (Bradarić et al., 2003). Additionally, they are more thermally stable than ammonium salts that they can be used in applications of high temperatures, i.e. exceeding 100 °C (Tsunashima and Sugiya, 2007). Lastly, alkylphosphonium salts are generally less dense than water. This is

beneficial in processing steps that involve decanting aqueous layers containing inorganic salt by-products.

Figure 2.5 shows a phase diagram for a binary chemical mixture to depict the eutectic composition. The two components of the mixture are denoted by α and β , T denotes temperature, and L denotes the liquid state. The point e is where the eutectic phenomenon is taking place, which is an expression of a certain composition of the two components (Smith and Hashemi, 2005, Buchinskaya and Fedorov, 2008).

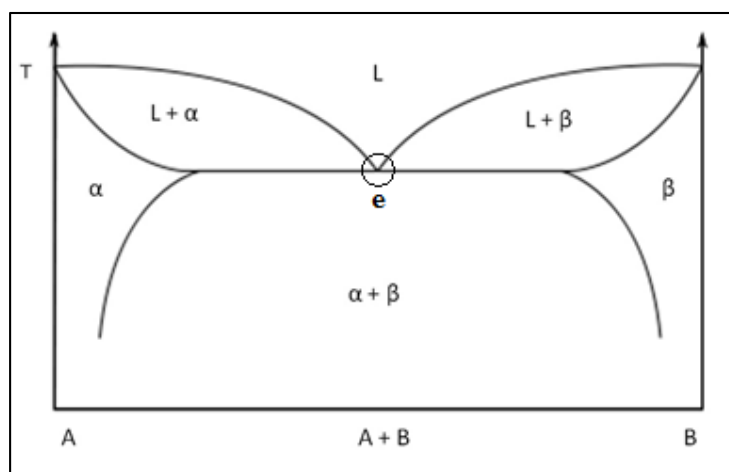


Figure 2.5: A phase diagram for a binary chemical mixture, adopted from Smith and Hashemi (2005).

The $\text{ChCl} + \text{urea}$ DES was reported to be able to dissolve many metal salts such as lithium chloride (solubility 2.5 mol/L) and copper (II) oxide (solubility 0.12 mol/L). In this capacity, the DES is used for metal cleaning prior to electroplating. Because the solvent is conductive, it also has a potential application in electropolishing. Organic compounds such as benzoic acid also have high solubility of 0.82 mol/L and this even includes cellulose (Abbott et al., 2003a).

Chen et al. (2010) described two methods of nucleophilic fluorination to prepare α -fluoroacetophenones from α -bromoacetophenones by using potassium fluoride with

polyethylene glycol 400 or tetra-n-butylammonium fluoride with zinc fluoride. A novel method for a one-pot fluorination to prepare α -fluoroacetophenones directly from acetophenones in DES was also developed by Chen et al. (2010). Morrison et al. (2009) studied the possible uses of DESs in improving the solubility of poorly soluble compounds for enhanced bioavailability in drug development. Five poorly soluble model compounds were studied. The solubility was improved by a magnitude of 5 to 22,000 folds in DESs in comparison to in water. As a conclusion, DESs were found to be promising vehicles for increasing exposure of poorly soluble compounds in preclinical studies.

The industrial applications of DESs are also extremely promising. They were applied as media for the deposition of zinc (Zn), chromium (Cr), tin (Sn), copper (Cu) and silver (Ag) metals in the electro and electroless plating of metals (Abbott et al., 2008, Abbott et al., 2009).

DESs had shown potential for large-scale applications, such as zinc electroplating (Abbott et al., 2001), batteries (Abbott et al., 2003b) as well as catalysts for Diels Alder reactions (Abbott et al., 2002). It has also recently been shown that these ideas can be extended to other metals by using hydrated salt mixtures (Abbott et al., 2003).

Their application to electropolish stainless-steel was also studied. A DES composed of ChCl and ethylene glycol showed three main advantages over the commercial alternative in this process. Firstly, high electrical current efficiencies were obtained. Secondly, a negligible gas evolution at the anode/solution interface during polishing was noticed. Lastly, the liquid used was non-corrosive and benign compared to the current aqueous acid solutions (Abbott et al., 2006). Additionally, DESs have been tested as reaction media for synthesizing lanthanide-organic frameworks. DESs were found to be able to act as unusual reaction media by serving as template-delivery

agents in a controlled manner. Thus, they could be used for the synthesis of materials that cannot be prepared using other standard techniques (Himeur et al., 2010). Furthermore, DESs have been used for the removal of residual palm oil-based biodiesel catalyst (Shahbaz et al., 2011).

2.3.1 Synthesis of deep eutectic solvents

As stated by Abbott et al. (2004), DESs are favorable over ILs for numerous reasons, in particular their method of preparation. The preparation is considered as a physical interaction between its components and no reactions take place. Thus the chemical structure is left intact while the hydrogen bonding is taking place. Abbott et al. (2004) has described a method for synthesizing DESs. This method also was used by Kareem et al. (2010, 2012a, 2012b) and Shahbaz et al. (2011a, 2011b, 2011c, 2012a, 2012b) to synthesize the DESs.

In comparison to the synthesis of IL which is more involved due to the multi-stage purification steps required to purify the resulting IL, the synthesis of DESs only requires a jacketed vessel equipped with either mechanical or magnetic stirring. As DES comprises two or more components, these components are usually heated to a certain temperature using the jacket around the mixing vessel, while mixing is carried out bring the components into direct contact. The time and temperature required for the synthesis varies from one DES to another. Some DESs require hours of stirring under high temperature, while others require only a short time at moderate temperatures. The product is a clear and homogenous liquid.

2.3.2 Physical properties of deep eutectic solvents

In section 2.3 it has been shown that DES is a combination of two or more components at specific molar ratios. It was proven that the change in one of these

components or the molar ratios with which the DES is prepared, leads to a change in the physical properties of the resulting DES (Kareem et al., 2010). Thus, the physical properties of DES, like those of IL, are tunable. This means, for instance, if a liquid extraction process needs a solvent with a viscosity not more than 0.15 Pa.s at room temperature, it is possible to synthesize specific DES with such viscosity, depending on previous knowledge of this very DES.

2.3.2.1 Melting (freezing) point

ILs and DESs are defined as molten salts that melt below 100 °C. This means that the melting point is a defining feature for them. Characterization studies were carried out as attempts to highlight the important physical properties DESs possess. Abbott et al. (2003) showed that DESs of ChCl + urea had some unique solvent's properties. It was shown since then that the self-association taking place between the salt and the HBD leads to a freezing point depression in the eutectic mixture which further leads to DES formation. It was also shown that the molar ratio of salt:HBD is the key factor that controls the melting point of DES.

For a mixture of ChCl + urea, Abbott et al. (2003) showed that the melting point of a DES with 68 % mol of urea has the minimum melting point which is 12 °C. Other concentrations of urea in the mixture lead to different DESs with higher melting points. This trend in the profile of the melting points for a specific mixture of salt and HBD at different mole ratios is illustrated in Chapter 4 of this thesis. Shahbaz et al. (2010) in a study for the applicability of DESs as glycerol removal solvents from biodiesel also showed that for a DES prepared from ChCl with either ethylene glycol or 2,2,2 trifluoroacetamide, the variation of the salt:HBD molar ratio has the same influence on the melting point of the DES. A melting point of -66 °C was achieved for ChCl + ethylene glycol at a salt:HBD molar ratio of 1:2.

2.3.2.2 Density

Numerous works had dealt with the estimation of the densities of different DESs. It was found that some phosphonium DESs possess densities higher than the density of water (Kareem et al., 2010, Shabaz et al., 2012c). Similar to melting point, density of DES is also a function of the salt:HBD molar ratio. In the work of Abbott et al. (2011), they reported the density's profile versus the salt's concentration in a DES prepared from ChCl and glycerol. The density of this particular DES was at a maximum of 1.26 g/cm³ at zero % molar concentration of ChCl. The density started to decrease as the ChCl concentration increased till it reached 1.18 g/cm³ when the ChCl concentration approximated to 33% mol.

2.3.2.3 Viscosity

Viscosity is defined as the resistivity of a fluid, and it is a vry significant property for a proper process design.

Works that includ data for viscosities of DESs are limited, unlike those for densities and melting points. Viscosity profiles versus temperature are presented for 3 DESs in subsection 4.1.3. The viscosities are generally higher than that of water. At or around room temperature, the viscosities are recorded between 0.068 and 0.14 Pa.s.

Another work by Hayyan et al. (2012) presented a DES made of ChCl and d-fructose as a HBD. It was shown that the variation of the salt:HBD ratio has influenced the viscosity of the resulting DES. The lowest viscosity was attained at a salt:HBD of 2:1. Yet, the viscosity of this DES is much higher than other reported viscosities for various DESs.

In the review by Zhang et al. (2012), it is reported that the viscosity of binary eutectic mixtures is mainly governed by hydrogen bonds, van der Waals and

electrostatic interactions. It is further stated that the viscosity of ChCl-based DESs is very much dependent on the nature of the HBD. On the other hand, the researchers argued that the use of derived sugars such as xylitol and sorbitol or carboxylic acids such as malonic acid as HBDs led to DESs demonstrating high viscosities due to the presence of a more robust 3D intermolecular hydrogen-bond network. This could provide the reason for the variability of viscosity for a DES.

2.3.3 Applications of deep eutectic solvents

At the early stage of this research, there were few research papers available in the literature dealing with the applications of DESs. Up to that time, almost all the published papers on the applications of DESs were dealing with electrochemical applications, such as electrodeposition of metals in DESs media. A few other applications were also available in the literature at that time.

Over a span of less than three years, numerous research papers appear in the literature dealing with different applications of DESs. From reaction media to solvents for separation processes, the applications of DESs expanded to a far wider horizon than before, and up to the time of writing this thesis, there are still new applications cropping up.

The following list summarizes the usefulness and some of the significant applications of DESs.

a) DESs in synthesis

The ChCl:urea combination is a very popular DES for research work. It was used as a reaction medium for the organic-solvent-free, low-temperature synthesis and crystallization of $Zn(O_3PCH_2CO_2).NH_4$ (Liao et al., 2005). The reactants (zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) and phosphonic acid ($H_2O_3PCH_2CO_2H$)) exhibited excellent solubility in the eutectic mixture, forming homogenous solution. Colorless

crystals were formed after several hours and afforded good yield after several days. Liu et al. (2012) reported the use of this ChCl:urea DES as a medium for the successful synthesis of a high nuclear lanthanide-containing polyoxometalate aggregate $\{[(\text{CH}_3)_3\text{N}(\text{CH}_2)_2\text{OH}]_2(\text{NH}_4)_{12}\}[\text{Ce}_4(\text{Mo}_4)(\text{H}_2\text{O})_{16}(\text{Mo}_7\text{O}_{24})_4].8\text{H}_2\text{O}$. This method avoids the disadvantages of poor solubility, lower yields, additional noxious organic reagents, and thus it is convenient and environmentally friendly. Another use of this DES is reported by Wei et al. (2012). Platinum (Pt) nanoflowers were synthesized in a DES medium by an “electrochemically shape-controlled” synthesis technique. Uniform Pt nanoflowers with sharp single crystal petals and high density of atomic steps were produced. These nanoflowers exhibit higher electrocatalytic activity and stability than commercial Pt black catalyst toward ethanol electrooxidation. Furthermore, the growth of Pt nanoflowers in DESs was in a simple electrochemical route, straightforward and controllable in terms of nanoflowers’ shape and size. These findings led to the belief that this technique using ChCl:urea DES as a medium can be applied in shape-controlled synthesis of other noble metal nanoparticles with high catalytic activity. Moreover, Wang et al. (2010) found that this DES is able to serve as a reaction medium for the synthesis of polyoxometalate (POM)-based hybrids. The traditional synthesis of these hybrids is achieved by two methods. Both of which exhibit high temperature use and possess other disadvantages such as low yields, insolubility of final products, the hard repetibility and control, the unclarity of reaction mechanism and the potential explosion of the organic solvent and organic reactants.. Thus, using a DES as a reaction medium was found to be excellent for reducing the application temperature to as low as 30 °C as well as eliminating the possibility of explosions as DESs are of negligible vapour pressure.

Abbott et al. (2006a) reported the use of this very DES in a process called cationic functionalization of cellulose. Different processes such as paper industry, cosmetics,

textiles, flotation and flocculation and drilling fluids are processes which use this functionalization process. For instance, in the textile industry, cationic functionalization of cellulose is used in the removal of acidic dyes from aqueous effluents, which is a necessary process to reduce the environmental impact of these dyes (Laszlo, 1994). Such approach uses large amounts of organic solvents with the drawback of low yields and the loss of product as a result of solubility in the reaction mixture. The work showed that this DES acted as both reagent and solvent in the mentioned process; whereby all the available hydroxyl groups on cellulose were modified. More interest in this DES is found in the work of Singh et al. (2012), whereby rapid synthesis of nitroaldol compounds, i.e. intermediates for the preparation of variety of compounds like nitroalkenes, 2-aminoalcohols and 2-nitroketones, were conducted in this DES as medium for this synthesis.

Disale et al. (2012) reported the use of another DES based on ChCl as a catalyst for the one pot three-component synthesis of α -aminophosphonates under solvent-free condition at room temperature. ChCl was mixed with zinc chloride (ZnCl) and the resulting DES was used in three-component Kabachnik–Fields reaction as a catalyst. The reactions were completed in a short time and the products were obtained in good to excellent yields. Zhao et al. (2012) presented a work that used a ChCl-based DES to ionothermally synthesize molecular sieves. It was reported that mesoporous SAPO-5 molecular sieve can be ionothermally synthesized by microwave heating in a DES of ChCl and pentaerythritol.

The transesterification activities of cross-linked proteases, i.e. subtilisin and α -chymotrypsin, immobilized on chitosan were individually examined in DESs of choline ion and glycerol. Cross-linked subtilisin exhibited a high activity and selectivity in 1:2 choline chloride/glycerol DES in the presence of 3% (v/v) water whereas free subtilisin gave poor selectivity in the same DES. Subtilisin was also found to be more active in

1:2 ChCl:glycerol DES than in choline acetate:glycerol DES, and subtilisin was also more compatible with DESs than α -chymotrypsin. In addition, the DESs showed excellent suitability for subtilisin biocatalysis (Zhao et al., 2011).

Another ChCl DES formed with imidazolidone as HBD was used as a medium for the synthesis of three-dimensional zinc phosphate. This compound, designated as ZnPO₄-EU1, with DFT topology was successfully produced ionothermally by in situ generation from imidazolidone. The precise synthesis conditions, such as crystallization time and temperature, as well as phosphate:zinc molar ratio, were systematically investigated (Liu et al., 2008).

A ChCl:ZnCl₂ DES was used as a fluorination reagent. α -fluoroacetophenones was produced in the reported DES as medium for its synthesis. Compared with two other commercially available reagents, i.e. potassium fluoride and tetrabutylammonium fluoride trihydrate, this DES was advantageous due to its improvement for the reaction's yield (Chen et al., 2010). In another work by Himeur et al. (2010), three isostructural materials Ln(TMA)(DMU)₂ were synthesised ionothermally using a ChCl:dimethyl urea DES as the medium.

b) Electrodeposition in DESs

Electrodeposition of metals in a DES environment is a popular research topic, and some significant research papers are summarized in this subsection.

The DESs made from ChCl and either urea or ethylene glycol was a subject to many electrodeposition studies. The electrodeposition of zinc-tin alloys in these DESs as media was conducted by Abbott and colleagues (Abbott et al., 2007a). It was shown that zinc and tin can be electrodeposited from these liquids as well as in the form of Zn-Sn alloys. Composite materials were also found to be able to deposit in DESs media,

Al_2O_3 was used as an example. Abbott et al. (2009) showed that the same DESs can be used as electrochemical solvents for the electrodeposition of copper. The current efficiency for copper deposition was found to be close to 100%. Composites of copper with Al_2O_3 and SiC were also produced. The loading of these species in the resulting electroplated films was found to be strongly dependent on the concentration of particulate in solution but largely independent of the concentration of copper metal ion or timescale. Another study by Steichen et al. (2011) used ChCl:urea DES with 1:2 molar ratio to electrodeposit copper (Cu) and Gallium (Ga) for a low cost preparation of CuGaSe_2 (CGS) semiconductors. These semiconductors are used in thin film solar cells. The coelectrodeposition of Cu–Ga films from DESs was conducted in a one-step process for the first time. A precise control of the film stoichiometry over a large gallium composition range and the high current efficiency of the electrodeposition process in the DES were also ascertained. More importantly, it was discovered that the reported electrodeposition process allows the fabrication of metallic Cu–Ga precursor films that can be selenized to high quality CuGaSe_2 absorbers without any significant Ga loss during the annealing step.

More research on ChCl:urea DES with a molar ratio of 1:2 as an electrodeposition medium is found in the work of Gómez and colleagues (Gómez et al., 2011). This DES was found to be exhibiting an electrochemical window that permits the deposition analysis of cobalt (Co), samarium (Sm) and samarium-cobalt (SmCo) system. The electrodeposition was carried out without interference from parallel reactions and under a temperature of 70 °C in order to stimulate mass transfer and to lower solution viscosity. The DES was found to possess the capability to permit the electrodeposition in non-aggressive conditions for alloys containing some transition metal. The same DES was also studied for its applicability as a medium for the electrodeposition of pure nickel

(Ni) (Yang et al., 2011). Nicotinic acid was added as a brightener for the deposited surface, whereby a shiny surface was formed after the deposition was completed.

ChCl:ethylene glycol DES was used as a medium for nickel (Ni) and cobalt (Co) electrodeposition. You et al. (2012) presented a study that demonstrated facile electrodeposition of Ni-Co alloys from this DES containing $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ at room temperature.

ChCl:glycerol DES was studied for its possible role in the electrodeposition of copper (Cu) on platinum (Pt) electrodes (Pollet et al., 2008). The electrodeposition process was conducted thrice. Firstly, under normal conditions without any driving force. The deposition was found to be driven only by diffusion. Secondly and thirdly, ultrasound waves at 20 and 850 kHz, respectively, were added as a driving force. It was found that the ultrasound waves served as driving force to accelerate the electrodeposition.

Saravanan et al. (2011) studied and ascertained the possibility of electrochemically depositing Fe-Ni-Cr alloy on mild steel substrate. A new form of DES was developed by mixing ChCl, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, KCl and ethylene glycol whereby a green-coloured DES was formed by stirring under heating. The deposited alloy's composition was approximately 53-61% Fe, 34-41% Ni, and 4-15% Cr.

Other studies on the electrodeposition of metals from DESs media were also reported (Bozzini et al., 2012, Abbott et al., 2011b, Yang et al., 2012, Gu et al., 2012, Wei et al., 2012, Cojocararu et al., 2011), not forgetting to mention that Haerens et al. (2009) studied the environmental impact of the DES made from ChCl and ethylene glycol. The later work took into account the DES carried by the washing water for the finished surfaces and how does it affect the water cleanliness. It was found that drag-out is the most influencing parameter on the environmental impact of the process, as it is

three times higher compared to classical solutions due to the higher viscosity of the DES.

c) Electroless deposition in DESs

In contrast to the electrodeposition of metals in DESs mediums, the electroless deposition in DESs was reported once only. DESs of ChCl with ethylene glycol or urea were applied in the electroless deposition of metallic silver on copper substrates from a solution of Ag^+ ions (Abbott et al., 2007b). Electroless silver deposits were obtained at several microns by dip-coating in these DESs without the use of catalysts of strong inorganic acids.

d) DESs as electrolytes

A ChCl:glycerol DES was used as an electrolyte for solar cells. Energy conversion efficiency of 3.88% at full sunlight was achieved by employing this DES. The DES-based electrolyte system is found to have good conductivity and high diffusion coefficient (Jhong et al., 2009). A study in 2012 by Ju and colleagues (Ju et al., 2012) showed that DESs of ChCl and HBDs such as glycerol or malonic acid or urea possess a very wide electrochemical window (2V) and thus they can serve as electrolytes for various electrochemical applications, particularly as electrolytes of electrical double-layer capacitors (EDLCs). It was shown that by adding γ -Butyrolactone as a diluent to the DESs, it worked perfectly in decreasing the viscosities and increasing the ionic conductivity of the DESs. This increased their potentials as electrolytes, especially when it improved the performance of the EDLCs.

e) DESs for electropolishing

It was found that for a DES made from choline chloride + ethylene glycol, it is possible to electropolish stainless steel due to three main benefits: a) high current

efficiencies are obtained, b) gas evolution at the anode/solution interface during polishing is negligible and c) the liquid used is comparatively benign and non-corrosive compared to the current aqueous acid solutions (Abbott et al., 2006b).

f) DESs as drug solubilization vehicles

Morrison et al. (2009) showed that DESs could improve the solubility of poorly soluble compounds by 5 to 22000 folds when compared with the solubility in water. Because the components in DES are pharmaceutically acceptable, they could potentially be used as vehicles for oral dosing of rats during early development pharmacokinetic investigations.

g) DESs as co-solvents for enzyme-catalyzed hydrolysis

Choline chloride-based DESs were tested as co-solvents in enzyme catalyzed hydrolysis of a chiral (1,2)-trans-2-methylstyrene oxide. Ethane-diol, urea and ethylene glycol were used as HBDs to make these DESs. The reaction mixture included DES, epoxide and potato epoxide hydrolase StEH1. The effect of the DESs on enzyme function was primarily elevations of K_M , up to 20 fold, and with lesser effects on turnover numbers, i.e. two-fold variation. The DES solutions dissolved 1.5-fold higher epoxide concentrations as compared to phosphate buffer (Lindberg et al., 2010).

h) DESs as solvents for extraction

The idea of applying ILs as extracting solvents was a subject of broad research and many specific extraction processes had undergone a solvent replacement with ILs. The work of Meindersma (2005) was a complete report on IL selection in pilot plant design and economic feasibility study on the process of aromatic hydrocarbons extraction from naphtha. However, literature survey reveals a much fewer number of scientific papers dealing with the use of DESs as solvents for extraction. Abbott et al. (2007c) presented

the first published work on this matter, whereby DESs made from glycerol and different salts, including ChCl, all at salt:HBD molar ratio of 1:1, were applied as extraction solvents to extract excessive glycerol found in the biodiesel produced from vegetable oils. This glycerol originated from the transesterification reaction. This reaction converts the vegetable oils into triglycerides, in the presence of potassium hydroxide (KOH) as catalyst. Glycerol is a side product of this reaction. This glycerol is to be removed from the biodiesel for quality enhancement purpose. The proposed procedure by Abbott and colleagues was to use the above mentioned DESs as liquid-liquid extraction solvents to extract the glycerol from the biodiesel. The DES-glycerol mixture was then separated by phase splitting. The results of that work showed the success of the proposed procedure with glycerol removal from biodiesel, as given in Table 2.2.

Table 2.2: Mole fraction of glycerol (X_{glycerol}) found in biodiesel after extraction with different DESs (Abbott et al., 2007c).

Salt of eutectic	X_{glycerol}
Not treated	0.15
Pr ₄ NBr	0.08
EtNH ₃ Cl	0.00
ClEtMe ₃ NCl	0.00
Choline chloride	0.05
Acetylcholine chloride	0.03

In 2010, another study on the same subject was published by Abbott and colleagues. Hayyan et al. (2010) presented a work that focused on the ChCl:glycerol DES but with a variation of the salt:HBD ratio, i.e. 1:1, 1:1.25, 1:1.5, 1:2, and 1:3. The biodiesel:DES molar ratio was also varied to study the effect of this variation (1:1, 1:1.5, and 1:2). The results showed that a salt:HBD ratio of 1:1 gave the best extraction yield. Moreover, biodiesel:DES ratio was found to be more important than the DES composition ratio in affecting the efficiency of extraction.

Shahbaz et al. (2010) reported the use of various DESs for the removal of residual potassium hydroxide (KOH) from palm oil-based biodiesel. ChCl and methyltriphenylphosphonium bromide were used to synthesize 18 DESs for the later study. The results revealed that the removal efficiency of KOH by all used DESs increased with the increase in DES:biodiesel molar ratio. The mole fraction of hydrogen bond donors (HBD) in mixture of salt:HBD was also to affect the separation efficiency in a direct proportional relationship. An average removal efficiency for KOH of 98.59% was achieved using these DESs.

Shahbaz et al. (2011) presented another trial of DESs in the glycerol removal from biodiesel issue. However, a different salt other than ChCl was used. DESs made from phosphonium salts are rarely studied. In this work, methyltriphenylphosphonium bromide as salt was studied to form DESs with three different HBDs, i.e glycerol, ethylene glycol, and triethylene glycol. The effect of DES type on the removal of free glycerol, bound glycerol, and total glycerol were examined. The results showed that the ethylene glycol and triethylene glycol DESs were successful in removing all free glycerol from the biodiesel. However, all tested DESs were able to reduce the content of monoglycerides (MGs) and diglycerides (DGs). Moreover, all the DESs showed tendency to reduce the DGs more effectively than removing MGs. A maximum removal efficiency of MGs and DGs was attained by triethylene-glycol-based DESs at a DES:biodiesel molar ratio of 3:1 and 0.75:1, with 37.9 and 53.4% removal, respectively.

As mentioned earlier in this subsection, DESs were introduced to LLE early in 2007. But their utilisation in the liquid-liquid extraction was limited to biodiesel purification operations, such as removal of glycerol and the remaining catalyst. In this work, the implementation of DESs into the liquid-liquid extraction of aromatic

hydrocarbons from naphtha (Kareem et al., 2012a) is introduced. A phosphonium salt is used in contrast to many other research groups in the world that focused on ammonium salts only. DESs formed by methyltriphenylphosphonium bromide (salt) and ethylene glycol (HBD) at different salt:HBD molar ratios of 1:4, 1:6 and 1:8 were synthesized and applied as extraction solvents. Ternary system of benzene + hexane + DES was studied to demonstrate this process. The DES:naphtha mass ratios were 1:1 and 1:2. It was found that the DES of molar ratio of 1:6 salt:HBD gave the best separation performance compared to sulfolane, the commercial solvent for this extraction, at DES:naphtha mass ratio of 1:1, which means that it is not necessary to use a big amount of solvent for this extraction. The research was extended to include another phosphonium salt, i.e. tetrabutylphosphonium bromide, combined with either ethylene glycol or sulfolane as HBDs (Kareem et al., 2012b). Various salt:HBD molar ratios were used to synthesize numerous DESs. These DESs were then applied in ternary systems of toluene + heptane + DES at a range of temperatures from 30 to 60 °C. High selectivities of the DESs towards toluene were achieved, yet not as high as sulfolane. However, the advantage was that the DESs did not suffer any loss to the raffinate layer. This eliminates the need for a further separation process for the product stream after the extractor.

i) DESs for ionic conductivity enhancement

The ChCl:urea DES was the subject of another related research. Series of polymer electrolytes composed of corn starch (CS), lithium bis(trifluoromethanesulfonyl)imide (LITFSI) and DES were fabricated by a solution casting technique. The addition of DES was beneficial in enhancing the room temperature ionic conductivity by increasing the amorphous elastomeric phase in CS:LITFSI matrix. There was an improvement in the ionic transport mechanism, and an appreciable amount of ion conducting polymer electrolytes was produced (Ramesh et. al., 2012).

j) DESs in carbon dioxide (CO₂) capture

Among the early studies on the use of ChCl:urea DES in the capture process of CO₂ gas emitted from various processes was that of Li et al. (2008). Three ChCl:urea DESs were synthesized at salt:HBD molar ratios of 1:1.5, 1:2 and 1:2.5. The pressure was varied at three temperatures (40, 50 and 60 °C) and the solubility was measured as a function of pressure. In general, it was shown that CO₂ has a good solubility in these DESs at low pressures. However, the solubility increased with escalating pressure. Further finding was that the different salt:HBD molar ratios did not give a significant difference in the solubility of CO₂ in the DES. Su et al. (2009) reported a work similar to the earlier work of Li et al. In their study, it was confirmed that CO₂ has a good solubility in the ChCl:urea DES. The work was conducted at 25, 30 and 35 °C. The solubility was found to behave in an inverse proportional manner with the concentration of water in the DES. Thus, a method for solvent recovery was proposed, which is by adding water to the CO₂-rich solvent, the CO₂ will be released.

2.4 The application of DESs in the extraction of aromatic hydrocarbons from hydrocarbons mixtures

The production of ethylene is usually carried out by the thermal cracking of long-chain hydrocarbons, and naphtha is the feedstock. It was shown in section 1.1 that many of ethylene cracker feeds contain aromatic compounds with concentration of 10 – 25 wt%. This range of concentrations depends on the source of the feed (naphtha or gas condensate). Due to their strong bonds, the aromatic compounds present in naphtha are not converted to olefins. Additionally, small amounts of these aromatic compounds are formed during the cracking process in the cracker furnaces (Zimmermann & Walzl, 2005). These aromatics occupy a large part of the capacity of the steam furnaces and put an extra load on the separation section of the C₅⁺ aliphatic compounds. In addition, the

presence of aromatics in the feed to the cracker has a negative influence on the thermal efficiency. Aromatic compounds present in the feed tend to foul the radiation sections, in particular coking of the coils, and the transfer line exchangers.

Several advantages could be gained if a major part of the aromatic compounds present in these feeds are separated upstream of the furnaces. The positive aspects will be higher capacity, higher thermal efficiency, less fouling, increasing economic efficiency, long life for the heat exchangers and lower environmental impact. The energy requirement of a thermal cracker is about 8.5 GJ/ton feed. The improved margin for the removal of 10% aromatic hydrocarbons from the feed to the naphtha cracker will be around \$ 35/ton of feed or \$ 80 M per year for a cracker with a feed capacity of 300 ton/h, due to the lower operational costs, as was indicated by Dutch State Mines (Meindersma, 2005). Although separation of aromatic and aliphatic hydrocarbons after the furnace section is an industrial practice, no suitable technology is currently available for the separation of aromatic compounds from the feed to cracker plants (Meindersma, 2005). The schematic diagram of a naphtha cracker was shown in Figure 2.1. At first, metal impurities in the feed are hydrogenated and removed by molecular sieves. The remaining feed stream is heated up to 60 °C and enters the furnace section where aliphatic hydrocarbons are converted by the high temperature, between 850 and 900 °C, into smaller molecules, preferably ethylene and propylene. After the furnace section, the product stream has to be cooled down in several steps.

In industry, the aromatics are separated after the ethylene cracking process. It is not industrially economical to remove the aromatics after the process due to the reasons mentioned earlier.

The conventional process for aromatics removal is liquid-liquid extraction with sulfolane or ethylene glycol as solvent. This process is suitable for the range of 20 –

65% aromatic content. For 65 – 90% aromatics, extractive distillation is preferred and for >90% aromatics, azeotropic distillation will be the choice (Weissermel and Arpe, 2003).

Thus, it is clear that there was no suitable separation process for the aromatics from naphtha at low concentrations. The only way to improve the economic feasibility of extraction technology at low aromatics content is by the development of new solvent systems that exhibit a dramatically higher aromatic distribution coefficient and/or a higher aromatic/aliphatic selectivity than sulfolane and ethylene glycol. Reviewing the literature, it was shown that aqueous cyclodextrin solutions and ILs could have the potential to compete with sulfolane and ethylene glycol.

Liquid-liquid extraction as a separation technique was widely used in industry for the aromatic hydrocarbon separation and purification. This was because of the mild operation conditions and due to the simplicity of this process (Zhang et al., 2007). Industrially-used extractants are mostly conventional polar organic solvents, such as sulfolane, ethylene glycol, tetraethylene glycol and N-methylpyrrolidone (Ali et al., 2003). These organic solvents are generally volatile, toxic and/or flammable.

The research on the development of liquid-liquid extraction solvents to extract aromatics hydrocarbons from mixtures of different hydrocarbons was a subject of study over a long period of time. It can be tracked back to the 1950's when Deal and colleagues presented a study on the application of sulfolane as extractant (Deal et al., 1959). The 1960's witnessed other advancements on this topic which were presented by Muller and Hochfeld (1967). This was an attempt to combine different solvents to achieve improved extraction yield. The period of 1970's and 1980's had its share of contribution to the knowledge of this topic as well (Rawat et al., 1976, Dang et al., 1977, Rawat and Gulati, 1981, Nagpal and Rawat, 1981, Awwad et al., 1988).

Tetraethylene glycol was utilized as liquid-liquid extraction solvent for aromatics separation from naphtha reformat by Al-Sahhaf and Kapetanovic (1996). A maximum selectivity of 10.64 at 45 °C was achieved out of the various experiments that were conducted. Tetraethylene glycol was also applied by Wang et al. (1998) as liquid-liquid extraction solvent in aromatics extraction. Five ternary and two multicomponent mixtures were studied. The work of Wang and coworkers focused on preparing data for applying UNIFAC model for liquid-liquid equilibrium (LLE) correlation. In addition, Yorulmaz and Karpuzcu (1985) compared between diethylene glycol and sulfolane as solvents for this process. It was shown that sulfolane is superior to diethylene glycol in terms of selectivity and yield.

Zhang et al. (2007) and other researchers realized the importance of developing new extractants with a high distribution coefficient of aromatic hydrocarbons, high selectivity towards aromatics and with a negligible solvent loss.

The use of room temperature ionic liquids (RTILs) in liquid-liquid extraction of aromatics from aliphatic hydrocarbons was investigated by numerous researchers (Alberto et al., 2007, Cláudia et al., 2007, Meindersma et al., 2004). Low activity coefficients at infinite dilution in several ionic liquids were reported for aromatic hydrocarbons, while aliphatic hydrocarbons showed high activity coefficients in the same ionic liquids (Meindersma, 2005, Huddleston et al., 1998, Selvan et al., 2000, Krummen et al., 2002, Letcher et al., 2003, David et al., 2003, Heintz et al., 2001, Kato and Gmehling, 2004, Shyu et al., 2001, Arlt et al., 2002). This fact indicated that ILs can be utilized as extractants for aromatic hydrocarbons from hydrocarbons mixtures.

Meindersma (2005) investigated the application of ILs in the extraction of aromatics from aliphatic hydrocarbons. The work identified three suitable ILs for a more detailed screening for the separation of aromatic and aliphatic hydrocarbons,

notably 1,3-dimethylimidazolium methylsulfate, 1-ethyl-3-methylimidazolium ethylsulfate and 4-methyl-N-butylpyridinium tetrafluoroborate ([mebupy]BF₄), because they all demonstrated a higher aromatic/aliphatic selectivity than sulfolane. In the present work, the main focus is on the ternary systems of benzene + hexane + IL and toluene + heptane + IL.

2.4.1 Ternary systems of benzene + hexane + ILs

To investigate a solvent for its separation capability of aromatics from naphtha, ternary systems are created which compromise aromatics + aliphatics + solvent. Here the solvent is IL. Researchers tend to use their own perception to make these systems. For systems of benzene + hexane + IL, Arce et al. (2007a) analyzed the separation of benzene from hexane using the ionic liquid 1-ethyl-3-methylimidazolium bis{(trifluoromethyl) sulfonyl}amide at 25 °C and 40 °C. The distribution coefficients attained were found to be not more than 1.38 with selectivity of 33.56 at low concentration of aromatics and 25 °C. The use of the ILs 1-ethyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide ([EMIM][NTf₂]), 1-ethyl-3-methyl-imidazolium iodide ([EMIM][I₃]) and 1-butyl-3-methyl-imidazolium iodide ([BMIM][I₃]) in ternary systems of benzene + hexane + ILs has been reported in Selvan et al. (2000) and Arce et al. (2007b), with satisfactory results. Nonetheless, for industrial use, the best reported IL will be [EMIM][NTf₂] because of its low viscosity and other favorable physico-chemical properties. Arce et al. (2007b) studied the effects of varying the structure of ILs by using different functional groups in the cation for this process of aromatics separation. Meindersma et al. (2006) compared the suitability of using sulfolane with 4-methyl-N-butylpyridinium tetrafluoroborate ([MBPy][BF₄]), 1-ethyl-3-methyl-imidazolium ethylsulfate ([EMIM][EtSO₄]), 1,3-dimethyl-imidazolium methylsulfate ([MMIM][CH₃SO₄]) and 1-butyl-3-methyl-imidazolium methylsulfate ([BMIM][CH₃SO₄]) as solvents in liquid–liquid extraction at 40 °C and 70 °C. The

results in showed that out of these four ILs, [MBPy][BF₄] possessed the best extraction yield. Additionally, the results showed that all studied ILs were superior to sulfolane. Domànska et al. (2007) reported the use of the ammonium-based IL ethyl(2-hydroxyethyl) dimethyl ammonium bis{(trifluoromethyl)sulfonyl}imide for the extraction of benzene, *p*-xylene, or *m*-xylene from hexane or octane at 25 °C. A feasible separation of aromatics using this IL was reported, and explained as it is due to its high selectivities and distribution ratios. Pereiro and Rodríguez (2010) applied the IL [BMpyr][NTf₂] for the extraction of benzene, toluene, or ethylbenzene from their mixtures with heptane at 25 °C. A selectivity of 19.54 is the highest obtained in that work for the ternary mixture benzene + heptane + [BMpyr][NTf₂]. Lastly, Arce et al. (2008) investigated the application of two immiscible ILs as a mixture to serve as a solvent for this process. The system of benzene + hexane + {[C₂mim][NTf₂] + [P₆₆₆₁₄][NTf₂]} at 25 °C was studied. The results indicated that no improvements in the separation of aromatics were achieved in comparison to {[C₂mim][NTf₂]} alone. However, the authors argued that a superior performance might exist using three (liquid) phases of proper combinations of solutes and ionic liquids. Table 2.3 shows a summary of some of published works related to the use of ILs in the separation of aromatics.

2.4.2 Ternary systems of toluene + heptane + ILs

The literature is rich with publications on the application of different ILs in the separation of toluene from toluene + heptane mixtures. Zhang et al. (2007) reported the use of various chloroaluminate-based ILs as solvents for extracting aromatics from different aromatics/aliphatics mixtures. For the toluene + heptane mixture, the test was carried out at 20 °C utilizing Et₃NHCl-2AlCl₃ as extractant. The distribution coefficient of toluene in the mentioned IL increased to 1.1 at low toluene concentration. This is a good distribution coefficient value and the solvent should be further studied for its process design aspects and economic feasibility. Table 2.4 summarizes some of these

ternary systems and their experimental results (Selvan et al., 2000, García et al., 2010a, García et al., 2010b, García et al., 2011, García et al., 2010c, Meindersma et al., 2006).

Table 2.3: Summary of previous researches on benzene/hexane mixtures. β is the distribution coefficient and S is the selectivity.

IL	Extraction System	Temp. (°C)	Best β	Best S	Ref.
[EMpy][ESO ₄] ¹	B + Hex + [EMpy][ESO ₄]	10, 20, 25, 30	1	37.96 @ 10 °C	Gonzales et al., 2009
[EMpy][ESO ₄] ¹	B + Hep + [EMpy][ESO ₄]	10, 25	0.87	103.17 @ 10 °C	
[3-Mebupy][DCA] ²	B + Hex + [3-Mebupy] [DCA]	30, 50	1.45	54.1 @ 30 °C	Hansmeier et al., 2010
[3-Mebupy][DCA] ²	Xy + Hex + [3-Mebupy] [DCA]	30, 55	0.53	22.6 @ 30 °C	
[hmim][BF ₄] ³	B + Hep or Dodec or Hexadec + [hmim][BF ₄]	25	0.76 0.66 0.57	17.59 for Hep 14.15 for Dodec 21.93 for Hexadec	Letcher and Reddy, 2005
[hmim][PF ₆] ⁴	B + Hep or Dodec or Hexadec + [hmim][PF ₆]	25	0.87 0.75 0.67	14.2 for Hep 18.78 for Dodec 39.94 for Hexadec	

1: 1-ethyl-3-methylpyridinium ethylsulphate, 2: 3-methyl-N-butylpyridinium dicyanamide, 3: 1-hexyl-3-methylimidazolium tetrafluoroborate, 4: 1-hexyl-3-methylimidazolium hexafluorophosphate, 5: 1-methyl-3-octylimidazolium hexafluorophosphate, 6: 1-ethyl-3-methylimidazolium ethylsulfate

The extracted aromatic hydrocarbon can be reclaimed by temperature elevation of the ionic liquid/aromatic mixture within only a few degrees (Arlt et al., 2002).

Matsumoto et al. (2005) reported another technique of aromatics separation using ILs. Supported liquid membrane based on the ILs [Et₂MeMeON][Tf₂N], [Hmim][PF₆], [Bmim][PF₆] and [Omim][PF₆] was used for this separation. The selectivity towards the aromatic compounds was greatly improved when the liquid membrane was supported by ILs.

Table 2.4: A summary of previous researches from the literature on toluene/heptane mixtures. β is the distribution coefficient and S is the selectivity.

IL	Temp. (°C)	Best S with its β		Ref.
		S	β	
1-Ethyl-3-methylimidazolium Triiodide	45	67.28	0.882	Selvan et al., 2000
1-Butyl-3-methylimidazolium Triiodide	35	109.7	6.036	
2-methyl-N-butylpyridinium tetrafluoroborate	40	60.0	0.524	Garcia et al., 2010b
3-methyl-N-butylpyridinium tetrafluoroborate	40	55.0	0.666	
4-methyl-N-butylpyridinium tetrafluoroborate	40	57.9	0.646	
N-ethylpyridinium bis(trifluoromethylsulfonyl)imide	40	45.3	1.10	Garcia et al., 2010a
2-methyl-N-ethylpyridinium bis(trifluoromethylsulfonyl)imide	40	45.8	1.19	
3-methyl-N-ethylpyridinium bis(trifluoromethylsulfonyl)imide	40	37.1	1.25	
4-methyl-N-ethylpyridinium bis(trifluoromethylsulfonyl)imide	40	38.3	1.29	
1-methyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	40	39.9	0.691	
1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide]	40	30.3	0.934	Garcia et al., 2011
1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	40	20.0	1.200	
1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	40	12.4	1.469	
N-butylpyridinium tetrafluoroborate	40	74.4	0.427	Garcia et al., 2010c
N-hexylpyridinium tetrafluoroborate	40	25.6	0.670	
4-methyl-N-butylpyridinium tetrafluoroborate	40	53.09	0.441	Meindersma et al., 2006
4-methyl-N-butylpyridinium tetrafluoroborate	75	39.32	0.476	
1-ethyl-3-methylimidazolium ethylsulfat	40	55.29	0.237	
1-ethyl-3-methylimidazolium ethylsulfate	75	35.55	0.206	
1,3-dimethylimidazolium methylsulfate	40	65.74	0.088	
1,3-dimethylimidazolium methylsulfate	75	56.28	0.081	

Recently, DESs have been recognized as alternatives to traditional solvents and ILs themselves (Hou et al., 2008). As was shown before, DESs have been applied in numerous chemical processings. All of these DESs are of ammonium salts, mainly choline chloride. However, to date, there has been no reported work on the application

of DESs in the liquid-liquid extraction of aromatic hydrocarbons from hydrocarbons mixtures, especially the DESs based on phosphonium salts.

The current work represents the first study on using phosphonium-based DES in the separation of aromatics. As the ILs have been investigated for their applicability in liquid-liquid extraction of aromatics, and produced superior results in comparison to sulfolane and ethylene glycol; it was found necessary to study the application of DESs in this process as well. Knowing that the DES is composed of salt and HBD, ethylene glycol ($C_2H_6O_2$) was chosen to be a HBD for the salt methyltriphenylphosphonium bromide ($C_{19}H_{18}P.Br$). Figure 2.6 shows the chemical structure of these two compounds.

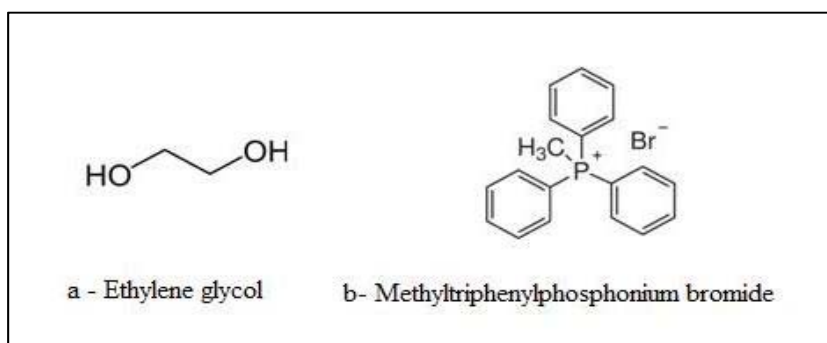


Figure 2.6: Chemical structure of ethylene glycol (a) and methyltriphenylphosphonium bromide (b).

The DESs of the present study were prepared in different salt:HBD mole ratios in order to study the effect of varying this ratio on the separation process.

CHAPTER III

RESEARCH METHODOLOGY

The procedures undertaken to achieve the objectives of this work are reported in this Chapter. Together with the resources and the required equipment, a complete description of the methodology that had led to the completion of this work is described here. Two main sections will be introduced in this chapter. Section 3.1 describes the methodology of synthesizing and characterizing some DESs, while section 3.2 describes the methodology of applying some DESs for liquid-liquid extraction of aromatic hydrocarbons.

3.1 Synthesis and characterization of DESs

3.1.1 Chemicals

Methyltriphenylphosphonium bromide, benzyltriphenylphosphonium chloride, glycerine, ethylene glycol, sulfolane and 2,2,2 trifluoroacetamide were supplied by Merck Chemicals (Germany). Tetrabutylphosphonium bromide and ethyltriphenylphosphonium iodide were supplied by Sigma–Aldrich (USA). All chemicals are synthesis-grade with high purity (> 99 %) and were used without any further purification.

3.1.2 Synthesis of DESs

It was reported by Abbott et al. (2004) that DESs can be synthesized by stirring two components of a DES, i.e. salt and hydrogen-bond donor, at a certain temperature until a homogeneous colorless liquid is formed. This method was utilized in this work to successfully synthesize different DESs, and followed by many researches that adopted

the same procedure. It is a very good method for synthesizing DESs, as it is easy to follow and less expensive in comparison to the synthesizing of ILs in which reactors and separation facilities are necessary.

The significant parameters that are to be considered in the synthesis of DES are mixing, mixing time, mixing speed and mixing temperature. Certain DESs require mechanical stirring; some of them can be formed by shaking the mixing vessels while others need only magnetic stirring to be produced. The extent and type of mixing depend on the type of the salt and the HBD used in the synthesis of DES. There is no specific rule that can be applied in this case and the proper mixing type and conditions are determined through experience. The same applies for the temperature of synthesis.

In general, a DES is said to be completely formed and is ready for use when the salt and HBD combine together to give a homogenous and colourless liquid.

The equipment used in the synthesis of DESs are summarized in Table 3.1.

Table 3.1: Equipment in the DESs synthesis.

Stirring Type	Equipment and apparatus	Make
Mechanical	Mechanical agitators, stirring speed controllers, jacketed vessels, oil/water bath.	Locally fabricated speed controller and mechanical agitators. Protech water bath.
Shaking	Incubating shaker, sealed vials.	Adolf Kühner AG, Schewir ASF-1-V incubating shaker
Magnetic	Hotplate magnetic stirrers, magnetic bars, sealed vessels.	IKA C-MAG HS7 S2 hotplate stirrer.

3.1.3 Characterization of DESs

Abbott et al. (2004) stated that a deep eutectic mixture results from the formation of complex anions which decrease the lattice energy and the freezing point of the system.

If a DES is made out of one salt and one HBD, the mole ratio of these two components

in the mixture, i.e. salt:HBD, is a key factor in determining the physical properties of the resulting DES. To explain this, the melting temperature as an important property is a clear example. For the DES methyltriphenylphosphonium bromide:ethylene glycol, if the salt:HBD mole ratio is 1:2, the melting temperature of this DES is not the same if the salt:HBD mole ratio is 1:3.

A DES can be characterized by measuring the important physical properties with the change in temperature. Numerous laboratory equipment were utilized to carry out the characterization study. Table 3.2 lists the equipment, the measurements obtained, and the uncertainties in the measurements.

Table 3.2: Devices used for characterization of DESs with their uncertainties.

Property	Device	Estimated Uncertainty
Density	Anton Paar DMA 4100 Density Meter (U-Tube)	$\pm 0.0001 \text{ g.cm}^{-3}$
Freezing temperature	Mettler Toledo Differential Scanning Calorimetry (DSC)	$\pm 0.19 \text{ }^{\circ}\text{C}$
Conductivity	Eutech Cyberscan Con 11 hand-held meter	$\pm 70 \text{ }\mu\text{S.cm}^{-1}$
pH	Eutech Cyberscan pH 300 hand-held meter	± 0.04
Refractive index	Mettler Toledo RE 40D Refractometer	± 0.0027
Viscosity (Relative)	Brookfield R/S plus Rheometer	(3 to 5) % of measured value
Dissolved oxygen	Eutech DO600 hand-held meter	$\pm 0.03 \text{ mg.L}^{-1}$

In the following sub-sections, the detailed procedures for measuring each physical property are described:

a) Density

Anton Paar U-tube density meter is a device utilizing sophisticated systems to weigh the mass of the injected liquid sample in the U-tube. The device can only be

used for samples which are liquid at room temperature as the procedure involves injection of the sample in the device using a syringe until the U-tube is full of the sample. Then, by using a pre-programmed method, a temperature at or above the room temperature can be set and the measurement of the density at that temperature is given by the device. The values of the density and the specific gravity at that specific temperature are then displayed on the screen of the device. The minimum and maximum operating temperatures are 25 °C and 65 °C, respectively.

b) Freezing temperature

The differential scanning calorimetry (DSC) device is a system that measures the heat flow emitted from a sample over a range of temperatures. A sample of less than 10 mg is placed inside a special pan made mainly from aluminium and a hole is made in the cover of that pan. The temperature of the sample is gradually raised. The hole allows the heat emitted to transfer outside the pan whereby special sensors will measure this heat and record it. If the sample is liquid at room temperature, then it must be cooled down till it freezes. The measurement starts from a point at which the sample is in the solid state. If the sample is solid at room temperature, then the heating program may start from the ambient temperature to a temperature at which the sample is in the liquid state. When the heating program starts, the sample starts to emit a certain amount of heat till it reaches the glass transition point whereby the solid state starts to change to liquid state with only few molecules of the sample. At this glass transition point, the amount of heat emitted will be reduced sharply to assist in converting the state of the sample, and thus the DSC records this reduction as a drop in the curve of the heat flow. When the entire sample has melted down, the heat emission will be uniform again. This sudden drop in the heat flow curve will be identified on the x-axis which represents the

temperature, and this temperature will be the melting or freezing temperature of the sample.

c) Conductivity

The measurement of the electrical conductivity of a liquid is accomplished by immersing a probe connected to a device that generates an electrical current and sends it to two metal ends in the probe. Eutech cyberscan con 11 hand-held meter is one brand of conductivity meter that applies this technique to measure the electrical conductivity of a liquid. The meter gives the conductivity in simens/unit length. The temperature range for the meter is 0 °C - 100 °C. In the present work, the measurement of the electrical conductivity for each DES was done in a temperature range of 5 °C to 95 °C. The change in temperature was achieved by placing a test tube inside a water bath and the sample of the DES was placed inside this test tube. The temperature was then varied by the control panel of the water bath and when the desired temperature was achieved, 5 minutes of time were allowed before the measurement is taken to ensure that the temperature of the DES sample was the same as of the water in the water bath.

d) pH and dissolved oxygen

Both pH and Dissolved Oxygen (DO) were measured by using hand-held meters that utilise probes with membranes. The temperature variation for measuring pH and DO was the same as that used for measuring the electrical conductivity.

e) Viscosity

Brookfield R/S Plus rheometer was used to measure viscosity. The temperature control was achieved by external water bath that was connected to jacket-like cell. The stainless steel testing tube was placed inside the jacket cell. A certain amount

of time was allowed after the desired temperature was reached in the water bath to ensure that the cell, test tube and the DES sample were all at same desired temperature. Only then, the rheometer was run and measurements of the dynamic viscosity taken.

f) Refractive index

The refractive index (n_D) was measured using Metler Toledo refractometer. This meter has a lens surrounded by a heating element to control the temperature of the sample being characterized. The temperature control is limited between 15 °C and 65 °C and the sample must be liquid to allow the characterization. The device sends a beam of light through the lens to the sample and measures the angle by which the reflected light is returning back to the device. This angle is then converted to a refractive index.

3.2 Application of DESs as solvents in the liquid-liquid extraction of aromatics

Coulson and Richardson (1978) showed that there are numerous physical processes for separating miscible compounds, such as distillation and liquid-liquid extraction.

Naphtha is a mixture of different hydrocarbons. Some of them have close boiling temperatures. Benzene and hexane have boiling points of 80.1 °C and 68 °C, respectively; and toluene and heptane boil at 110 °C and 98.4 °C, respectively. Hence, distillation is not a suitable separation method for separating the aromatics from naphtha. The most suitable operation for this separation was found to be a liquid-liquid extraction to extract the aromatic compounds. This is achieved by utilizing a selective solvent that has more tendency to dissolve aromatics than aliphatics when brought in direct contact with the naphtha. Universal Oil Products, a Honeywell company, has

established an extraction process utilizing sulfolane as a selective solvent for aromatic hydrocarbons separation from naphtha (Meindersma, 2005).

In the present work, laboratory-scale experiments were carried out to test the applicability of some DESs as solvents in liquid-liquid extraction to replace sulfolane. The liquid-liquid equilibrium (LLE) experiments are conducted in batch mode according to the following procedure:

a) Synthesis of DESs

This step was explained in subsection 3.1.2.

b) LLE tests

In order to study the LLE of a ternary system, three components must be identified as the two miscible compounds and the solvent of extraction. To represent aromatic hydrocarbons, benzene and toluene were selected and as aliphatic hydrocarbons, hexane and heptane were chosen. Thus, the ternary systems should either be benzene + hexane + DES or toluene + heptane + DES. For each system, different concentrations of the aromatics in the hydrocarbon mixture must be considered for LLE experiments. This is to generate numerous data sets which are necessary to plot the ternary diagram of any ternary system. This was carried out by choosing different mass concentration percentages of aromatics in the mixture. Usually, low concentrations of aromatics are recommended. It is because one of the main arguments regarding the use of sulfolane is that it is not able to remove traces of aromatics from naphtha. Thus, the removal of traces of aromatics is proposed by using DESs. By weighing proper amounts of aromatic and aliphatic hydrocarbons, concentrations of as low as 2% wt could be easily prepared. The mixtures were prepared using pure toluene, benzene, hexane and heptane. The prepared mixtures

were kept inside scintillation vials with tight caps to prevent the hydrocarbons from escaping to the atmosphere. DES was then added to the mixtures in a feed:DES mass ratio of 1:1 or 1:2. The vials were then secured by tightening their caps and shaken in an incubating shaker for 3 hours at constant temperature. The LLE experiments were conducted at different temperatures ranging from 27 °C to 60 °C. The vials were kept at the same temperature inside the incubator for another three hours to allow the two phases to separate completely. During these three hours, two immiscible layers were clearly formed. These layers are the solvent, also known as bottom, extract or DES phase, and hydrocarbons, which may be termed as top or raffinate phase. Samples from each layer were taken by syringes. The weight of each sample was around 0.1 g. The samples were placed in special vials for gas chromatography (GC) analysis and they were diluted by acetone.

The samples of the top and bottom layers were analyzed using HP 6890 GC equipped with Alltech Econo-Cap EC-Wax column of dimensions 30 m x 0.32 mm x 0.25 μm , and a Flame Ionization Detector (FID). The GC run was managed according to the operating conditions listed in Table 3.3. This is to prevent the overlapping of different peaks in the chromatogram. A method for this type of analysis was developed specially for toluene, benzene, heptane, hexane, ethylene glycol and sulfolane. The GC was calibrated using samples of toluene, benzene, hexane, heptane, ethylene glycol and sulfolane with known concentrations. Each of these samples must be analyzed at 4 or 5 different known concentrations in order to generate a calibration curve. An example of a calibration curve is given in Figure 3.1. The readings from the GC for the samples taken for the LLE experiments were converted to concentrations by the use of a calibration equation.

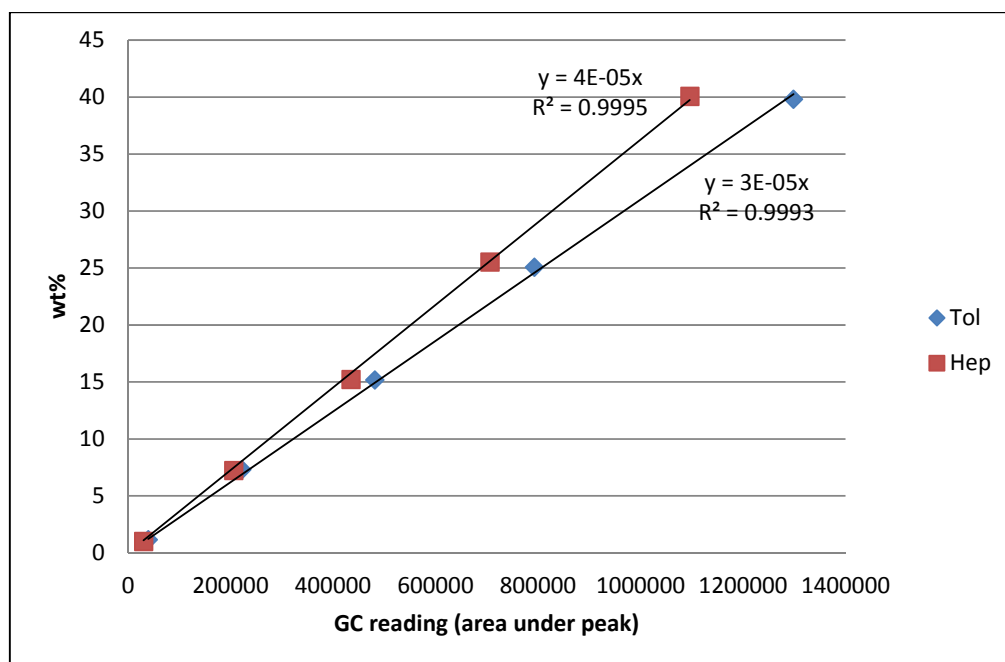


Figure 3.1: A sample of a calibration curve for heptane and toluene.

Table 3.3: Operating conditions for gas chromatograph.

Parameter	Set
Oven Temperature	50 °C (5 min) ramped to 200 °C at (15 °C/min)
Carrier Gas	Helium at (3 mL/min)
Injector Temperature	250 °C
Detector Temperature	250 °C

By doing these analyses and converting areas under the peaks, the laboratory work was considered to be completed. Further calculations were carried out to determine the distribution coefficient β , selectivity S and, in some cases efficiencies of separation η .

3.2.1 Calculation of distribution coefficients, selectivities and efficiencies of separation

The distribution coefficient of the aromatics β_{aro} and the selectivity S are the characterization parameters that measure the suitability of any solvent to perform liquid-liquid extraction efficiently. They can be calculated using the following equations (Hansmeier et al., 2010):

$$\beta_{\text{aro}} = \frac{x_{\text{aro}}^{\text{extract}}}{x_{\text{aro}}^{\text{raffinate}}} \quad (3.1)$$

$$\beta_{\text{ali}} = \frac{x_{\text{ali}}^{\text{extract}}}{x_{\text{ali}}^{\text{raffinate}}} \quad (3.2)$$

$$S = \beta_{\text{aro}} / \beta_{\text{ali}} \quad (3.3)$$

where x is mole or mass fraction of aromatic (aro) or aliphatic (ali) hydrocarbons.

The efficiency η can be expressed as the percentage of what ideally could be expected. In this present work, η is calculated from the difference in the amounts of toluene entering the process in the feed stream and the amount leaving it in the raffinate layer (Treybal, 1981):

$$\eta = \frac{Tol_{in} - Tol_{out}}{Tol_{in}} \times 100\% \quad (3.4)$$

3.2.2 Consistency of the LLE data

It is important in chemical engineering applications to predict and correlate the ternary LLE data, like those of liquid-liquid extraction. Neumerous methods were proposed in the literature for this purpose (Sørensen et al., 1979, Magnussen et al., 1980, Zamaro and Campanella, 2002). The Hand (1930) and Othmer – Tobias (1942) correlations are well-known empirical correlations for tie lines in liquid-liquid equilibrium (Treybal, 1951). Their usage for ascertaining the consistency of the experimental LLE data is common in researches on ternary systems (Brandant, 1985, Escudero and Cabezas, 1994, Kirbaslar et al., 2000, González et al., 2009).

Hand correlation was presented in 1930 as the first correlation of its kind. Equation 3.5 gives the mathematical expression of Hand's correlation.

$$\ln \left(\frac{w_{Tol}^I}{w_{Hep}^I} \right) = c + d \cdot \ln \left(\frac{w_{Tol}^{II}}{w_{DES}^{II}} \right) \quad (3.5)$$

Othmer – Tobias correlation was developed and presented in 1942, using ternary solubility data of liquid-liquid systems. It was shown that a straight line results from plotting a logarithmic function that correlates the solubilities of the solute and the solvent in two different liquid phases. Equation 3.6 gives this correlation:

$$\ln \left(\frac{1-w_{Hep}^I}{w_{Hep}^I} \right) = a + b \cdot \ln \left(\frac{1-w_{DES}^{II}}{w_{DES}^{II}} \right) \quad (3.6)$$

where w_{Tol}^{II} and w_{DES}^{II} are the mass fractions of toluene and the DES in the lower layer (DES-rich phase), w_{Tol}^I and w_{Hep}^I are the mass fraction of toluene and n-heptane in the upper layer (hydrocarbon-rich phase), a and b are the fitting parameters of the Othmer–Tobias correlation and c and d are those of the Hand correlation.

These correlations were used to ascertain the reliability of the liquid - liquid extraction experimental data for some DESs at different temperatures.

3.2.3 LLE data correlation

An isothermal liquid-liquid flash calculation at given temperature and pressure was done to calculate the theoretical compositions after the liquid-liquid extraction. This flash consists from the following system of equations (Felder and Rousseau, 2004):

Mass balance:

$$x_i - (1 - \omega)x_i^I - \omega x_i^{II} = 0 \quad i = 1, N_C \quad (3.7)$$

Equilibrium equation:

$$x_i^I \gamma_i^I - x_i^{II} \gamma_i^{II} = 0 \quad i = 1, N_C \quad (3.8)$$

Equation of summation:

$$\sum x_i^I - \sum x_i^{II} = 0 \quad (3.9)$$

where:

ω is the liquid-liquid splitting ratio,

x_i is the composition of component i in the mixture,

x_i^I is the composition of component i in the liquid phase I,

x_i^{II} is the composition of component i in the liquid phase II,

γ_i^I is the activity coefficient of component i in the liquid phase I,

γ_i^{II} is the activity coefficient of component i in the liquid phase II, and

N_C is the number of constituents.

Numerous equations were developed to correlate the activity coefficients. Despite the availability of big number of equations, those which are in common use are based on the concept of local composition introduced by Wilson (1964). From these equations are the universal quasi-chemical (UNIQUAC) equation of Abrams and Prausnitz (1975), the universal functional activity coefficient (UNIFAC) method in which activity coefficients are calculated from group contributions (Fredenslund et al., 1975) and the non-random two liquid (NRTL) equation of Renon and Prausnitz (1968). However, NRTL thermodynamic equation was found to be more useful for correlating the experimental data of LLE than UNIQUAC and UNIFAC. LLE data are correlated by minimizing an objective function based on the squared differences between calculated and experimental compositions. Follows this, binary parameters would be used to calculate the compositions for the ternary data, resulting in a good representation of the data. NRTL was also used for systems containing ILs (Aznar, 2007, Pereiro et al., 2007).

In the NRTL calculations, the DESs were considered as pseudo-pure components. The model development was achieved using Simulis® thermodynamics environment,

which is a thermo-physical properties calculation server provided by ProSim (www.prosim.com, 2013) and available as an MS-Excel add-in.

The interaction parameters τ_{ij} , τ_{ji} and α_{ij} were estimated from “6M” experimental data points, where M represents the number of tie lines. This is achieved by minimizing the quadratic criterion between calculated and experimental solubilities of each constituent in each phase, as follows:

$$\text{Criterion} = \frac{1}{6M} \sum_i \sum_j \sum_k \left(s_{ijk}^{\text{exp}} - s_{ijk}^{\text{cal}} \right)^2 \quad (3.10)$$

where s is the solubility expressed in mole fraction and the subscripts i , j , and k designate the component, phase, and the tie lines, respectively (Pereiro and Rodriguez, 2009). The value of the third non-randomness parameter α_{ij} in the NRTL model was optimized between 0 and 0.5.

CHAPTER IV

RESULTS AND DISCUSSIONS

Twenty one DESs were synthesized and utilized for different parts of this research. To simplify the text, each DES was given an abbreviation. These DESs are summarized in Table 4.1.

Table 4.1: DESs studied in different parts in this work.

Salt	Hydrogen-Bond Donor	Mole Ratio (Salt:HBD)	Abbreviation
methyltriphenylphosphonium bromide	glycerine	1:1.75	DES 1
methyltriphenylphosphonium bromide	ethylene glycol	1:4	DES 2
methyltriphenylphosphonium bromide	2,2,2 trifluoroacetamide	1:8	DES 3
benzyltriphenylphosphonium chloride	glycerine	1:5	DES 4
benzyltriphenylphosphonium chloride	ethylene glycol	1:3	DES 5
benzyltriphenylphosphonium chloride	2,2,2 trifluoroacetamide	3:1	DES 6
methyltriphenylphosphonium bromide	ethylene glycol	1:6	DES 7
methyltriphenylphosphonium bromide	ethylene glycol	1:8	DES 8
tetrabutylphosphonium bromide	ethylene glycol	1:2	DES 9
tetrabutylphosphonium bromide	ethylene glycol	1:4	DES 10
tetrabutylphosphonium bromide	ethylene glycol	1:6	DES 11
tetrabutylphosphonium bromide	ethylene glycol	1:8	DES 12
tetrabutylphosphonium bromide	sulfolane	1:2	DES 13
tetrabutylphosphonium bromide	sulfolane	1:6	DES 14
tetrabutylphosphonium bromide	sulfolane	1:8	DES 15
ethyltriphenylphosphonium iodide	ethylene glycol	1:6	DES 16
ethyltriphenylphosphonium iodide	ethylene glycol	1:8	DES 17
ethyltriphenylphosphonium iodide	ethylene glycol	1:10	DES 18
ethyltriphenylphosphonium iodide	sulfolane	1:4	DES 19
ethyltriphenylphosphonium iodide	sulfolane	1:6	DES 20
ethyltriphenylphosphonium iodide	sulfolane	1:8	DES 21

Some of the synthesized DESs were studied for their physical properties initially. Starting from the results of this study, the DES synthesized from methyltriphenylphosphonium bromide as salt and ethylene glycol as HBD was selected to be used in liquid-liquid extraction experiments. This is due to the fact that this DES showed low viscosities and a low melting temperature. This salt was later changed with other two phosphonium salts, while using ethylene glycol as well as sulfolane as HBDs. Table 4.2 below shows the type of experiments for the various DESs synthesized here.

Table 4.2: The utilization of different DESs in this work.

DESs	Experiment type
1 - 6, 9, 18	Physical properties estimation
2,7 - 21	Liquid-liquid extraction

The results of this study are organized into two main sections. Section 4.1 comprises the results of the synthesis and characterization of some of the DESs summarized in Table 4.1. Following this, Section 4.2 presents the results of applying DESs as solvents for extracting aromatic hydrocarbons from aromatics/aliphatics mixtures. This is accomplished in ternary systems of aromatic + aliphatic + DES. Section 4.2 also reports the application of the non-random two liquid (NRTL) activity coefficients model for some of the ternary systems studied.

4.1 Synthesis and characterization of different DESs

Table 4.1 summarized the twenty one DESs prepared throughout this work. Some of these DESs are utilized in a study for their physical properties. It is possible to synthesize different DESs from the same salt and HBD combination by varying the salt:HBD molar ratio. This was explained in Subsection 3.1.3. It will be shown later in Section 4.2 that this change in the molar ratio has an effect on the separation capability of DES. Thus, it is impossible to synthesize and characterize all the possible DESs that can be prepared

out of a specific salt and HBD. This limitation suggested two alternatives to be adopted. Firstly, only the DES at the eutectic point, i.e. has the lowest melting temperature in its series, to be characterized. This is done for five DESs whereby a comprehensive study for their physical properties is completed. The identification of the deep eutectic point will be described in the following subsection. Secondly, the DESs that show good separation selectivity of aromatics from aromatics/aliphatics mixtures should be characterized. This adoption is carried out for other DESs which showed the best separation results for aromatics among a group of other DESs.

4.1.1 Identification of deep eutectic point

DESs 1 – 6 listed in Table 4.1 are chosen from different salt:HBD mole ratios of the same salt and HBD. This is because these DESs are at the eutectic point. This point for different combinations of salt and HBD is identified by plotting the profile of the melting temperature at different salt:HBD mole ratios versus the mole ratio itself. The minimum value for the curve of the melting temperature represents the mole ratio that lies at the eutectic point. DESs 1 – 6 are all representing the eutectic point for their individual series of DESs. Figure 4.1 shows a schematic plot for the melting temperatures of six DESs series. The minimum values are clear on the curves. One curve only, i.e. the curve of benzyltriphenylphosphonium chloride + 2,2,2 trifluoroacetamide, is not showing a minimum point. In this case, increasing the mole ratio of the salt or the HBD is not producing DES as expected, i.e. colorless and homogeneous liquid.

4.1.2 Measurement of melting temperatures

Some of the DESs shown in Table 4.1 are synthesized from methyltriphenylphosphonium bromide and benzyltriphenylphosphonium chloride as salts and glycerin, ethylene glycol and 2,2,2 trifluoroacetamide as HBDs. They are synthesized for several salt:HBD mole ratios. The profiles of the melting temperatures for the

resulting DESs are shown in Figure 4.1. DESs 1 – 6 in Table 4.1 are found to possess the mole ratio that lies at the eutectic point. The salt:HBD mole ratio represents the ratio in moles of the salt to that of the HBD in a particular DES combination. The melting temperatures of DESs 1 – 6 are shown in Table 4.3. It is concluded from Figure 4.1 that the melting temperature of the synthesized DESs is a function of the salt:HBD mole ratio. For example, for methyltriphenylphosphonium bromide + 2,2,2 trifluoroacetamide combination, the melting temperature of the mixture changes from as high as 91 °C when the mole ratio is 1:2 to – 69 °C when it is 1:8. Knowing that the melting temperature of methyltriphenylphosphonium bromide is 231 °C and for 2,2,2 trifluoroacetamide is 73 °C can make it easier to understand how a DES has a melting point lower than the melting points of its consisting compounds, i.e the salt and the HBD.

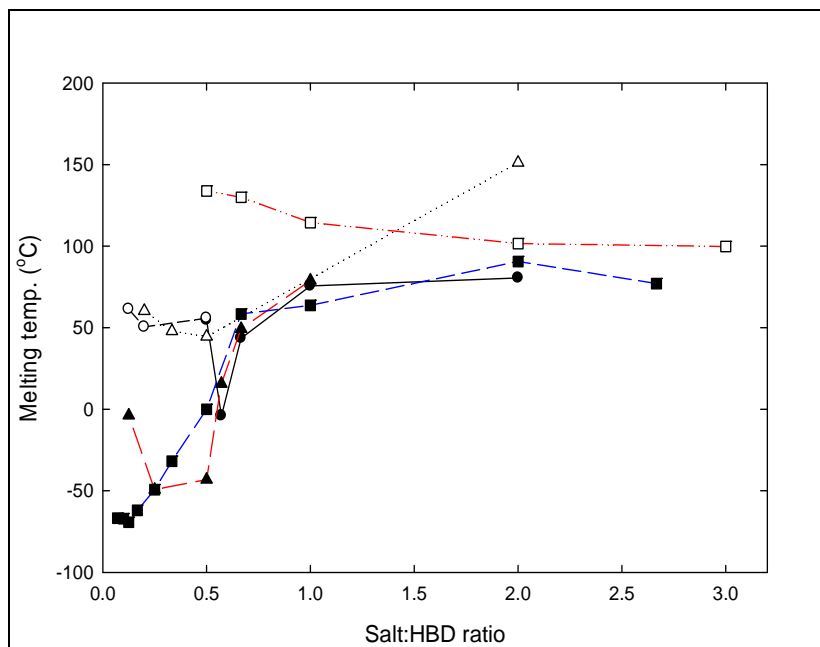


Figure 4.1: Profiles of melting temperatures of six DESs series. ●, is Methyl salt:Glycerine; ▲, is Methyl salt:Ethylene Glycol; ■, is Methyl salt:2,2,2 Trifluoroacetamide; ○, is Benzyl salt:Glycerine; △, is Benzyl salt: Ethylene Glycol; and □ is Benzyl salt: 2,2,2 Trifluoroacetamide.

Table 4.3: Melting temperatures for DESs 1 – 6.

DES	t (°C)
1	- 4.03
2	- 49.34
3	- 69.29
4	50.36
5	47.91
6	99.72

DES 2 which is a combination of methyltriphenylphosphonium bromide and ethylene glycol has an eutectic point occurring at a mole ratio of 1:4. At this ratio, the melting temperature is - 49.34 °C. When glycerine is used as HBD with the same salt, i.e. DES 1, the eutectic temperature is at a mole ratio of 1:1.75 and the melting temperature is - 4.03 °C. In comparison between DESs 1 and 2, it is found that the salt methyltriphenylphosphonium bromide needs less amount of glycerine than ethylene glycol to produce DES at the eutectic point. This decrease can be attributed to the larger number of hydroxyl groups in glycerine in comparison to that in ethylene glycol.

Some DESs are not characterized for their melting temperatures. This is because when they are applied in the liquid-liquid extraction experiments for aromatics removal, their selectivities towards the aromatic hydrocarbons are low in comparison to some other DESs. Thus, the DESs made from the same salt but different HBDs are subjected to selection criteria which is the selectivity towards aromatics. For the DESs synthesized from the salt tetrabutylphosphonium bromide and ethyltriphenylphosphonium iodide, only DES 9 and DES 19 are characterized for their melting temperatures. Table 4.4 shows the melting temperatures for these two DESs.

Table 4.4: Melting temperatures for DESs 9 and 19.

DES	T (°C)
9	-32.02
19	-30.68

4.1.3 Measurement of viscosities, densities, pH, electrical conductivities, refractive indices and dissolved oxygen contents

For convenience, the physical properties viscosity (μ), density (ρ), electrical conductivity (κ), refractive index (n_D) and dissolved oxygen content (DO) are represented by symbols in this section.

Due to the variation in the melting temperatures of DESs 1 – 5 which were characterized here, some of their physical properties were measured at different ranges of temperatures. This is because the measurements were limited to liquid-phase materials only. κ , μ , DO and pH of DESs 1, 2 and 3 were measured in a temperature range from 5 °C to 95 °C. n_D for these DESs was measured within the range of temperatures 15 °C to 65 °C, and ρ was measured within the range 25 °C to 85 °C, due to equipment limitations. On the other hand, the physical properties of DESs 4 and 5 that have relatively high melting temperatures were measured at temperatures at least 5 °C higher than their melting temperatures. As the operating temperatures of the density meter were limited between 25 °C and 85 °C, the densities of DESs 4 and 5 were not measured due to their high melting temperatures. The physical properties of DES 6 were not measured as it froze in a temperature higher than the limits of the measuring equipment. μ and n_D of DESs 9 and 18 were measured at temperatures 25 °C and 65 °C. This range of temperature is suitable in the extraction of aromatics from naphtha.

For DES 2, the eutectic temperature was at a mole ratio of 1:4, with a melting temperature of -50 °C. This DES was characterized by having a low μ of about 5.4 mPa·s at 65 °C. When glycerine was used as HBD with the same salt, i.e. DES 3, the eutectic temperature occurred at a mole ratio of 1:1.75 with a melting temperature of -4 °C. The decrease in the amount of the HBD needed for making the DES can be attributed to the larger number of hydroxyl groups in glycerine in comparison to that in ethylene glycol,

as was mentioned in subsection 4.1.2. However, μ of DES 3 was about 16.6 mPa·s at 65 °C, which was higher than that for DES 3 at the same temperature.

The measured μ of DESs 1 – 5, 9 and 18 are fitted using Arrhenius-like formula (Eq. 4.1) (Choi and Yoo, 2009, Thodesen et al., 2009, Saeed et al., 2009), and plotted in Figure 4.2.

$$\mu = \mu_o e^{\left(\frac{E_\mu}{RT}\right)} \quad (4.1)$$

where μ is the viscosity, μ_o is a constant, E_μ is the activation energy, R is the ideal gas constant and T is the temperature in Kelvin. Values of μ_o and E_μ are shown in Table 4.5 along with the sum of squared errors.

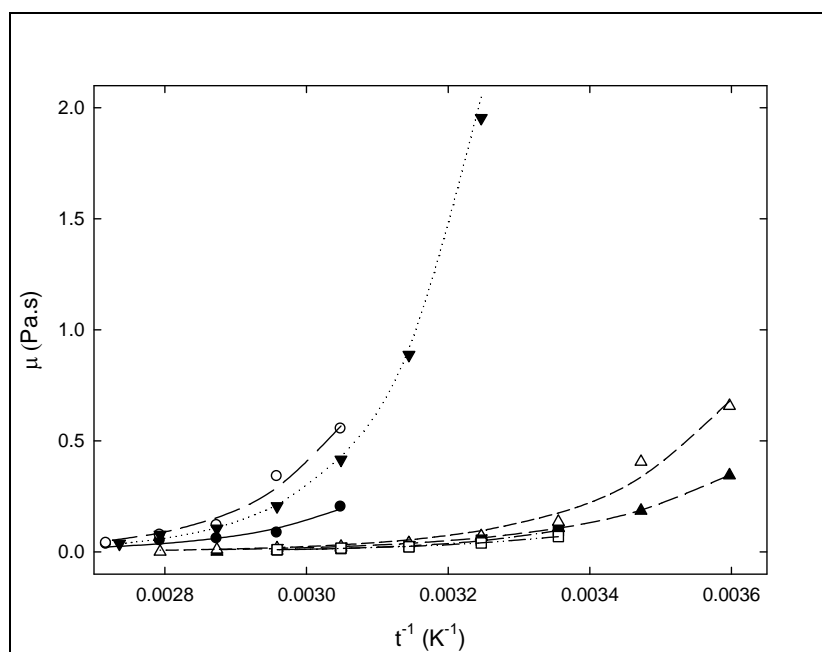


Figure 4.2: Dynamic viscosity μ of DESs 1, 2, 3, 4, 5, 9 and 18 as a function of inverse temperature, with Arrhenius fit curves. \blacktriangledown , \blacktriangle , Δ , \circ , \bullet , \square and \blacksquare refer to DESs 1, 2, 3, 4, 5, 9 and 18, respectively. Curves Eq. 4.1.

Values of κ of DESs 1 – 5 were measured at a temperature range of 5 – 95 °C. The behaviour of κ for the DESs based on methyltriphenylphosphonium bromide was different than that for those of DESs based on benzyltriphenylphosphonium chloride.

While DESs 1, 2 and 3 shows increasing κ with increasing temperature, κ of DESs 4 and 5 decrease with the increase of temperature, as shown in Figure 4.3. In addition, the conductivity of DESs 4 and 5 did not change considerably in the temperature range 70 °C to 95 °C. Similar to μ , Arrhenius type equation is used to fit κ values as shown below:

$$K = K_0 e^{\left(\frac{E_K}{RT}\right)} \quad (4.2)$$

where κ is the conductivity in $\text{mS}\cdot\text{cm}^{-1}$, κ_0 is a constant, E_K is the activation energy of conductivity and R is the gas constant. Values of κ_0 , E_K , and sum of squared errors are shown in Table 4.5.

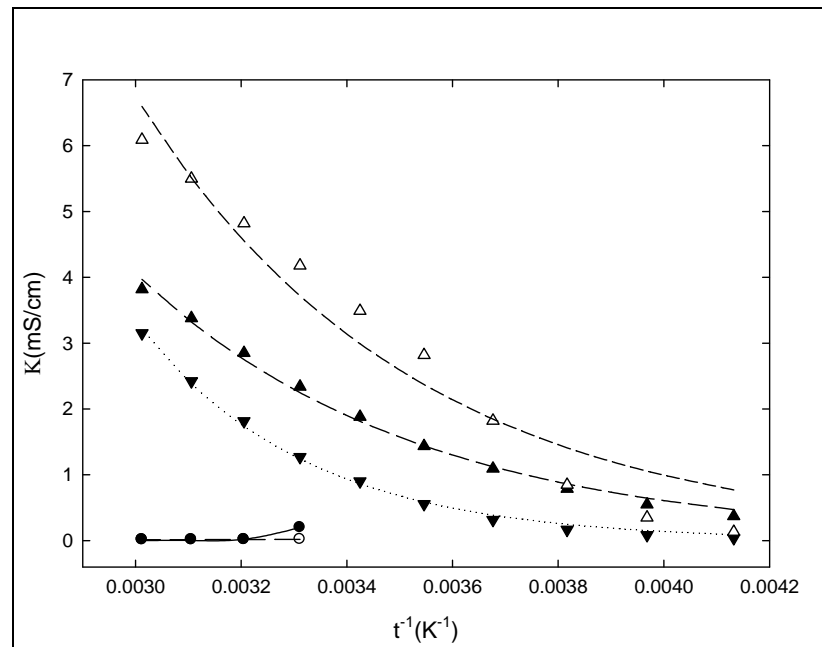


Figure 4.3: Conductivity κ of DESs 1, 2, 3, 4 and 5 as a function of inverse temperature, with Arrhenius fit. \blacktriangledown , \blacktriangle , \triangle , \circ and \bullet refer to DESs 1, 2, 3, 4 and 5, respectively. Curves, Eq. 4.2.

Table 4.5: Regression parameters for viscosity and conductivity. SSE is the sum of squared errors.

DES	μ_o (mPa.s)	E_μ (Pa.L.mol ⁻¹)	SSE
1	1.526x10 ⁻¹¹	6.562x10 ⁷	1.994x10 ⁻²
2	8.185x10 ⁻⁹	4.000x10 ⁷	2.387x10 ⁻⁴
3	1.149x10 ⁻⁴	4.668x10 ⁷	7.589x10 ⁻³
4	7.786x10 ⁻¹¹	6.193x10 ⁷	4.051x10 ⁻³
5	4.158x10 ⁻¹⁰	5.443x10 ⁷	9.374x10 ⁻⁴
9	5.418x10 ⁻⁹	4.053x10 ⁷	5.000x10 ⁻⁶
19	1.742x10 ⁻¹⁰	4.986x10 ⁷	1.406x10 ⁻⁵

DES	κ_o (mS.cm ⁻¹)	E_κ (Pa.L.mol ⁻¹)	SSE
1	47842.94	26.52	3.44x10 ⁻²
2	1214.79	15.80	7.42x10 ⁻²
3	2123.98	15.94	2.21
4	6.87x10 ⁻⁴	-8.29	6.34x10 ⁻⁹
5	9.99x10 ⁻³³	-180.96	2.54x10 ⁻²

The relatively high κ for DESs 1, 2 and 3 suggests that they are suitable for electrochemical applications, such as electrodeposition and electrofinishing.

Both the pH and DO for DESs 1 – 5 are measured as a function of temperature and are plotted in Figures 4.4 and 4.5, respectively. pH of DES 1 is around 7 and do not change much with the change in temperature. On the other hand, pH of DES 2 is very low, i.e. the DES is acidic, and it increases with increasing temperature. It is clear that the type of HBD has a strong effect on determining the acidity of the DES. pH values for DESs 1, 2, 3, 4 and 5 are fitted with linear equation (Eq. 4.3).

$$\text{pH} = a \cdot t (\text{°C}) + b \quad (4.3)$$

where t is the temperature and a and b are constants whose values are dependent on the type of DES. The values of a and b for the tested DESs are shown in Table 4.6. Figure 4.4 shows the pH profiles and their fittings.

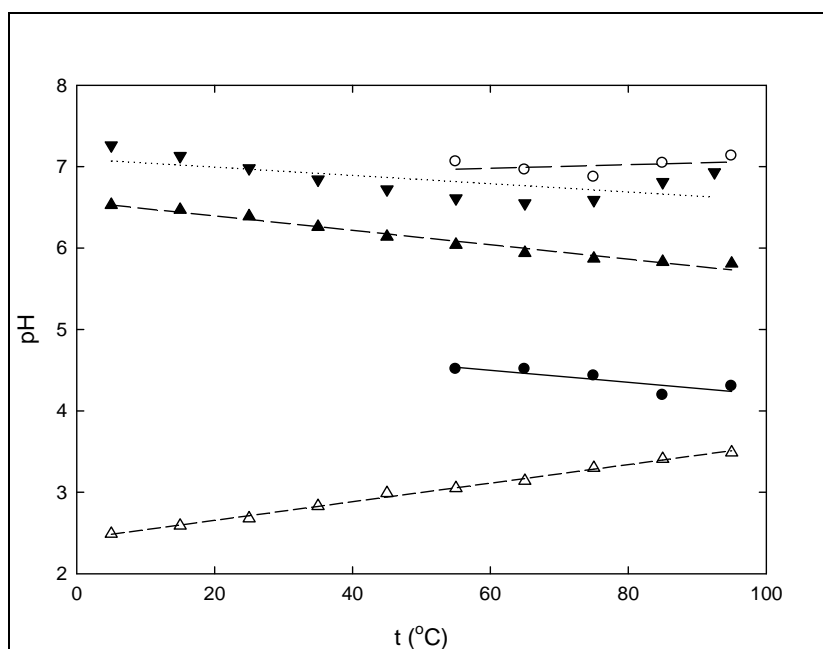


Figure 4.4: pH of DESs 1, 2, 3, 4 and 5 as a function of temperature t with linear fit. \blacktriangledown , \blacktriangle , Δ , \circ and \bullet refer to DESs 1, 2, 3, 4 and 5 respectively. Lines, Eq. 4.3.

Table 4.6: Regression parameters for Eq. (4.3).

DES	$a \times 10^4$	b
1	-49	7.088
2	-89	6.571
3	114	2.427
4	22	6.847
5	-22	5.763

Solubility of oxygen (DO) in DESs is an important parameter for applications involving oxidative reactions. In this case, the DES can be used as a solvent and sometimes as a reactant. DO profiles versus temperature for DESs 1 – 5 are plotted in Figure 4.5.

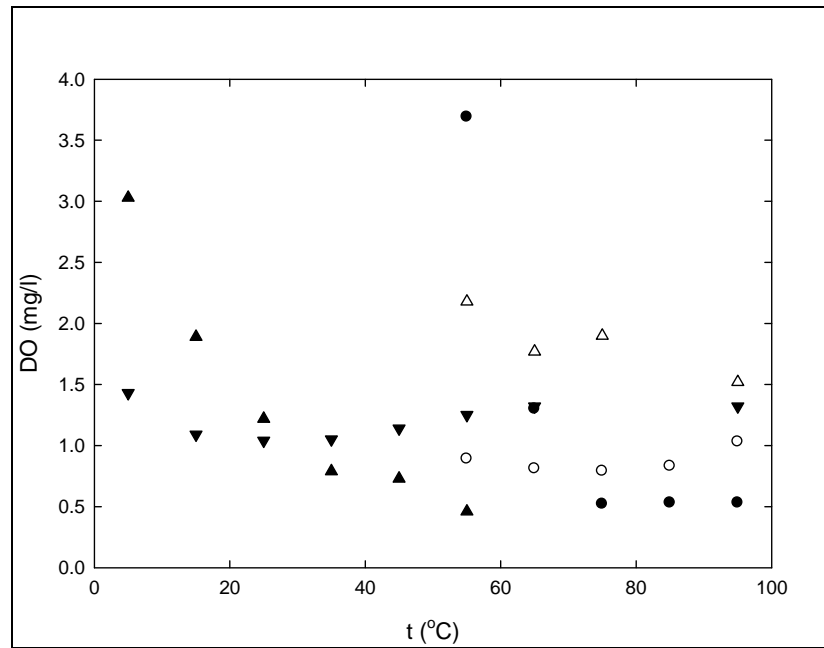


Figure 4.5: Dissolved oxygen DO in DESs 1, 2, 3, 4 and 5 as a function of temperature t. ▼, ▲, △, ○ and ● refer to DES 1, 2, 3, 4 and 5, respectively.

It is noticed that the DO values for DESs 1, 2, 3, 4 and 5 are smaller than those reported for common ILs (AlNashef et al., 2001). DO in DESs based on benzyltriphenylphosphonium chloride, i.e. DESs 4 and 5, show a very small variation with temperature. On the other hand, DO in DESs based on methyltriphenylphosphonium bromide, i.e. DESs 1, 2 and 3 is very sensitive to the temperature variations, i.e. 0.3 to 3 mg.L⁻¹ and 1 to 2 mg.L⁻¹ for DESs 1 and 2, respectively. Thus, the sensitivity of DO to temperature variation must be taken into consideration when dealing with applications involving dissolved oxygen at different temperatures. Measurements for ρ were conducted only for DESs 1, 2 and 3 due to equipment limitations. As expected, the change of ρ with temperature is a linear change. The ρ for these three DESs are fitted by a linear relationship as follows:

$$\rho \text{ (g/cm}^3\text{)} = a \cdot t \text{ (}^\circ\text{C)} + b \quad (4.4)$$

where ρ is the density, t is the temperature and a and b are constants that are dependent upon the type of DES. The values of a and b are shown in Table 4.7, and Figure 4.6 shows ρ profiles as function of temperature.

Table 4.7: Regression parameters for equation (4.4).

DES	$a \times 10^4$	b
1	-7	1.307
2	-7	1.250
3	-11	1.423

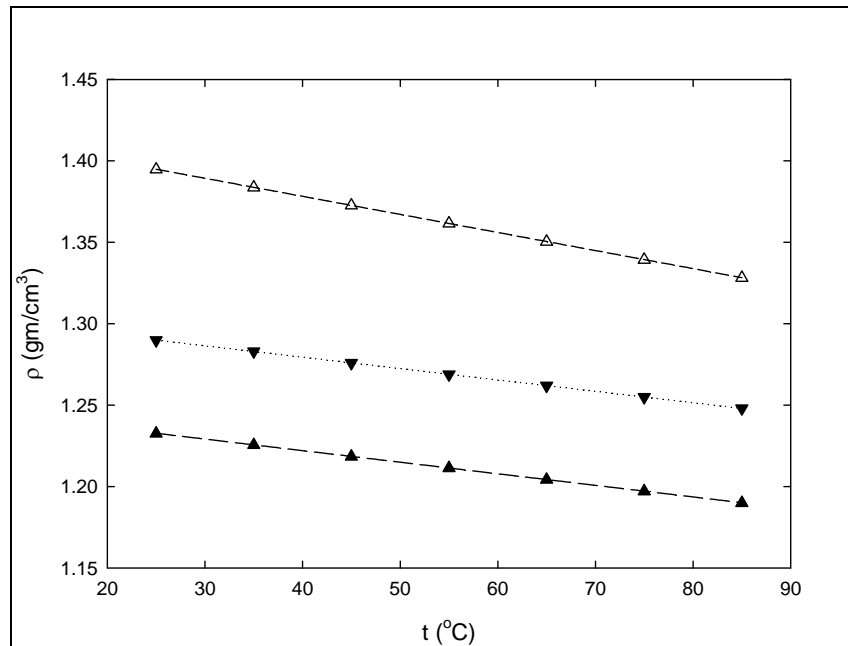


Figure 4.6: Density ρ of DESs 1, 2 and 3 as a function of temperature t . ▼, ▲, △ refer to DESs 1, 2 and 3, respectively. Lines, Eq. 4.4.

Lastly, n_D for DESs 1 – 5, 9 and 18 was measured within a range of temperatures. n_D is an important property for any application involving optical properties of the medium. It is used to calculate the focusing power of lenses, and the dispersive power of prisms. Since n_D is a fundamental physical property of a substance, it is often used to identify a particular substance, confirm its purity, or measure its concentration. Mostly, it is used to measure the concentration of a solute in an aqueous solution.

Typically, the values of the refractive indices are expected to decrease with increasing the temperature. This is because that the temperature change affects the density of the substances, which subsequently, affects their n_D . All the characterized DESs show the expected behavior, except DES 5 which shows an increase in its n_D value at 65 °C in comparison to that at 55 °C, as can be seen in Figure 4.7.

In general, the refractive index is proportional to the square root of electrical permittivity and magnetic permeability. These factors may change with temperature but not linearly, and therefore the refractive index does not always have a simple relationship with temperature. However, in these DESs, it is found that the relationship is almost linear and is fitted linearly, as shown in Eq. 4.5.

$$n_D = a \cdot t \text{ (}^\circ\text{C)} + b \quad (4.5)$$

where n_D is the refractive index, t is temperature in °C and a and b are constants that vary according to the type of DES. As n_D is a dimensionless property, a and b are dimensionless parameters as well. Table 4.8 shows the regression parameters for DESs 1, 2, 3, 9 and 19 for n_D fit. Figure 4.7 shows n_D profiles and their fitting by linear regressions.

Table 4.8: Regression parameters for equation (4.5).

DES	$a \times 10^4$	b
1	-2.446	1.574
2	-3.526	1.495
3	-3.456	1.567
9	-3.481	1.496
19	-3.632	1.525

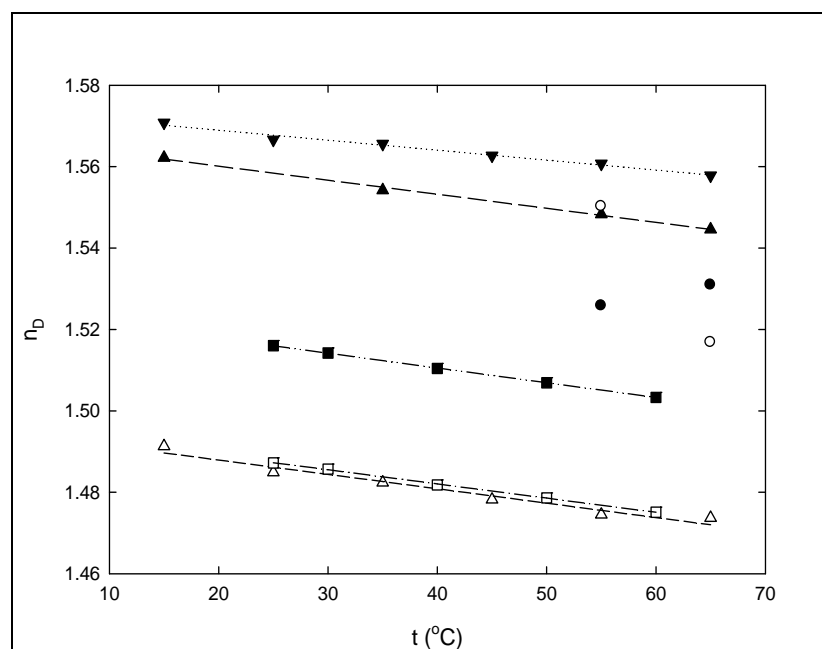


Figure 4.7: Refractive index n_D for DESs 1, 2, 3, 4, 5, 9 and 18 as a function of temperature t . \blacktriangledown , \blacktriangle , \triangle , \circ , \bullet , \square and \blacksquare refer to DESs 1, 2, 3, 4, 5, 9 and 18 respectively. Lines, eq. 4.5.

4.2 Application of DESs in the liquid-liquid extraction of aromatic hydrocarbons

Liquid-liquid extraction was conducted for mixtures of benzene and hexane or toluene and heptane. The aim was to extract the aromatic compound, i.e. benzene or toluene, from the mixtures. Because both ethylene glycol and sulfolane are commercial solvents used for the liquid-liquid extraction of aromatics from naphtha, they are both utilized as HBDs to synthesize various DESs. The salts of these DESs were chosen from phosphonium salts only. These DESs were the proposed solvents for the liquid-liquid extraction process. Referring to Table 4.1, DESs 2 and 7 – 21 are used in the liquid-liquid extraction studies. The objective of these studies was to investigate the enhancements to the already existing processes of aromatics extraction. The work is divided into 3 Subsections according to the phosphonium salt used in these DESs. They are:

- Subsection 4.2.1 Application of methyltriphenylphosphonium bromide-based DESs
- Subsection 4.2.2 Application of tetrabutylphosphonium bromide-based DESs
- Subsection 4.2.3 Application of ethyltriphenylphosphonium iodide-based DESs.

In order to establish the tie-line diagrams and to validate the liquid-liquid extraction data, there must be three data points for each set of experiments. This means that the DESs must be tested at the same temperature for at least 3 different concentrations of aromatics in the hydrocarbons mixtures. The literature survey presented in Chapter Two indicated that there is no suitable extraction process for low aromatic concentrations in naphtha. For this reason, different concentrations of aromatics in aromatics/aliphatics mixtures were considered. To be specific, aromatics concentrations were taken from as low as 2 wt % up to 90 wt %. The experiments in the present work were accomplished within the temperature range of 27 °C to 60 °C. The important parameters that characterize a suitable solvent for the liquid-liquid extraction are the distribution coefficient of aromatics and the selectivity of the solvent towards aromatics.

4.2.1 Application of methyltriphenylphosphonium bromide-based DESs

Three DESs made from the salt methyltriphenylphosphonium bromide with ethylene glycol as HBD were applied. The difference among these three DESs was the salt:HBD mole ratio. This enabled the study of the effect of increasing the ethylene glycol composition in the DES on the separation capability. The three DESs used in this Subsection are DES 2, DES 7 and DES 8 as illustrated in Table 4.1. The experiments in this section were carried out at 27 °C, 35 °C and 45 °C. Here, the mixture of benzene and hexane was chosen as a model for the naphtha and the objective was to extract the benzene from this mixture.

The distribution coefficient of benzene β_{ben} and the selectivity S for the experiments involving these three DESs were calculated according to the equations given in Subsection 3.2.1. Some of the physical properties of DES 2 were reported in Section 4.1. Ten different concentrations for benzene in the benzene/hexane mixtures were studied to cover a wide range of aromatics concentration in hydrocarbons mixtures. These concentrations are 2, 5, 7, 10, 15, 20, 30, 40, 60 and 90 wt%. This study was to investigate the ability of the mentioned DESs to selectively extract aromatic compounds from the naphtha fed to steam cracking unit to produce ethylene. The experiments were carried out twice at Feed:DES mass ratios of 1:1 and 1:2. The experimental results for the compositions in the ternary mixtures of the liquid-liquid extraction experiments are tabulated in three tables. Tables 4.9, 4.10 and 4.11 show the experimental results for DESs 2, 7 and 8. The tables also include distribution coefficients and selectivities calculated for these experiments at various temperatures, where x_1 , x_2 and x_3 refer to mole fraction of benzene, mole fraction of hexane and mole fraction of DES, respectively.

Analysis of samples using gas chromatography showed that the ethylene glycol which is one component of the DES has not been found in the raffinate layer after the liquid-liquid extraction experiments. It can be deduced that when ethylene glycol is employed in a DES, the interaction between the salt and HBD traps the ethylene glycol in the extract layer and prohibits it from transferring at low concentrations to the raffinate. Figure 4.8 below shows a simplified sketch of the extraction of aromatics by the DES. It is shown in the sketch that only hydrocarbons are transferring to the DES layer. This is very significant from an industrial view point. Currently, ethylene glycol is applied in industry as a liquid-liquid extraction solvent for the same process of aromatics extraction. It transfers to the raffinate layer causing what is called as “solvent loss”. By trapping the ethylene glycol in the extract layer, one important advantage in this extraction process is achieved.

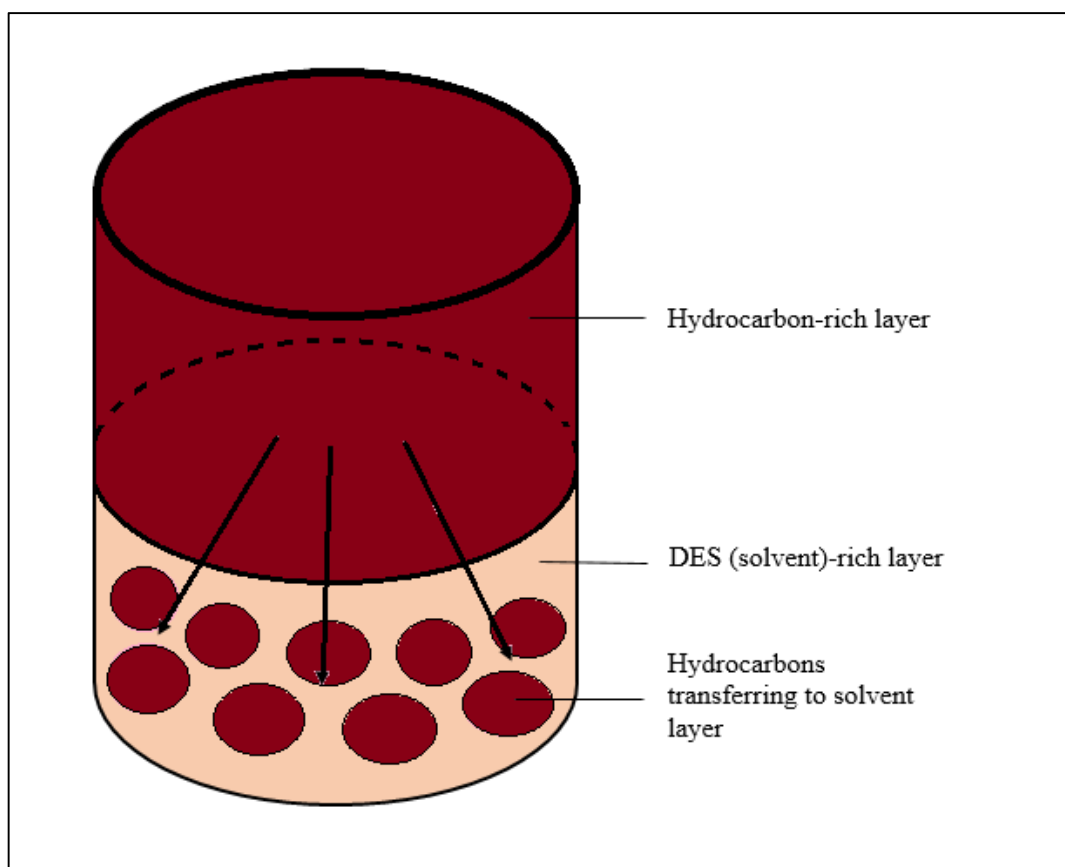


Figure 4.8: A simplified sketch of the extraction of aromatics by DESs.

For the purpose of comparison with commercially used solvents, β and S of sulfolane and N-formylmorpholine towards benzene in benzene/hexane mixtures were obtained from Chen et al. (2000) and Mahmoudi and Lotfollahi (2010). These data are compared to the results obtained in this investigation and are presented in Figures 4.9 through 4.12.

Table 4.9: Experimental mole fractions of the liquid-liquid extraction for the ternary system of benzene (x_1) + hexane (x_2) + DES 2 (x_3) at different temperatures.

Hydrocarbon-rich phase			DES-rich phase			β_{ben}	S
x_1	x_2	x_3	x_1	x_2	x_3		
T= 27 °C			Feed:DES			1:1	
0.0532	0.9468	0	0.0143	0.0027	0.9830	0.2688	98.27
0.0994	0.9006	0	0.0203	0.0020	0.9777	0.2042	85.82
0.1298	0.8702	0	0.0291	0.0025	0.9684	0.2242	67.99
0.3140	0.6860	0	0.0419	0.0022	0.9558	0.1334	53.48
0.4293	0.5707	0	0.0751	0.0028	0.9221	0.1749	33.14
0.5241	0.4759	0	0.0687	0.0025	0.9288	0.1311	22.11
0.7048	0.2952	0	0.0864	0.0023	0.9113	0.1226	17.19
0.9247	0.0753	0	0.1852	0.0012	0.8136	0.2003	12.36
T= 35 °C			Feed:DES			1:1	
0.0300	0.9700	0	0.0104	0.0035	0.9861	0.3467	87.09
0.0801	0.9199	0	0.0301	0.0055	0.9644	0.3758	68.50
0.1557	0.8443	0	0.0259	0.0043	0.9698	0.1663	46.30
0.2289	0.7711	0	0.1999	0.0195	0.7806	0.8733	23.04
0.4119	0.5881	0	0.3777	0.0174	0.6049	0.9170	32.52
0.9041	0.0959	0	0.5891	0.0039	0.4069	0.6516	15.87
T= 45 °C			Feed:DES			1:1	
0.0152	0.9848	0	0.0336	0.0241	0.9423	2.2105	93.68
0.0432	0.9568	0	0.0962	0.0244	0.8794	2.2269	87.36
0.0641	0.9359	0	0.1488	0.0259	0.8252	2.3214	83.37
0.0847	0.9153	0	0.2120	0.0280	0.7600	2.5030	77.69
0.1765	0.8235	0	0.2505	0.0162	0.7333	1.4193	69.02
0.2360	0.7640	0	0.3785	0.0217	0.5998	1.6038	61.29
0.3181	0.6819	0	0.5141	0.0206	0.4652	1.6162	48.44
0.4805	0.5195	0	0.5639	0.0197	0.4164	1.1736	38.64
0.6810	0.3190	0	0.7077	0.0111	0.2812	1.0392	26.25
0.9300	0.0700	0	0.8130	0.0034	0.1836	0.8742	18.39
T= 45 °C			Feed:DES			1:2	
0.0504	0.9496	0	0.0205	0.0137	0.9658	0.4065	28.19
0.0673	0.9327	0	0.0390	0.0243	0.9357	0.5938	22.77
0.1148	0.8852	0	0.0480	0.0208	0.9316	0.415	17.67
0.1670	0.8330	0	0.0810	0.0236	0.8957	0.4832	17.06
0.2481	0.7519	0	0.0930	0.0174	0.8899	0.3737	16.13
0.6069	0.3931	0	0.3290	0.0190	0.6516	0.5426	11.20
0.9143	0.0857	0	0.4320	0.0138	0.5543	0.4724	2.93

Table 4.10: Experimental mole fractions of the liquid-liquid extraction for the ternary system of benzene (x_1) + hexane (x_2) + DES 7 (x_3) at different temperatures.

Hydrocarbon-rich phase			DES-rich phase			β_{ben}	S
x_1	x_2	x_3	x_1	x_2	x_3		
T= 27 °C			Feed:DES			1:1	
0.0405	0.9595	0	0.0320	0.0140	0.9540	0.7901	55.83
0.0880	0.9120	0	0.1598	0.0319	0.8084	1.8159	51.77
0.1236	0.8764	0	0.2778	0.0389	0.6834	2.2476	46.55
0.1575	0.8425	0	0.3120	0.0450	0.6430	1.9810	39.93
0.3800	0.6200	0	0.4527	0.0232	0.5241	1.1913	31.73
0.4772	0.5228	0	0.5461	0.0188	0.4351	1.1444	31.59
0.6619	0.3381	0	0.5600	0.0101	0.4299	0.846	28.38
T= 35 °C			Feed:DES			1:1	
0.0217	0.9783	0	0.0084	0.0042	0.9875	0.3855	83.64
0.0553	0.9457	0	0.0245	0.0062	0.9693	0.4430	75.99
0.1120	0.8880	0	0.0558	0.0068	0.9374	0.4982	65.61
0.1380	0.8620	0	0.0494	0.0052	0.9454	0.358	57.83
0.3616	0.6384	0	0.1165	0.0041	0.8794	0.3222	45.72
0.4726	0.5274	0	0.1583	0.0045	0.8372	0.3350	42.67
0.6512	0.3488	0	0.2790	0.0045	0.7166	0.4284	32.99
T= 45 °C			Feed:DES			1:1	
0.0280	0.9720	0	0.0292	0.0493	0.9215	1.0429	19.27
0.0486	0.9514	0	0.0566	0.0593	0.884	1.1646	17.83
0.0900	0.9100	0	0.0966	0.0692	0.8341	1.0733	16.99
0.2543	0.7457	0	0.2187	0.0466	0.7347	0.8600	13.52
0.3399	0.6601	0	0.2377	0.0344	0.7279	0.6993	12.64
0.6576	0.3424	0	0.3110	0.0129	0.6761	0.4729	12.92
0.9182	0.0818	0	0.3945	0.0070	0.5985	0.4296	4.94
T= 27 °C			Feed:DES			1:02	
0.0517	0.9483	0	0.0812	0.0263	0.8926	1.5706	54.79
0.0770	0.9230	0	0.1060	0.0243	0.8697	1.3767	54.30
0.1973	0.8027	0	0.1964	0.0160	0.7877	0.9954	50.75
0.2937	0.7063	0	0.3311	0.0161	0.6528	1.1273	47.49
0.4258	0.5742	0	0.376	0.0119	0.6122	0.8830	43.65
0.5923	0.4077	0	0.4963	0.0101	0.4936	0.8379	33.78
0.9143	0.0857	0	0.5666	0.0045	0.4290	0.6197	11.86
T= 35 °C			Feed:DES			1:02	
0.0382	0.9618	0	0.089	0.0271	0.8839	2.3298	70.81
0.0697	0.9303	0	0.0992	0.026	0.8748	1.4232	60.07
0.1104	0.8896	0	0.1234	0.0244	0.8522	1.1178	46.58
0.1607	0.8393	0	0.1498	0.0265	0.8236	0.9322	30.5
0.3169	0.6831	0	0.3435	0.0253	0.6312	1.0839	20.05
0.4685	0.5315	0	0.363	0.0146	0.6224	0.7748	33.49
0.9184	0.0816	0	0.5514	0.0039	0.4447	0.6004	12.53

Table 4.11: Experimental mole fractions of the liquid-liquid extraction for the ternary system of benzene (x_1) + hexane (x_2) + DES 8 (x_3) at different temperatures.

Hydrocarbon-rich phase			DES-rich phase			β_{ben}	S
x_1	x_2	x_3	x_1	x_2	x_3		
T= 45 °C			Feed:DES			1:1	
0.0229	0.9771	0	0.0126	0.0097	0.9776	0.5502	49.09
0.0753	0.9247	0	0.0236	0.0064	0.97	0.3134	44.28
0.1292	0.8708	0	0.0652	0.0159	0.9189	0.5046	37.85
0.3573	0.6427	0	0.1706	0.018	0.8114	0.4775	15.31
0.4868	0.5132	0	0.1915	0.0119	0.7966	0.3934	13.66
0.6867	0.3133	0	0.2701	0.0077	0.7222	0.3933	18.68
0.9229	0.0771	0	0.3802	0.0022	0.6177	0.412	14.26
T= 27 °C			Feed:DES			1:2	
0.0203	0.9797	0	0.0135	0.0102	0.9763	0.665	66.77
0.068	0.932	0	0.0433	0.0095	0.9472	0.6368	61.3
0.1964	0.8036	0	0.1203	0.0083	0.8714	0.6125	53.91
0.3484	0.6515	0	0.2537	0.0121	0.7343	0.7282	43.69
0.4029	0.5971	0	0.2935	0.0115	0.695	0.7285	38.74
0.6119	0.3881	0	0.3901	0.0075	0.6023	0.6375	30.73
0.9051	0.0949	0	0.5344	0.0038	0.4618	0.5904	14.94
T= 45 °C			Feed:DES			1:2	
0.0492	0.9508	0	0.0639	0.0446	0.8915	1.2988	26.04
0.065	0.935	0	0.0091	0.0055	0.9854	0.1392	24.68
0.0949	0.9051	0	0.0076	0.0032	0.9892	0.0801	22.85
0.4005	0.5995	0	0.0332	0.0031	0.9637	0.0829	15.52
0.5422	0.4578	0	0.1889	0.0102	0.8009	0.3484	16.07
0.8951	0.1049	0	0.5184	0.0049	0.4767	0.5792	12.37

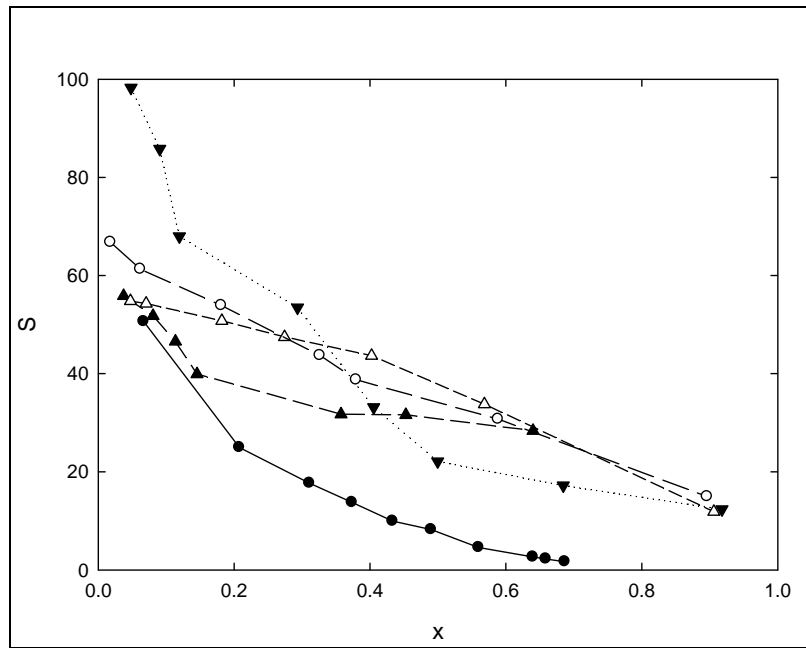


Figure 4.9: Selectivity S of ternary systems dependent on benzene composition in raffinate phase x at 27 °C compared to sulfolane at 25 °C as in Chen et. al. (2000). \blacktriangledown is Feed:DES 2 1:1, \blacktriangle is Feed:DES 7 1:1, \triangle is Feed:DES 7 1:2, \circ is Feed:DES 8 1:2 and \bullet is sulfolane.

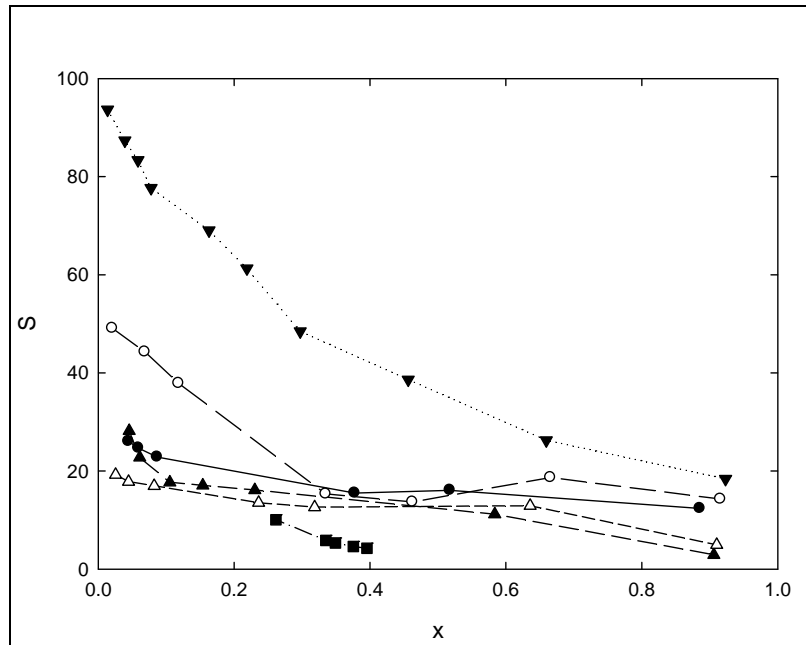


Figure 4.10: Selectivity S of ternary systems dependent on benzene composition in raffinate phase x at 45 °C compared to N-formylmorpholine at 45 °C as in Mahmoudi and Lotfollahi (2010). \blacktriangledown is Feed:DES 2 1:1, \blacktriangle is Feed:DES 2 1:2, \triangle is Feed:DES 7 1:1, \circ is Feed:DES 8 1:1, \bullet is Feed:DES 8 1:2 and \blacksquare is N-formylmorpholine.

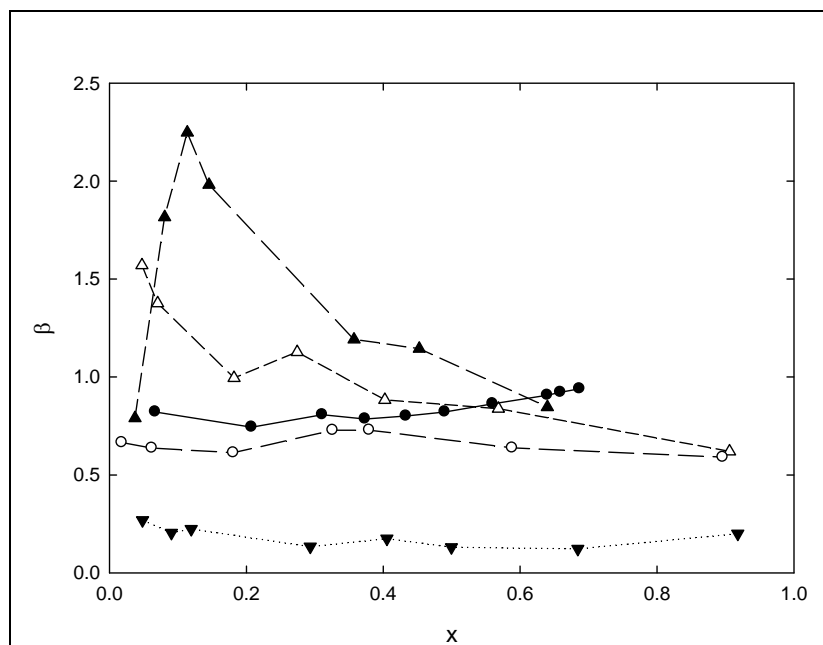


Figure 4.11: Distribution coefficient β of ternary systems dependent on benzene composition in raffinate phase x at 27 °C compared to sulfolane at 25 °C as in Chen et al. (2000). \blacktriangledown is Feed:DES 2 1:1, \blacktriangle is Feed:DES 7 1:1, Δ is Feed:DES 7 1:2, \circ is Feed:DES 8 1:2 and \bullet is sulfolane.

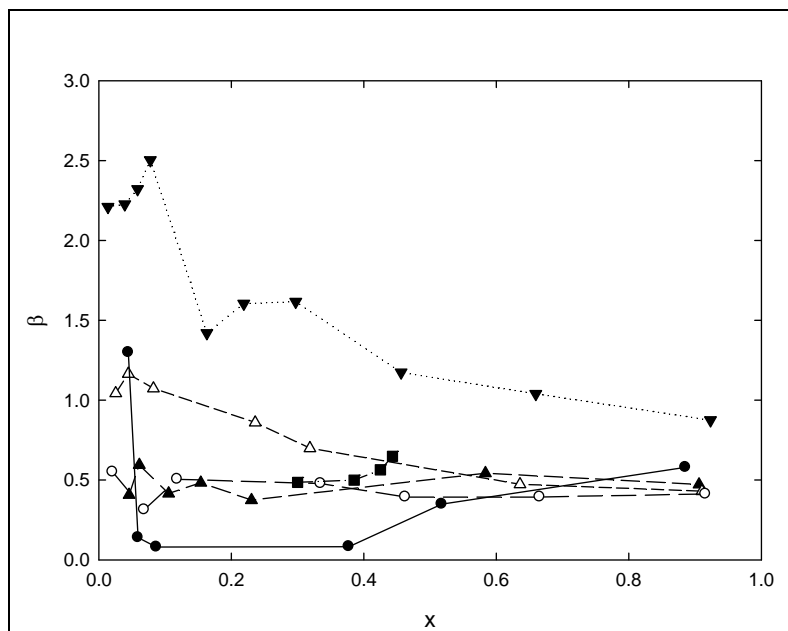


Figure 4.12: Distribution coefficient β of ternary systems dependent on benzene composition in raffinate phase (x) at 45 °C compared to N-formylmorpholine at 45 °C as in Mahmoudi and Lotfollahi (2010). \blacktriangledown is Feed:DES 2 1:1, \blacktriangle is Feed:DES 2 1:2, Δ is Feed:DES 7 1:1, \circ is Feed:DES 8 1:1, \bullet is Feed:DES 8 1:2 and \blacksquare is N-formylmorpholine.

It should be noted that the experimental data reported by Chen et al. (2000) for sulfolane were measured at 25 °C while in this work the experiments were conducted at a temperature of 27 °C. This small difference in temperature did not considerably affect the comparison.

From Table 4.9, it is found that for DES 2 at DES:Feed ratio of 1:1, 45 °C is the best temperature that provides the highest β_{aro} and S at low concentrations of aromatics. At 27 °C, a relatively higher S is achieved, however, β_{aro} is low.

In Figure 4.8, it can be seen that S of more than 80 is achieved at low concentrations of aromatic. In addition, it is also clear that some of the studied DESs are of higher selectivity towards benzene than the commercially used solvent, i.e. sulfolane. However, the selectivity is decreasing at higher concentrations of aromatics in the feed, a behavior similar to what has been found for other solvents (Dománska et al., 2007, Letcher and Reddy, 2005, and Meindersma et al., 2005). Moreover, it can be noted that the S of DES 2 when the Feed:DES mass ratio is 1:1 is higher than all the other DESs curves in the range 0 to 0.35 wt fraction and lower than the others at more than 0.4 wt fraction, as shown in Figure 4.8. This can be attributed to the amount of ethylene glycol in the used DESs. At lower aromatic concentrations, the amount of ethylene glycol present in DES 2 is sufficient for the extraction of aromatics and thus the selectivity of DES 2 is higher than other DESs. However, at higher concentrations, the amount of ethylene glycol in DES 2 required for the extraction of aromatics is insufficient and thus S decreases. The same argument can be used to explain the difference between DES 7 and DES 8 at feed:solvent mass ratio of 1:2.

Focus will be directed to low concentrations of aromatics as they represent a practical separation problem, as discussed earlier. Table 4.9 shows that at 45 °C and Feed:DES mass ratio of 1:2, the benzene distribution coefficient as well as the selectivity are

relatively low in comparison to the corresponding Feed:DES mass ratio of 1:1 at the same temperature. It can be concluded that for DES 2, the best operating conditions are at Feed:DES mass ratio of 1:1 and under the temperature of 45 °C, whereby selectivity of more than 93 is achieved at low aromatic concentration.

Figure 4.10 shows a comparison between selectivities achieved by some of the systems investigated and selectivity of N-formylmorpholine reported by Mahmoudi and Lotfollahi (2010). The selected systems are of a higher selectivity in comparison to N-formylmorpholine. These experimental findings support the contention that it is still possible to prepare new and novel non-conventional solvents able to compete with the industrial solvents.

Figures 4.11 and 4.12 show comparisons between the distribution coefficients in DESs 2, 7 and 8 and in sulfolane at 25 °C and in N-formylmorpholine at 45 °C, respectively. These figures show that the distribution coefficients of sulfolane and N-formylmorpholine are not the lowest. However, DES 7 is superior to sulfolane in both distribution coefficient and selectivity at Feed:DES mass ratio of 1:1 and 1:2 at 27 °C. Moreover, DES 2 is higher in distribution coefficient than N-formylmorpholine at 45 °C.

Interestingly, Table 4.9 shows different findings. For DES 7, the mass ratio 1:2 for Feed:DES is better in terms of distribution coefficients and selectivity. At 35 °C and Feed:DES mass ratio of 1:2, a selectivity value of greater than 70 with high distribution coefficients is achieved. While at 35 °C and Feed:DES mass ratio of 1:1, the selectivity is 83.6 at aromatic concentration of 0.0549 wt% in the feed and distribution coefficient is not as high as it is in Feed:DES mass ratio of 1:2. Other temperatures of application are not able to increase the distribution coefficient and the selectivity.

Table 4.11 gives the separation results using DES 8. It is clear that at Feed:DES mass ratio of 1:2 at 27 °C, the highest distribution coefficient and selectivity are achieved. At a Feed:DES mass ratio of 1:1 and 45 °C, it is possible to achieve selectivity of almost 50 but the distribution coefficient is low in comparison to that at 27 °C.

As a conclusion from all the data presented in Tables 4.9, 4.10 and 4.11, DES 2 achieved the best separation at a Feed:DES mass ratio of 1:1 and under a temperature of 45 °C. Thus, DES 2 can be considered as the best solvent among DESs 2, 7 and 8 that can be adopted for further investigation and analysis.

It is worth mentioning here that sometimes the distribution coefficient does not show a monotonic trend in its values. This is also noticed for selectivity profiles for certain cases. This behavior is similar to the findings reported in the literature for hydrocarbons separation (Domńska et al., 2007, Letcher and Reddy, 2005, and Meindersma et al., 2005). The fluctuation could be due to the interaction between the DES and the benzene which is polar in nature and temperature independent.

The experimental results presented above show that, in general, at low concentrations of aromatics in the feed, β is relatively higher than usual. Again, it is a good indication that the separation of aromatics at low concentrations is promising using the studied DESs. Also it can be seen that for DES 7 and DES 8, a Feed:DES mass ratio of 1:2 is the best in terms of β and S. Finally, DES 2 is the best solvent with selectivity more than 98 at low concentrations of aromatics. The fluctuations in selectivity and distribution coefficients seen in Figures 4.9 - 4.12 are common in the literature when ILs were used. The work of Meindersma et al. (2006) showed similar fluctuations.

Figures 4.13, 4.14 and 4.15 are the ternary diagrams for the selected systems at 27, 35 and 45 °C, respectively. They show clearly how a good separation of aromatics is achieved which further supports the argument presented in this section.

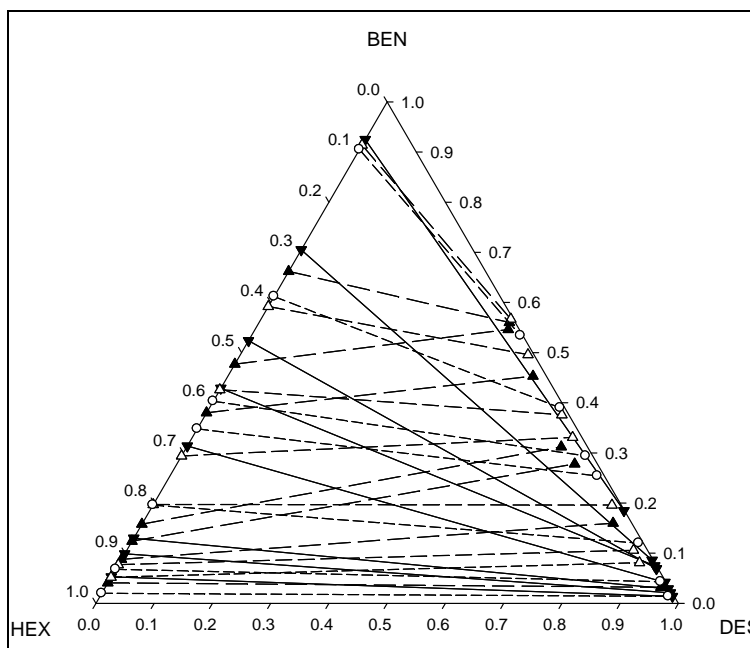


Figure 4.13: Experimental compositions of the ternary system benzene + hexane + DES at 27 °C. ▼ is Feed:DES 2 1:1, ▲ is Feed:DES 7 1:1, △ is Feed:DES 7 1:2 and ○ is Feed:DES 8 1:2.

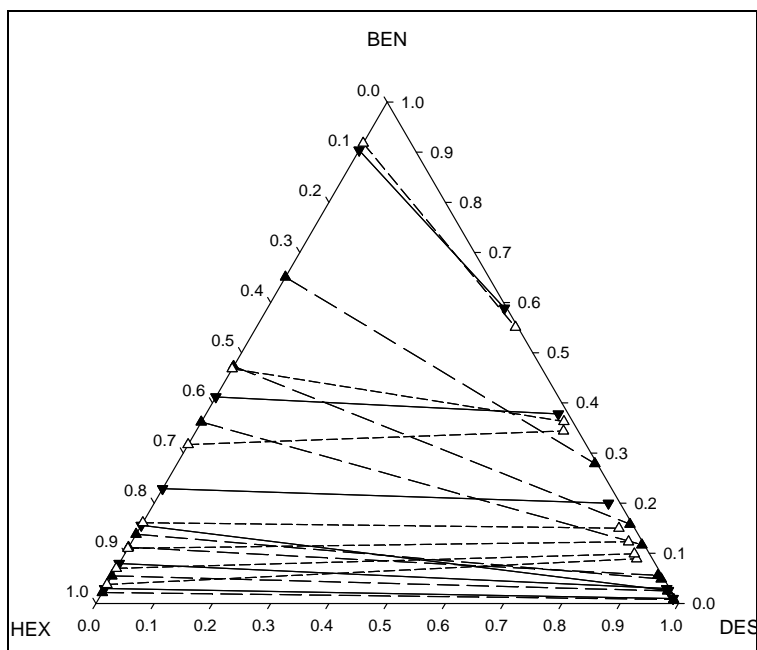


Figure 4.14: Experimental compositions of the ternary system benzene + hexane + DES at 35 °C. ▼ is Feed:DES 2 1:1, ▲ is Feed:DES 7 1:1 and Δ is Feed:DES 7 1:2.

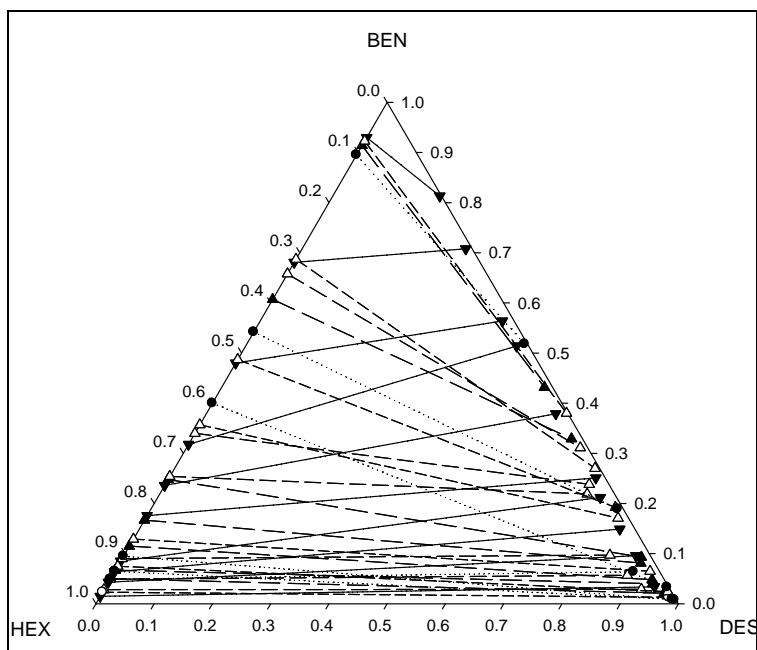


Figure 4.15: Experimental compositions of the ternary system benzene + hexane + DES at 45 °C. ▼ is Feed:DES 2 1:1, ▲ is Feed:DES 2 1:2, Δ is Feed:DES 7 1:1, ○ is Feed:DES 8 1:1 and ● is Feed:DES 8 1:2.

4.2.2 Application of tetrabutylphosphonium bromide-based DESs

In this Section, the distribution coefficient and selectivity for the other two DESs formed by mixing 1:2 mole ratio of tetrabutylphosphonium bromide as salt and ethylene glycol or sulfolane as HBDs, i.e. DES 9 and DES 13 in Table 4.1, are tested for the potential application as solvents for the liquid-liquid extraction of aromatic hydrocarbons from naphtha. Mixtures of toluene and heptane are used as models of naphtha. The difference between these two DESs is the HBD used to synthesize them. In DES 9, ethylene glycol is used while in DES 13, sulfolane is used as HBD. Liquid-liquid extraction experiments are conducted at 40 °C, 50 °C and 60 °C.

Here, the distribution coefficient and selectivity are calculated from the experimental data of the liquid-liquid extraction at different temperatures. The values of the viscosity μ and refractive index n_D of the DES that gave the best selectivity for the studied systems are measured at a temperature range from 20 °C to 60 °C. Toluene's concentrations that are used here are 2, 9, 16, 25, 40, and 60 wt%. Tables 4.12 and 4.13 present the experimental mole fractions of the systems toluene + heptane + DES 9 and toluene + heptane + DES 13, respectively, as well as the calculated distribution coefficients and selectivities.

Similar findings to those reported in Subsection 4.2.1 are found here. The GC analysis showed that the DES was not detected in the raffinate layer after the experiments. For the extract layer, the concentration of DES was calculated from the mass balance by considering three components in the layer. The concentrations of heptane and toluene were determined using GC analysis.

Table 4.12: Experimental mole fractions of the liquid-liquid extraction for the ternary system of toluene (x_1) + heptane (x_2) + DES 9 (x_3) at different temperatures.

Hydrocarbon-rich layer			Solvent-rich layer			β_{tol}	β_{hep}	S
Tol	Hep	DES	Tol	Hep	DES			
x_1	x_2	x_3	x_1	x_2	x_3			
40 °C								
0.017	0.983	0	0.010	0.065	0.925	0.565	0.066	8.52
0.041	0.959	0	0.039	0.059	0.901	0.954	0.062	15.38
0.086	0.914	0	0.046	0.059	0.895	0.542	0.065	8.40
0.206	0.794	0	0.112	0.062	0.826	0.544	0.078	6.96
0.341	0.659	0	0.184	0.064	0.753	0.539	0.097	5.58
0.534	0.466	0	0.288	0.063	0.650	0.538	0.135	4
50 °C								
0.017	0.983	0	0.009	0.058	0.933	0.494	0.059	8.35
0.073	0.927	0	0.035	0.06	0.905	0.484	0.065	7.48
0.087	0.913	0	0.048	0.069	0.882	0.555	0.076	7.29
0.533	0.467	0	0.287	0.066	0.647	0.538	0.141	3.81
0.344	0.656	0	0.197	0.073	0.730	0.573	0.111	5.16
0.209	0.791	0	0.115	0.07	0.816	0.549	0.088	6.24
60 °C								
0.017	0.983	0	0.009	0.067	0.924	0.541	0.068	7.95
0.074	0.926	0	0.047	0.082	0.871	0.641	0.089	7.24
0.087	0.913	0	0.056	0.082	0.862	0.649	0.090	7.24
0.211	0.789	0	0.125	0.079	0.795	0.595	0.101	5.92
0.341	0.659	0	0.195	0.071	0.734	0.571	0.108	5.30
0.536	0.464	0	0.266	0.063	0.671	0.495	0.136	3.64

Table 4.13: Experimental mole fractions of the liquid-liquid extraction for the ternary system of toluene (x_1) + heptane (x_2) + DES 13 (x_3) at different temperatures.

Hydrocarbon-rich layer			Solvent-rich layer			β_{tol}	β_{hep}	S
Tol	Hep	DES	Tol	Hep	DES			
x_1	x_2	x_3	x_1	x_2	x_3			
50 °C								
0.016	0.984	0	0.013	0.093	0.894	0.832	0.095	8.80
0.070	0.930	0	0.058	0.078	0.865	0.824	0.083	9.87
0.081	0.919	0	0.067	0.089	0.844	0.829	0.097	8.56
0.197	0.803	0	0.156	0.082	0.762	0.789	0.103	7.68
0.328	0.672	0	0.248	0.080	0.672	0.758	0.119	6.36
0.511	0.489	0	0.377	0.082	0.541	0.737	0.168	4.39
60 °C								
0.016	0.984	0	0.012	0.083	0.904	0.792	0.084	9.38
0.071	0.929	0	0.059	0.090	0.852	0.821	0.097	8.50
0.083	0.917	0	0.067	0.092	0.842	0.806	0.100	8.08
0.200	0.800	0	0.156	0.084	0.760	0.777	0.105	7.37
0.327	0.673	0	0.244	0.082	0.674	0.746	0.123	6.09
0.516	0.484	0	0.379	0.087	0.534	0.733	0.180	4.08

Figure 4.16 shows the profiles of the distribution coefficients for the results listed in Tables 4.12 and 4.13, while Figure 4.17 shows the profiles of the selectivities for the same results. Generally, the distribution coefficient decreases with the increase of toluene concentration in the raffinate layer. An explanation to this behavior was given by Holbrey et al. (2003) when they used ILs for aromatics/aliphatics separation and noticed a similar behavior. They concluded that ILs and aromatics, in this case is toluene, will organize the molecules in a sandwich structure, whereby the cations of the ILs and the aromatics interact through π - π interactions while the anions of the ILs are arranged around this complex. By increasing the composition of the aromatics, the distance between the aromatics and the anions become larger, resulting in a reduction in the interaction's strength and thereby in the distribution coefficient (Garcia et al., 2010). It is also evident from Figure 4.16 that increasing temperature has slight effect on the distribution coefficient. It can be concluded from this that the application of these two DESs for the separation of aromatics and aliphatics is possible at low temperatures. However, DES 20

at salt:HBD mole ratio of 1:2 is solid at 40 °C and can only be used at 50 °C or higher. From the work of Meindersma (2005), the average distribution coefficient in a temperature range from 40 °C to 75 °C was around 0.3. From the present work, as shown in Tables 4.12 and 4.13, a higher distribution coefficient is achieved through the DESs under investigation.

By definition, the selectivity is the product of dividing β_{tol} on β_{hep} . Thus, decreasing β_{tol} and increasing β_{hep} result directly in decreasing the selectivity. From the experiments, as the toluene started to appear in lesser amount in the extract layer and in an increasing composition in the raffinate layer, the likelihood of the solvent, in this case DES, to selectively dissolve toluene decreased as well. In this case, the lowest selectivity is for the lowest distribution coefficient and vice-versa. It is important to have high selectivity at lower concentrations of aromatics. As was discussed by Meindersma (2005), there is no suitable separation process for low concentrations of aromatics in naphtha.

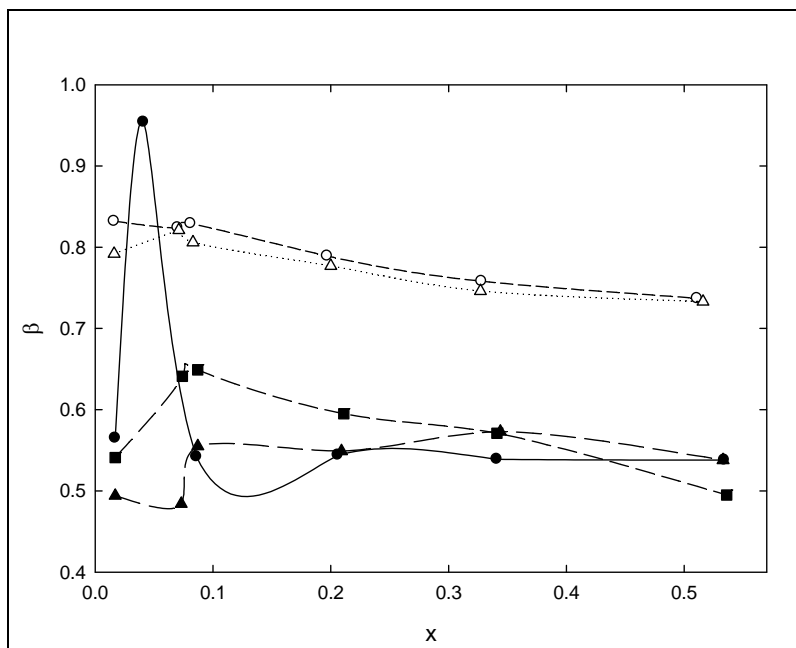


Figure 4.16: Toluene's distribution coefficient β_{tol} dependent on toluene composition in raffinate phase x . ∇ is DES 9 at 40 °C, \blacktriangle is DES 9 at 50 °C, \triangle is DES 9 at 60 °C, \circ is DES 13 at 50 °C and \bullet is DES 13 at 60 °C.

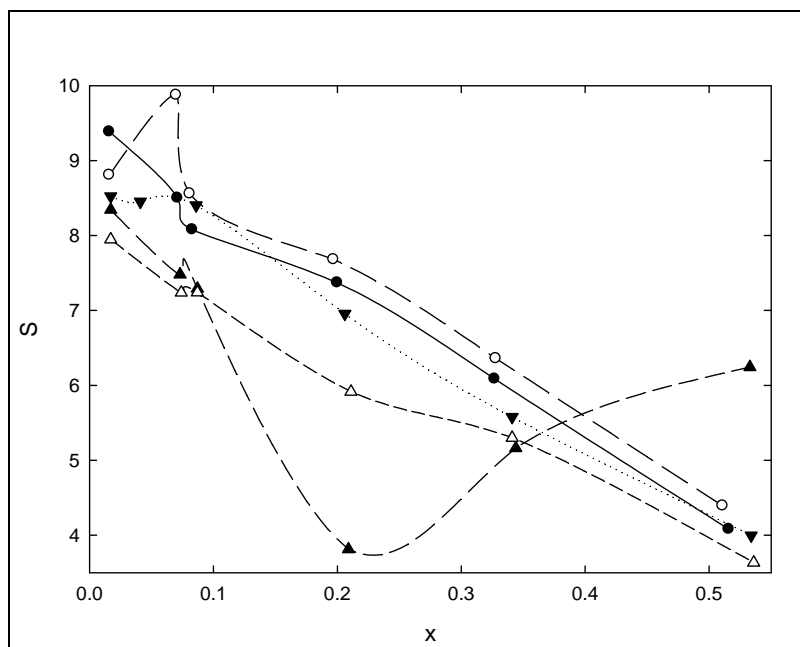


Figure 4.17: Selectivity S dependent on toluene composition in raffinate phase x . ▼ is DES 9 at 40 °C, ▲ is DES 9 at 50 °C, △ is DES 9 at 60 °C, ○ is DES 13 at 50 °C and ● is DES 13 at 60 °C.

4.2.2.1 Consistency of the experimental data

The Othmer – Tobias and Hand correlations described in Subsection 3.2.2 were applied to establish the reliability of the experimental liquid - liquid extraction data for the DESs under investigation at different temperatures.

The fitting parameters of these correlations are given in Table 4.14 for DESs 16 and 20 at different temperatures, together with their correlation factor, R^2 . As can be seen, both equations provide similar and satisfactory fitting since the regression coefficients are very close to unity. This confirms the degree of consistency of the experimental data. With one exception, the R^2 value for the system toluene + heptane + DES 16 at 40 °C whereby R^2 is 0.9613.

Table 4.14: Constants of the Othmer – Tobias and Hand correlations and the correlation factor (R^2).

Othmer-Tobias Correlation Parameters		
<i>a</i>	<i>b</i>	R^2
{Toluene + Heptane + DES 9} at 40 °C		
0.4984	-2.189	0.9613
{Toluene + Heptane + DES 9} at 50 °C		
0.5917	-2.0613	0.994
{Toluene + Heptane + DES 9} at 60 °C		
0.4203	-2.1946	0.9969
{Toluene + Heptane + DES 9} at 50 °C		
0.6056	-1.7807	0.9944
{Toluene + Heptane + DES 9} at 60 °C		
0.5855	-1.7874	0.9903
Hand Correlation Parameters		
<i>c</i>	<i>d</i>	R^2
{Toluene + Heptane + DES 9} at 40 °C		
1.301	3.04	0.976
{Toluene + Heptane + DES 9} at 50 °C		
1.088	2.4	0.99
{Toluene + Heptane + DES 9} at 60 °C		
1.107	2.405	0.981
{Toluene + Heptane + DES 9} at 50 °C		
1.122	2.137	0.999
{Toluene + Heptane + DES 9} at 60 °C		
1.126	2.154	1

4.2.2.2 Liquid-liquid equilibrium modeling

Liquid-liquid equilibrium (LLE) calculations were performed by solving the isothermal liquid-liquid flash at the given temperature and pressure, as described in Subsection 3.2.3.

The deviation from ideality in the liquid phase was expressed using the NRTL model based on the local composition concept. The model development was achieved within Simulis[®] Thermodynamics environment, a thermophysical properties calculation server provided by ProSim (www.prosim.com, 2012) and available as an MS-Excel add-in.

The regression process described in Subsection 3.2.3 is followed here. The binary interaction parameters τ_{ij} , τ_{ji} and α_{ij} were estimated from “6M” experimental data points, where M represents the number of tie lines, by minimizing the quadratic criterion between calculated and experimental solubilities of each constituent in each phase:

$$Criterion = \frac{1}{6M} \sum_i \sum_j \sum_k (s_{ijk}^{exp} - s_{ijk}^{cal})^2 \quad (3.10)$$

with s is the solubility expressed in mole fraction and the subscripts i, j , and k designate the component, phase, and the tie lines, respectively.

Tables 4.15 and 4.16 show the values of the binary interaction parameters obtained using the NRTL model with each ternary system. The temperature dependence is neglected for the fitting parameters in this temperature window and the interaction between toluene and heptane is considered independent of the solvent.

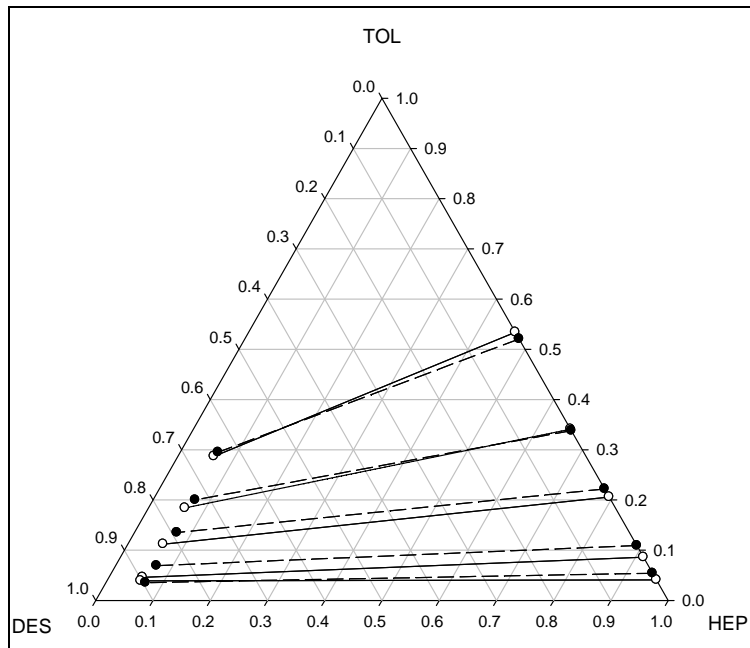
Table 4.15: NRTL binary interaction parameters for the ternary system toluene + heptane + DES 9 (criterion = $3.71e^{-5}$).

i	j	τ_{ij}	τ_{ji}	α_{ij}
1	2	22.02	-38.84	0.390
1	3	1773.85	-429.55	0.188
2	3	3134.15	802.67	0.254

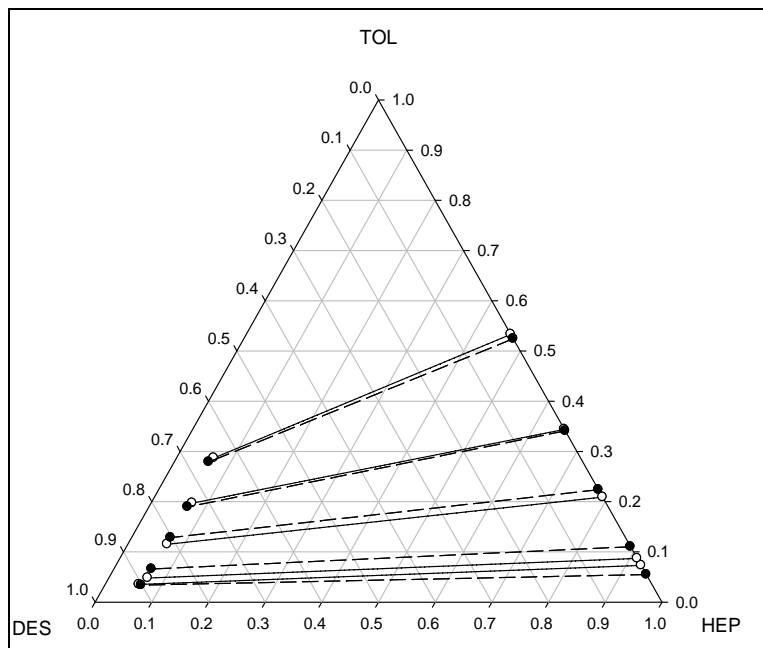
Table 4.16: NRTL binary interaction parameters for the ternary system toluene + heptane + DES 13 (criterion = $1.31e^{-5}$).

i	j	τ_{ij}	τ_{ji}	α_{ij}
1	2	22.02	-38.84	0.390
1	3	1426.74	-578.34	0.178
2	3	3128.40	616.88	0.230

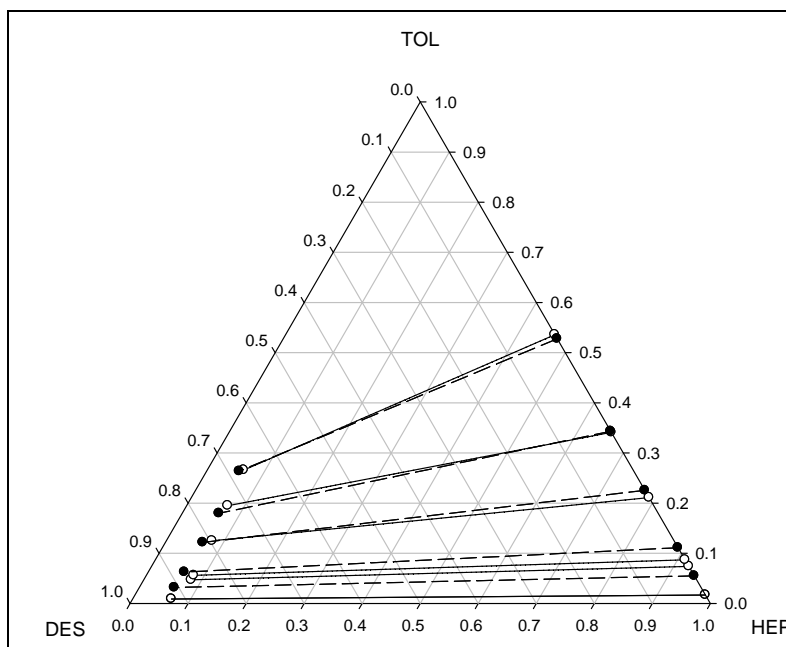
Figures 4.18 and 4.19 show the ternary diagrams, including the calculated compositions by NRTL correlation. It can be seen from these Figures that the calculated compositions have good agreement with the experimental ones. Additionally, the tie-lines of both compositions coincide in most of the cases.



(a)

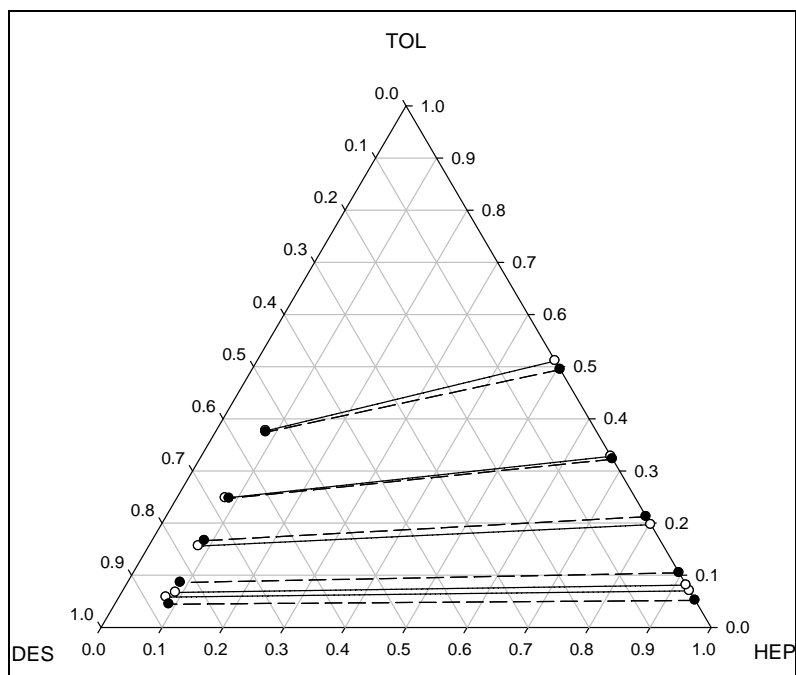


(b)

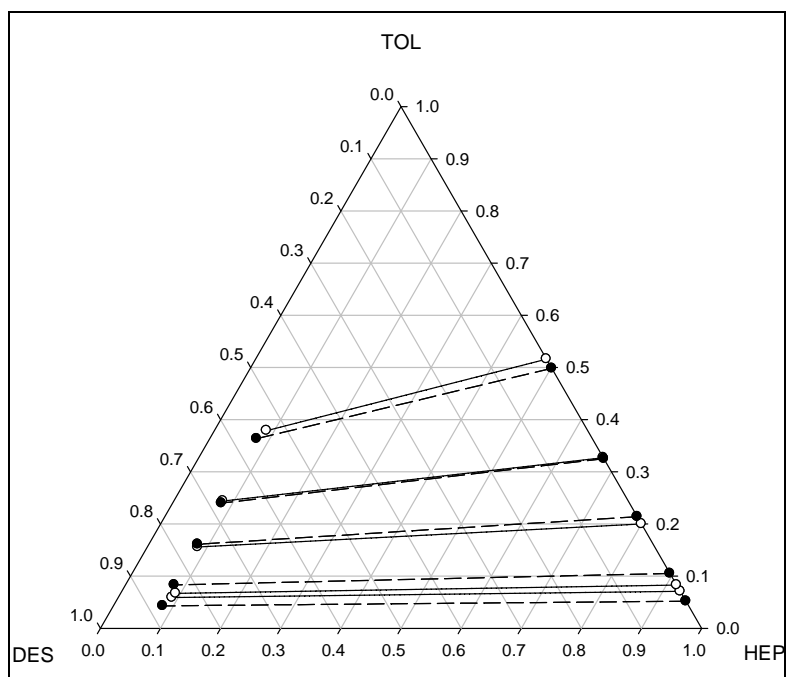


(c)

Figure 4.18: Experimental and calculated compositions of the ternary system toluene + heptane + DES 9 at 40 °C (a), 50 °C (b) and 60 °C (c). Solid lines indicate experimental tie lines, and dashed lines indicate calculated data by the NRTL model.



a



b

Figure 4.19: Experimental and calculated composition of the ternary system toluene + heptane + DES 13 at 50 °C (a) and 60 °C (b). Solid lines indicate experimental tie lines, and dashed lines indicate calculated data by the NRTL model.

4.2.2.3 Additional screening

It has been shown that a DES is a mixture of salt and HBD that can form a eutectic mixture with unique solvent properties. The salt:HBD mole ratio incorporated can be varied, resulting in DESs possessing different physical properties. The melting temperature for the DES could be lower or higher than that at the deep eutectic point if the salt:HBD mole ratio is varied. Thus, there is no limit for the ratios that can form a DES from the same salt and HBD. For this reason, additional molar ratios to synthesize more DESs from the same constituents have been selected. salt:HBD mole ratios of 1:4, 1:6 and 1:8 were chosen and additional DESs were synthesized. The objective was to investigate the effect of increasing the salt:HBD mole ratio in the DES on the separation capability. DESs 10, 11, 12, 14 and 15 in Table 4.1 are accordingly synthesized.

The liquid-liquid extraction experiments were conducted for one concentration of toluene at different temperatures. This was to reduce the number of experimental runs needed to cover a large range of concentrations. As the focus of the study was on low to moderate concentrations of aromatics in hydrocarbons mixtures, a concentration of 9% by weight of aromatics was used.

Tables 4.17 and 4.18 show the experimental distribution coefficients and selectivities for different ratios of salt:HBD. In addition, Figures 4.20 and 4.21 show a plot of the distribution coefficients and selectivities listed in Tables 4.17 and 4.18, respectively. These Figures show that, in terms of the distribution coefficient, the DES with the lowest content of HBD has the highest distribution coefficient. However, in terms of the selectivity, the opposite is correct; i.e. for a higher HBD content in the DES, a higher selectivity is achieved. As a conclusion, increasing the HBD in the DES is not contributing to an improvement in the total selectivity of the solvent towards the toluene.

Table 4.17 : Additional experimental data (Distirbution coefficients of toluene and heptane β_{tol} , β_{hep}) for DESs 9, 10, 11, 12, 13, 14 and 15 at 9% wt toluene in feed.

Temp(°C)	DES 9		DES 10		DES 11		DES 12		DES 13		DES 14		DES 15	
	β_{tol}	β_{hep}	β_{tol}	β_{hep}	β_{tol}	β_{hep}	β_{tol}	β_{hep}	β_{tol}	β_{hep}	β_{tol}	β_{hep}	β_{tol}	β_{hep}
30	-	-	0.479	0.026	0.435	0.020	0.381	0.015	-	-	0.243	0.015	0.209	0.024
40	0.954	0.062	0.508	0.041	0.185	0.021	0.349	0.029	-	-	0.247	0.019	0.081	0.013
50	0.484	0.065	0.478	0.029	0.415	0.024	0.362	0.016	0.824	0.083	0.246	0.026	0.191	0.013
60	0.641	0.089	0.499	0.034	0.403	0.023	0.283	0.021	0.821	0.097	0.245	0.020	0.659	0.037

Table 4.18 : Additional experimental data (selectivity S) for DESs 9, 10, 11, 12, 13, 14 and 15 at 9% wt toluene in feed.

Temp (°C)	DES 9	DES 10	DES 11	DES 12	DES 13	DES 14	DES 15
	S	S	S	S	S	S	S
30	-	18.7	22.27	25.89	-	16.02	8.53
40	15.38	12.44	8.63	12.04	-	13.28	6.46
50	7.48	16.48	17.64	22.12	9.87	14.52	14.51
60	7.24	14.84	17.59	13.43	8.5	12.1	17.6

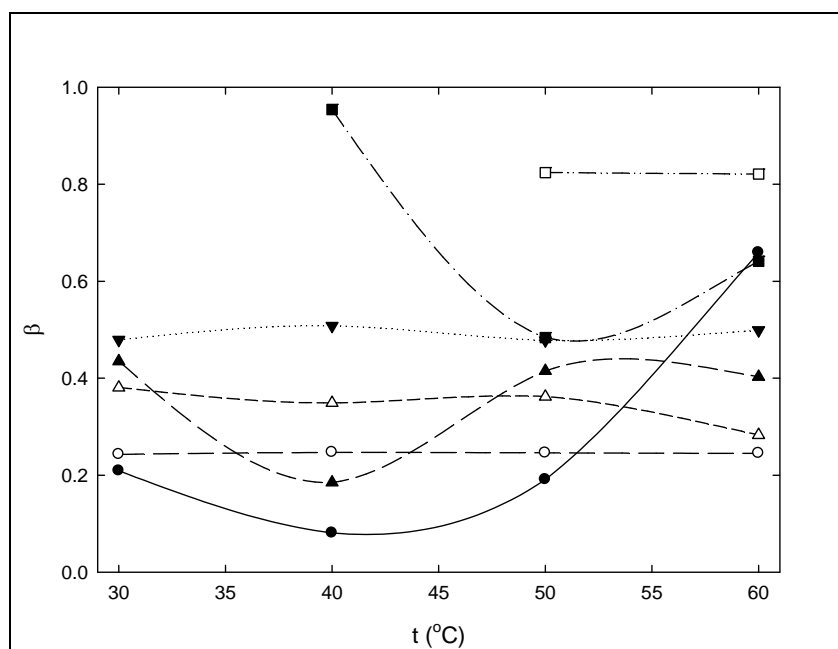


Figure 4.20: Effect of varying the salt:HBD molar ratio on the distribution coefficient β at different temperatures. ■ is DES 9, ▼ is DES 10, ▲ is DES 11, △ is DES 12, □ is DES 13, ○ is DES 14 and ● is DES 15.

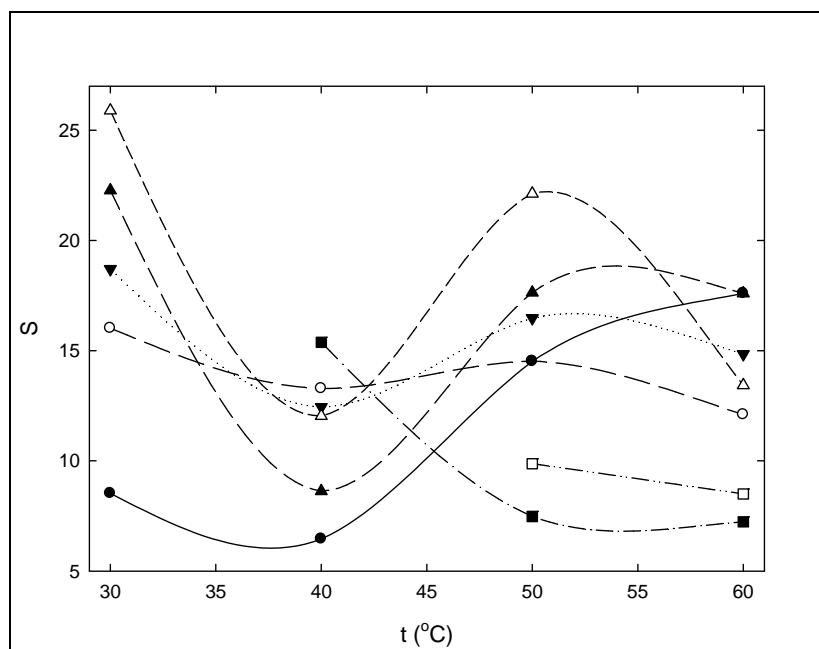


Figure 4.21: Effect of varying the salt:HBD mole ratio on the selectivity S at different temperatures. ■ is DES 9, ▼ is DES 10, ▲ is DES 11, △ is DES 12, □ is DES 13, ○ is DES 14 and ● is DES 15.

4.2.3 Application of ethyltriphenylphosphonium iodide-based DESs

The present work includes the application of other DESs synthesized from ethyltriphenylphosphonium iodide as a salt and ethylene glycol or sulfolane as HBDs, namely DESs 16, 17, 18, 19, 20 and 21 in Table 4.1. As in the previous section, the effect of increasing HBD concentration in the DES was investigated. The liquid-liquid extraction experiments were carried out only for three concentrations of aromatics for each system. Mixtures of toluene + heptane were used as models for naphtha. The experiments were carried out at four different temperatures, i.e. 30 °C, 40 °C, 50 °C and 60 °C. Tables 4.19 to 4.24 show the experimental concentrations of the ternary systems of toluene + heptane + DES in the two layers formed after the extraction.

In addition to these experimental concentrations, the Tables present the distribution coefficients, selectivities and efficiencies for all the experiments. As in the cases discussed in Subsections 4.2.1 and 4.2.2, there were no losses of DESs to the raffinate layer in these sets of experiments. Analysis by GC for the raffinate layer (hydrocarbon-rich phase) proved the presence of toluene and heptane only with no traces of ethylene glycol or sulfolane.

Table 4.19: Experimental mole fractions of the liquid-liquid extraction for the ternary system of toluene (x_1) + heptane (x_2) + DES 16 (x_3) at different temperatures.

Hydrocarbon-rich phase			DES-rich phase			β_{tol}	β_{hep}	S	η
Tol	Hep	DES	Tol	Hep	DES				
x_1	x_2	x_3	x_1	x_2	x_3				
30 °C									
0.0886	0.9114	0	0.0112	0.0049	0.9839	0.1269	0.0054	23.71	17.54
0.1221	0.8779	0	0.0026	0.0026	0.9948	0.0212	0.0029	7.23	13.30
40 °C									
0.0206	0.9794	0	0.0025	0.0033	0.9942	0.1236	0.0033	37.02	35.68
0.0888	0.9112	0	0.0065	0.0031	0.9904	0.0729	0.0034	21.18	11.16
0.1475	0.8525	0	0.0582	0.0227	0.9191	0.3943	0.0267	14.80	5.32
50 °C									
0.0155	0.9845	0	0.0025	0.0069	0.9906	0.162	0.007	23.05	12.84
0.0702	0.9298	0	0.0108	0.0056	0.9836	0.1536	0.006	25.41	16.34
0.1303	0.8697	0	0.0796	0.0622	0.8582	0.611	0.0715	8.548	8.75
60 °C									
0.0155	0.9845	0	0.0023	0.0052	0.9924	0.1506	0.0053	28.29	18.75
0.0691	0.9309	0	0.0099	0.0109	0.9793	0.1429	0.0117	12.26	25.64
0.1308	0.8692	0	0.0170	0.0062	0.9767	0.1301	0.0072	18.13	14.59

Table 4.20: Experimental mole fractions of the liquid-liquid extraction for the ternary system of toluene (x_1) + heptane (x_2) + DES 17 (x_3) at different temperatures.

Hydrocarbon-rich phase			DES-rich phase			β_{tol}	β_{hep}	S	η
Tol	Hep	DES	Tol	Hep	DES				
x_1	x_2	x_3	x_1	x_2	x_3				
50 °C									
0.0208	0.9792	0	0.0022	0.0148	0.9830	0.1042	0.0151	6.90	12.22
0.0708	0.9292	0	0.0093	0.0304	0.9603	0.1312	0.0327	4.01	17.99
0.2036	0.7964	0	0.0431	0.1103	0.8466	0.2117	0.1385	1.53	51.19
60 °C									
0.0152	0.9848	0	0.0019	0.0058	0.9923	0.1222	0.0059	20.75	10.40
0.0676	0.9324	0	0.0084	0.0060	0.9856	0.1237	0.0064	19.24	17.65
0.1584	0.8416	0	0.0187	0.0051	0.9762	0.1182	0.0060	19.57	26.85

Table 4.21: Experimental mole fractions of the liquid-liquid extraction for the ternary system of toluene (x_1) + heptane (x_2) + DES 18 (x_3) at different temperatures.

Hydrocarbon-rich phase			DES-rich phase			β_{tol}	β_{hep}	S	η
Tol	Hep	DES	Tol	Hep	DES				
x_1	x_2	x_3	x_1	x_2	x_3				
50 °C									
0.0865	0.9135	0	0.0193	0.0031	0.9776	0.2227	0.0034	65.83	23.32
0.0910	0.9090	0	0.0088	0.0051	0.9861	0.0967	0.0056	17.35	10.88
0.2038	0.7962	0	0.0217	0.0041	0.9741	0.1066	0.0052	20.58	12.66
60 °C									
0.0225	0.9775	0	0.0020	0.0034	0.9946	0.0885	0.0035	25.43	10.09
0.0910	0.9090	0	0.0082	0.0035	0.9883	0.0901	0.0038	23.52	11.27
0.2563	0.7437	0	0.0224	0.0034	0.9742	0.0874	0.0045	19.39	9.79

Table 4.22: Experimental mole fractions of the liquid-liquid extraction for the ternary system of toluene (x_1) + heptane (x_2) + DES 19 (x_3) at different temperatures.

Hydrocarbon-rich phase			DES-rich phase			β_{tol}	β_{hep}	S	η
Tol	Hep	DES	Tol	Hep	DES				
x_1	x_2	x_3	x_1	x_2	x_3				
30 °C									
0.0143	0.9857	0	0.0081	0.0126	0.9793	0.5655	0.0128	44.21	39.357
0.0816	0.9184	0	0.0316	0.0116	0.9569	0.3866	0.0126	30.66	28.252
0.1853	0.8147	0	0.0702	0.0242	0.9056	0.3789	0.0297	12.76	29.854
40 °C									
0.0195	0.9805	0	0.0076	0.0196	0.9728	0.3904	0.0200	19.51	86.192
0.0823	0.9177	0	0.0333	0.0193	0.9474	0.4042	0.0211	19.20	47.806
0.1456	0.8544	0	0.0725	0.0257	0.9018	0.4975	0.0301	16.53	27.413
50 °C									
0.0192	0.9808	0	0.0074	0.0140	0.9786	0.3875	0.0142	27.23	62.343
0.0823	0.9177	0	0.0315	0.0184	0.9501	0.3831	0.0200	19.14	44.797
0.1833	0.8167	0	0.0669	0.0131	0.9200	0.3649	0.0160	22.81	46.061
60 °C									
0.0143	0.9857	0	0.0063	0.0193	0.9745	0.4404	0.0195	22.54	51.472
0.0624	0.9376	0	0.0304	0.0146	0.9551	0.4870	0.0155	31.37	25.67
0.1446	0.8554	0	0.0627	0.0161	0.9212	0.4338	0.0188	23.08	25.132

Table 4.23: Experimental mole fractions of the liquid-liquid extraction for the ternary system of toluene (x_1) + heptane (x_2) + DES 20 (x_3) at different temperatures.

Hydrocarbon-rich phase			DES-rich phase			β_{tol}	β_{hep}	S	η
Tol	Hep	DES	Tol	Hep	DES				
x_1	x_2	x_3	x_1	x_2	x_3				
30 °C									
0.0178	0.9822	0	0.0069	0.0085	0.9846	0.3881	0.0087	44.75	34.149
0.0801	0.9199	0	0.0311	0.0166	0.9524	0.3879	0.0180	21.52	30.645
0.1791	0.8209	0	0.0723	0.0178	0.9099	0.4037	0.0217	18.61	39.909
40 °C									
0.0623	0.9377	0	0.0314	0.0142	0.9543	0.5044	0.0152	33.22	80.224
0.1422	0.8578	0	0.0710	0.0228	0.9062	0.4991	0.0266	18.77	48.333
50 °C									
0.0180	0.9820	0	0.0077	0.0120	0.9803	0.4278	0.0122	35.11	-
0.0800	0.9200	0	0.0294	0.0111	0.9595	0.3681	0.0120	30.55	26.559
0.1406	0.8594	0	0.0620	0.0125	0.9255	0.4413	0.0145	30.36	40.854
60 °C									
0.0145	0.9855	0	0.0068	0.0185	0.9746	0.4735	0.0188	25.19	62.805
0.0617	0.9383	0	0.0276	0.0165	0.9559	0.4469	0.0176	25.36	24.27
0.1422	0.8578	0	0.0615	0.0148	0.9238	0.4322	0.0172	25.12	54.195

Table 4.24: Experimental mole fractions of the liquid-liquid extraction for the ternary system of toluene (x_1) + heptane (x_2) + DES 21 (x_3) at different temperatures.

Hydrocarbon-rich phase			DES-rich phase			β_{tol}	β_{hep}	S	η
Tol	Hep	DES	Tol	Hep	DES				
x_1	x_2	x_3	x_1	x_2	x_3				
30 °C									
0.0179	0.9821	0	0.0070	0.0158	0.9772	0.3912	0.0161	24.36	51.555
0.0790	0.9210	0	0.0320	0.0828	0.8852	0.4048	0.0899	4.50	50.909
0.1762	0.8238	0	0.0681	0.0114	0.9205	0.3866	0.0138	28.05	51.328
40 °C									
0.0134	0.9866	0	0.0065	0.0264	0.9671	0.4830	0.0268	18.02	29.417
0.0606	0.9394	0	0.0291	0.0228	0.9481	0.4808	0.0243	19.80	45.266
0.1390	0.8610	0	0.0685	0.0354	0.8961	0.4926	0.0412	11.97	31.165
50 °C									
0.0135	0.9865	0	0.0077	0.0163	0.9760	0.5686	0.0165	34.40	58.176
0.0798	0.9202	0	0.0309	0.0125	0.9566	0.3878	0.0135	28.65	57.475
0.1377	0.8623	0	0.0730	0.0683	0.8588	0.5297	0.0792	6.69	62.245
60 °C									
0.0134	0.9866	0	0.0067	0.0743	0.9190	0.4955	0.0753	6.58	51.156
0.0638	0.9362	0	0.0377	0.0210	0.9413	0.5911	0.0225	26.32	41.257
0.1419	0.8581	0	0.0681	0.0193	0.9127	0.4797	0.0225	21.35	26.735

4.2.3.1 Consistency of the experimental data

Hand's correlation was applied to ascertain the experimental data, as mentioned in subsection 3.2.2. Equation 3.5 was used to correlate the experimental data. Table 4.25 shows the fitting parameters and the correlation factor, R^2 .

As can be seen in Table 4.25, a satisfactory fitting is achieved for most of the systems. The values of the correlation factor exceeded 0.99 in these systems, indicating the degree of consistency of the experimental data.

4.2.3.2 Effects of various factors on the separation

The effects of several factors on the separation of aromatics were investigated. The results of the experiments presented in Tables 4.19 – 4.24 are discussed under the effect of temperature, effect of the concentration of toluene in the feed and effect of the type of the DES.

a) Effect of temperature

The effect of temperature on the separation factors, i.e. the distribution coefficient β_{tol} , selectivity S and efficiencies of separation η , is clear for DES 16. The increase in temperature has increased the values of the distribution coefficient noticeably. As the distribution coefficient is low at 30 and 40 °C, it is significantly increased up to 8 folds at 50 °C, while an increase in temperature to 60 °C lowers the value of the distribution coefficient again. On the other hand, the corresponding values of the selectivity at 50 °C and 60 °C are lower than the value gained at 40 °C. It is noticed in Table 4.19 that 40 °C and 50 °C are the best out of the 4 different temperatures studied. The value of the separation efficiency is higher at 40 °C than that for 30 °C. It can be concluded that 40 °C is an optimum for this system, i.e. toluene + heptane + DES 16. This is lower than the temperature usually used for sulfolane as industrial solvent in the aromatics + aliphatics + sulfolane systems (Meindersma, 2005).

Table 4.25: Constants of the Hand correlation and the correlation factor (R^2)

c	d	R^2
{Toluene + Heptane + DES 16} at 30°C		
-0.1263	-3.1467	0.8956
{Toluene + Heptane + DES 16} at 40°C		
0.5812	1.1854	0.7811
{Toluene + Heptane + DES 16} at 50°C		
0.6033	0.9234	0.8961
{Toluene + Heptane + DES 16} at 60°C		
1.1056	4.8328	0.9977
{Toluene + Heptane + DES 17} at 50°C		
0.7948	2.7777	0.9974
{Toluene + Heptane + DES 17} at 60°C		
1.0797	4.9636	0.9989
{Toluene + Heptane + DES 18} at 50°C		
0.6308	2.0544	0.3147
{Toluene + Heptane + DES 18} at 60°C		
1.106	5.6628	0.998
{Toluene + Heptane + DES 19} at 30°C		
1.2375	4.4633	0.998
{Toluene + Heptane + DES 19} at 40°C		
0.9312	2.6654	0.9961
{Toluene + Heptane + DES 19} at 50°C		
1.0715	3.6413	0.9989
{Toluene + Heptane + DES 19} at 60°C		
1.0297	3.1907	0.996
{Toluene + Heptane + DES 20} at 30°C		
1.0242	3.5599	1
{Toluene + Heptane + DES 20} at 40°C		
1.356	5.0844	0.9928
{Toluene + Heptane + DES 20} at 50°C		
1.0349	3.5748	0.9929
{Toluene + Heptane + DES 20} at 60°C		
1.0716	3.706	0.9998
{Toluene + Heptane + DES 21} at 30°C		
1.0381	3.8164	0.9949
{Toluene + Heptane + DES 21} at 40°C		
1.0189	3.4746	1
{Toluene + Heptane + DES 21} at 50°C		
1.0536	3.6825	0.9695
{Toluene + Heptane + DES 21} at 60°C		
1.0476	3.5713	0.9908

The system of toluene + heptane + DES 17 has better selectivity at 60 °C than 50 °C, in contrast with the system toluene + heptane + DES 18. Tables 4.20 and 4.21 show that

the distribution coefficient and the selectivity at 60 °C are generally higher than the corresponding the distribution coefficient and selectivity at 50 °C for DES 17. However, the opposite is true for DES 18, whereby the selectivity reaches 65.829 at low aromatics concentration and at 50 °C. Values of separation efficiencies are also higher at 60 °C than at 50 °C for DES 17 but the distribution coefficient is generally better at 50 °C.

Tables 4.22, 4.23 and 4.24 show the experimental results for DESs where Sulfolane is the HBD. Table 4.22 shows the results for the system toluene + heptane + DES 19. This system does not show any particular trends for the selectivity or the distribution coefficient. While 30 °C is the best temperature for the selectivity, the distribution coefficient is at its highest values at 60 °C and the separation efficiency is highest at 40 °C. Table 4.23 shows that 40 °C is the optimum temperature for applying DES 20 in the system toluene + heptane + DES 20. All three separation factors, i.e. the distribution coefficient β_{tol} , selectivity S and efficiencies of separation η are at their highest values at 40 °C. While for DES 21, it is observed in Table 4.24 that at 50 °C, the distribution coefficient is reaching 0.53 and 0.569. These are higher values than all the values for the distribution coefficient in this system, except one value at 60 °C. The values of the selectivities at 50 °C are also higher than the other values at 30 °C, 40 °C and 60 °C. Furthermore, the separation efficiency at 50 °C is higher than that at other temperatures. It can be concluded that 50 °C is the optimum temperature for this system.

b) Effect of the concentrations of toluene in the feed

Various studies (Domanska et al., 2007, Meindersma et al., 2005, and Letcher and Reddy, 2005) have reported that the values of the distribution coefficient and the selectivity tend to decrease with increasing aromatics concentrations in the feed stream. In general, the results obtained from the present work followed the same trend. The values of the distribution coefficient decreases with increasing aromatics concentration for DES

16 at all temperatures and similarly the values of the selectivity follow the same trend with increasing concentration. With the exception of experiments at 50 and 60 °C, selectivities values trend is different (Table 4.19). DES 17 has a similar trend of decreasing selectivity, while for the distribution coefficient it is increasing with decreasing aromatics concentration at 50 °C only, as can be seen in Table 4.20. DES 18 is the last of the DESs synthesized from ethylene glycol as HBD. The values of the selectivities are not following the common trend when the temperature is 50 °C, but only at 60 °C the values of the selectivities decrease with increasing aromatics concentration.

c) Effect of type of DES

The results of the extraction are described according to the effects of the salt:HBD mole ratio to make a DES and the HBD involved.

Sulfolane as a HBD has good influence on both the distribution coefficient and the selectivity. DESs 19, 20 and 21 that incorporate Sulfolane in their structures resulted in selectivity of up to 60 with distribution coefficient of more than 1 at salt:HBD mole ratio of 1:6 and at a temperature of 50 °C. Other selectivity achieved with this HBD was up to 44 and distribution coefficient of more than 0.565 was achieved at 30 °C. Increasing this ratio to 1:8 had a negative effect on the distribution coefficient and the selectivity. At 1:8 mole ratio, the selectivity dropped to a maximum value of 34.397 at 50 °C and minimum of 4.504 at 30 °C. This suggests that the increased amount of sulfolane has no benefit but worsen the separation capability of the DES. In Subsection 4.1.1 the method of determining the eutectic point of a salt + HBD mixture was described. It was also shown that this eutectic point should exhibit DES with the minimum melting temperature possible for this mixture. In the case of the mixture of ethyltriphenylphosphonium iodide + sulfolane, the salt:HBD mole ratio of 1:6 could be the eutectic ratio and this explains the better separation performance at this ratio.

Ethylene glycol as a HBD for the same salt, i.e. ethyltriphenylphosphonium iodide, showed the best separation performance in terms of the distribution coefficient and the selectivity at a salt:HBD mole ratio of 1:10. In this case, the selectivity reached slightly above 65 at 50 °C and above 25 at 60 °C, with distribution coefficient of 0.223 and 0.089, respectively. In comparison to salt:HBD mole ratios of 1:6 and 1:8, 1:10 ratio was superior as the best selectivity they showed was slightly above 37 with distribution coefficient of 0.124 at 40 °C for the 1:6 ratio.

4.2.3.3 Analysis of the distribution coefficient and the selectivity

Most of the DESs showed high distribution coefficients and selectivities under different conditions in comparison to sulfolane as conventional solvent. The distribution coefficient for sulfolane was given as 0.398 at 25 °C, 0.415 at 40 °C and 0.395 at 50 °C (Tripathi et al., 1975), even though the validity of the values given at 25 °C are questionable as sulfolane is solid at this temperature and only melts around 28 °C. The selectivity reported by Tripathi and co-workers was found to be slightly above 44, 37 and 28 at 25 °C, 40 °C and 50 °C respectively. In the present work, the selectivity of DES 20 at 40 °C reached 60 and at 50 °C it is 35.11, while for DES 18 the selectivity at 50 °C reached 65. This proves the superiority of the studied DESs made from ethyltriphenylphosphonium iodide + sulfolane or ethylene glycol to sulfolane itself. The added advantage has been mentioned in Subsection 4.2.1, i.e. the sulfolane and ethylene glycol were absent in the raffinate layer which means the process did not experience solvent loss.

A comprehensive study for the distribution coefficients and the selectivities achieved for DESs 16 – 21 is presented here:

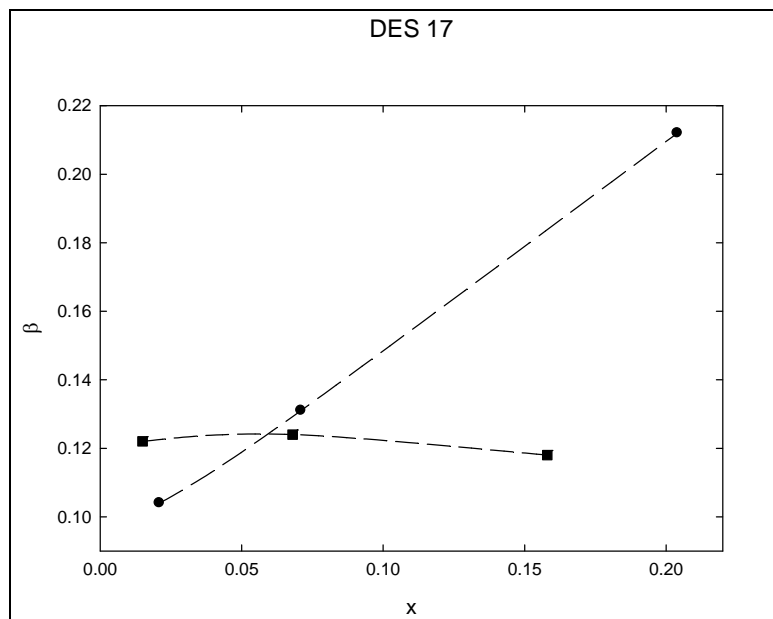
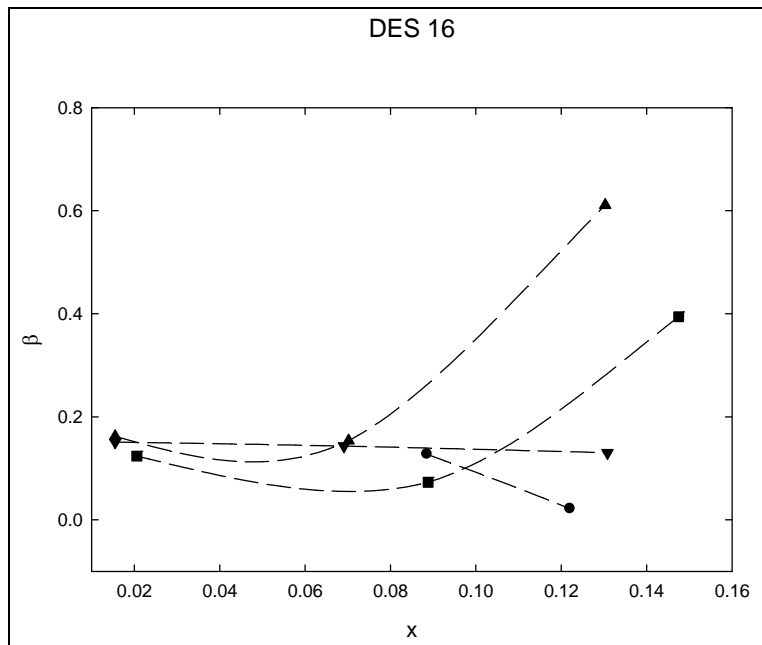
a) Distribution coefficient, β

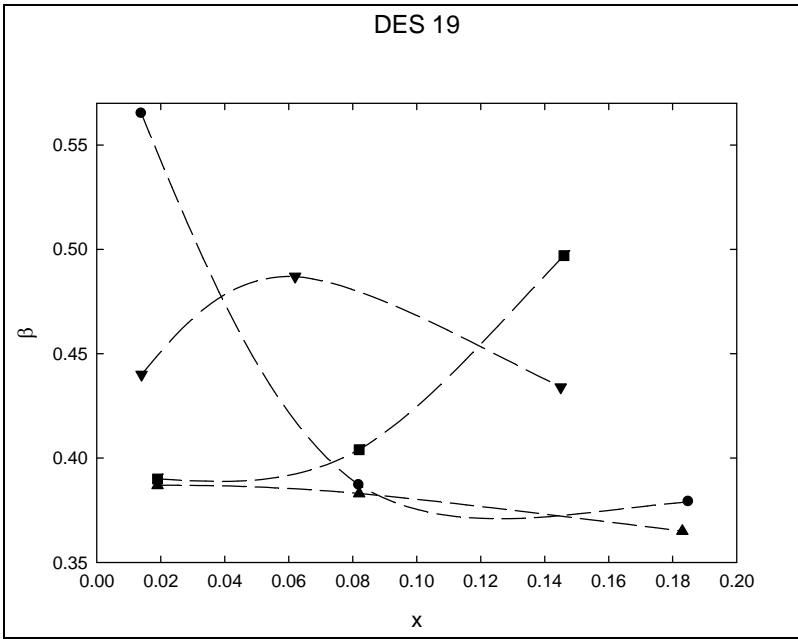
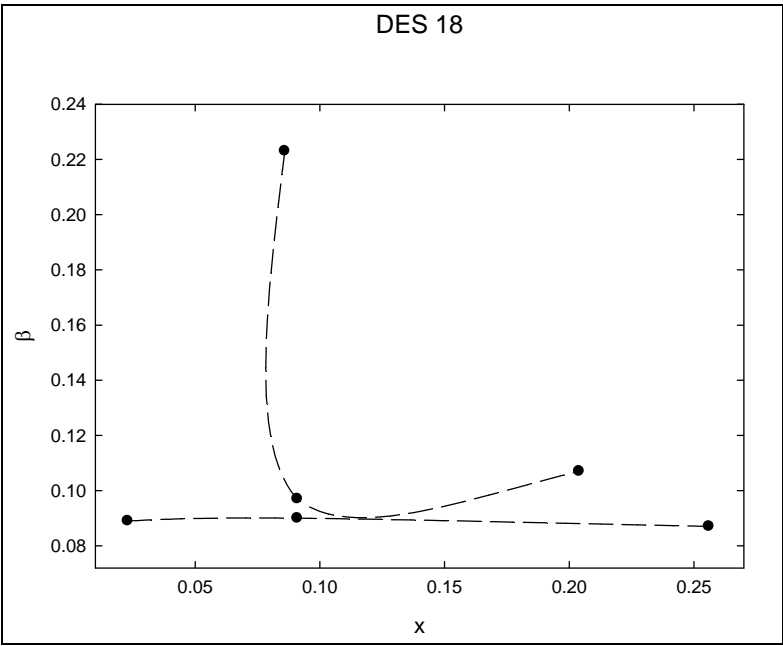
Figure 4.22 shows the distribution coefficients dependent on the composition of toluene in the raffinate layer at different temperatures. In most of the cases, the distribution coefficient is decreasing when the composition is increasing in the raffinate layer. There is one exception for DES 17 at 50 °C, whereby the distribution coefficient increases from slightly above 0.1 to around 0.21 with increasing toluene composition. In other cases such as DESs 18, 19, 20 and 21, a fluctuation in the distribution coefficient could be noticed from the plots in Figure 4.22.

An explanation for the decrease in the distribution coefficient with the increase in the aromatics composition was given by Holbrey et al. (2003) and was discussed in Subsection 4.2.2.

The distribution coefficients illustrated in Figure 4.21 show unique results for the above-mentioned DESs. They illustrate high values of the distribution coefficient in comparison to other solvents in the literature. From the work of Meindersma (2005), it can be seen that the average distribution coefficient within a temperature range from 40 °C to 75 °C is approximately 0.3, while in the present work it is shown that a higher distribution coefficient is achieved by employing DESs. This finding may indicate a very good potential for the applicability of these DESs as solvents for aromatics separation. Further work will be required for the optimization of the operating conditions in the extraction process.

Among the six DESs that are studied, DES 20 which was synthesized by mixing ethyltriphenylphosphonium iodide + sulfolane at a salt:HBD molar ratio of 1:6 showed the best distribution coefficient with a value of 1.046, while the lowest distribution coefficient was that of DES 16 synthesized from mixing ethyltriphenylphosphonium iodide + ethylene glycol at salt:HBD of 1:6.





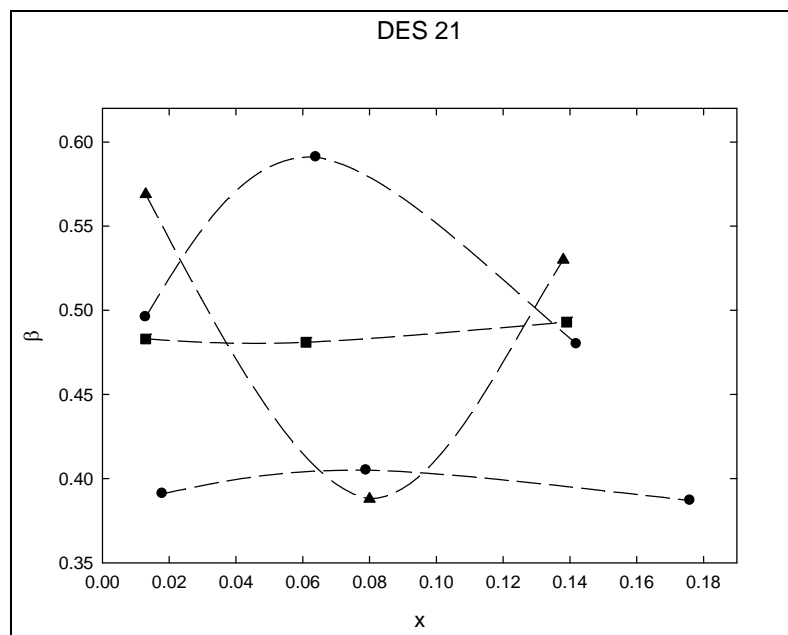
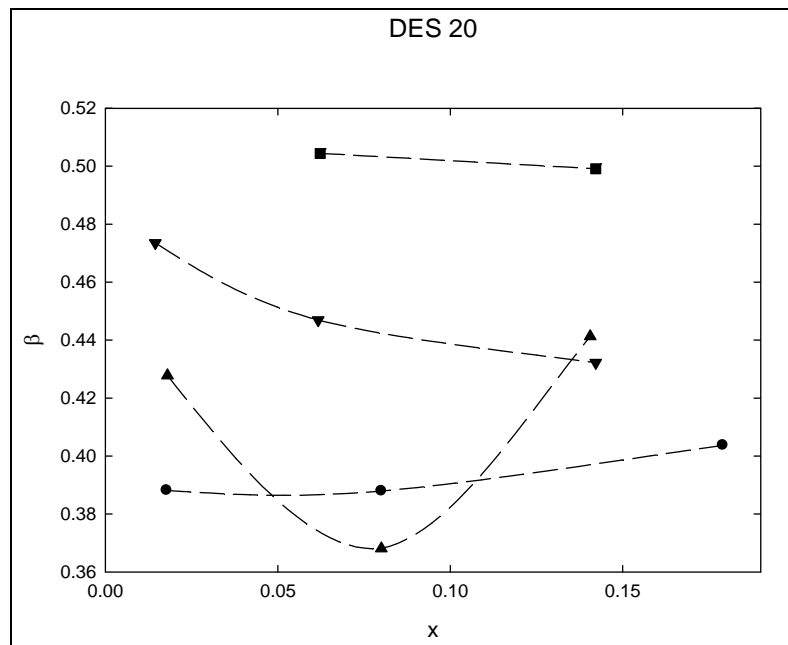


Figure 4.22: The distribution coefficient β dependent on the composition of toluene in the raffinate layer x for DESs 16, 17, 18, 19, 20 and 21. ● is 30 °C, ■ is 40 °C, ▲ is 50 °C and ▼ is 60 °C.

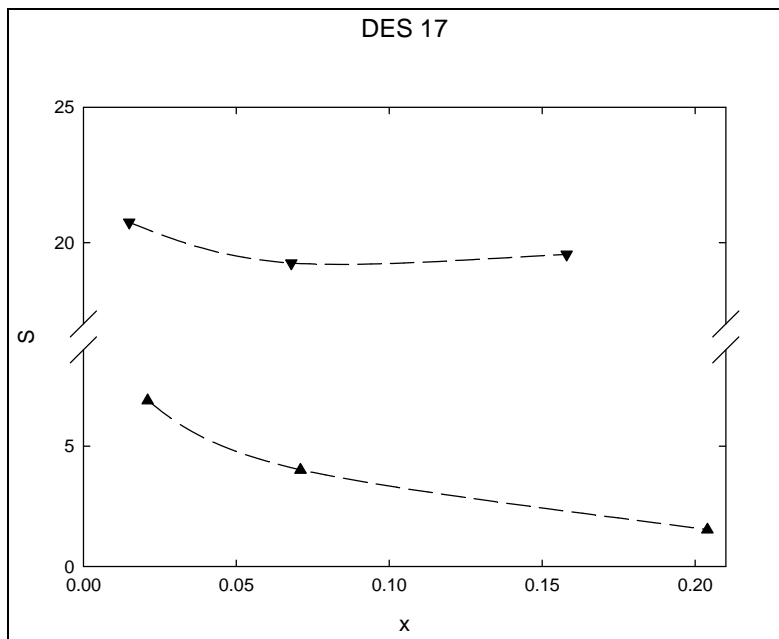
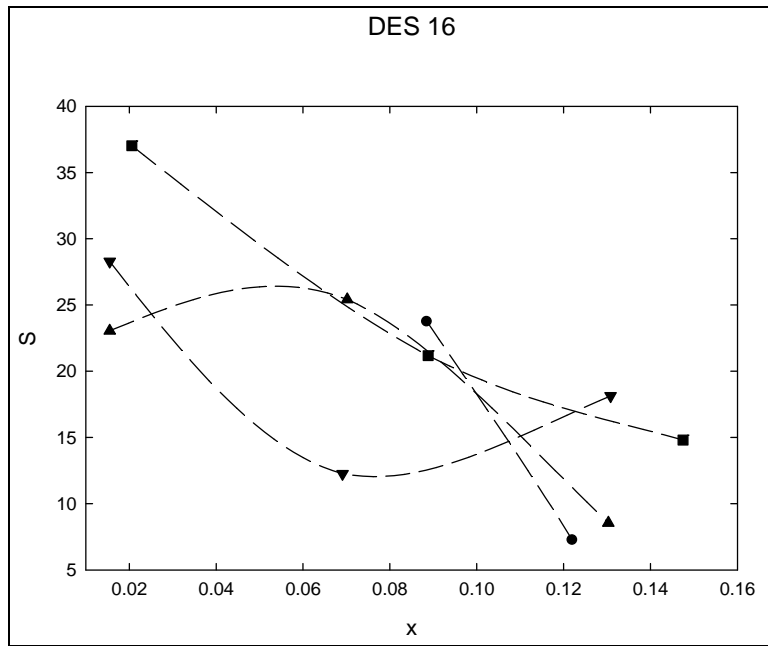
It is also evident from Figure 4.22 that increasing the temperature has a slight effect on the distribution coefficient except for the cases of DES 19 and DES 21. It can be

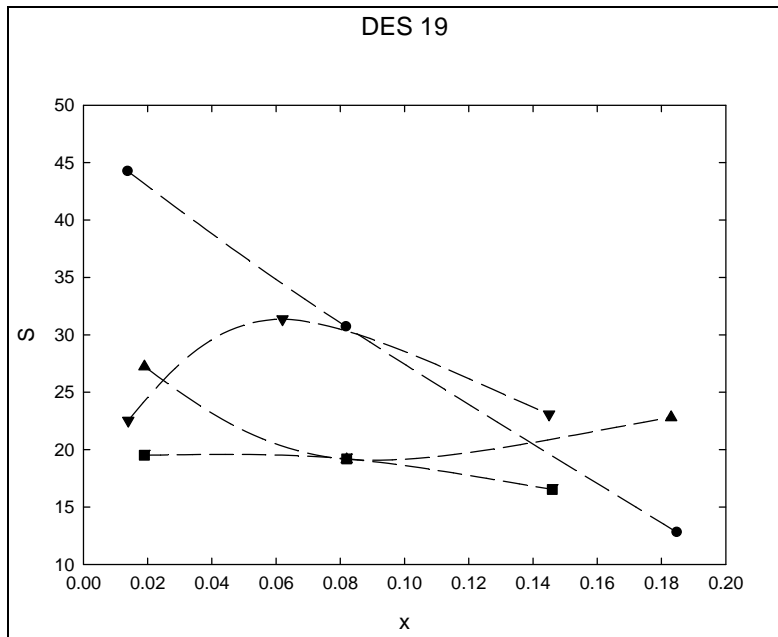
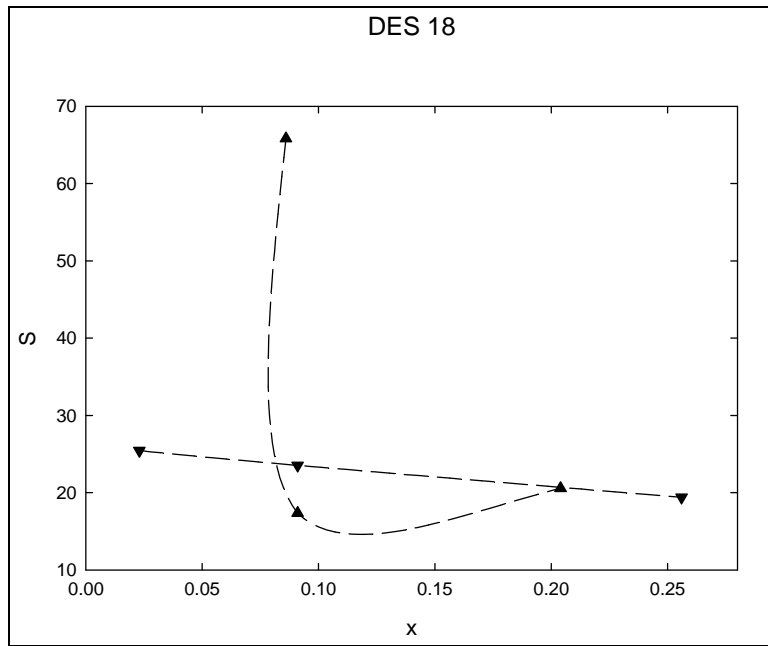
concluded that the application of these DESs for the separation of aromatics is possible at low temperatures.

b) Selectivity, S

Figure 4.23 shows profiles of selectivity dependent on the composition of toluene in the raffinate layer. By definition, the selectivity S is a product of dividing β_{tol} on β_{hep} , which was given by Eq. 3.3. Thus, decreasing the toluene's distribution coefficient results directly in decreasing the selectivity. As the toluene starts to appear in lesser amount in the extract layer over the increasing composition in the raffinate layer, the likelihood of the solvent (in this case DES) to selectively dissolve toluene decreases as well. In this case, the lowest S is for the lowest β_{tol} and vice-versa.

The best selectivity is found for DESs 18 and 20 at low concentration of aromatics in the raffinate layer. A selectivity value of more than 60 is higher in comparison to the reported values (Tripathi et al., 1975).





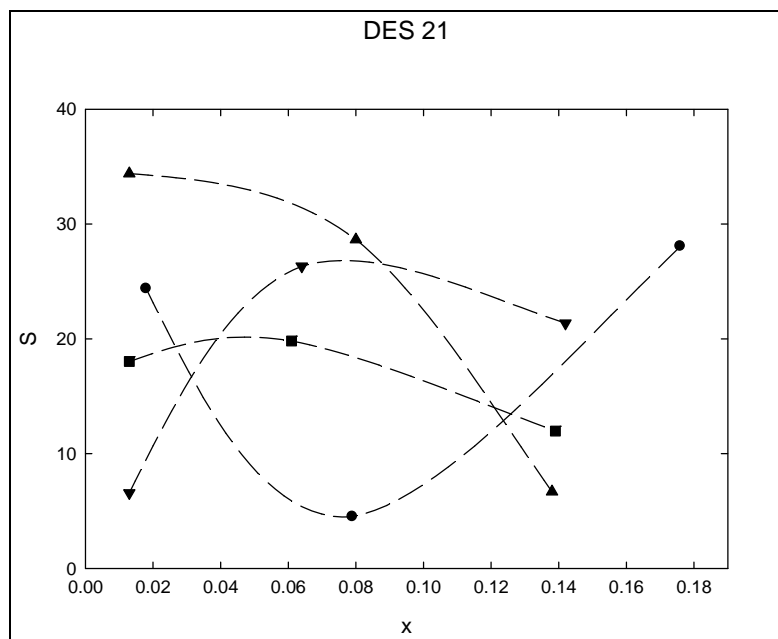
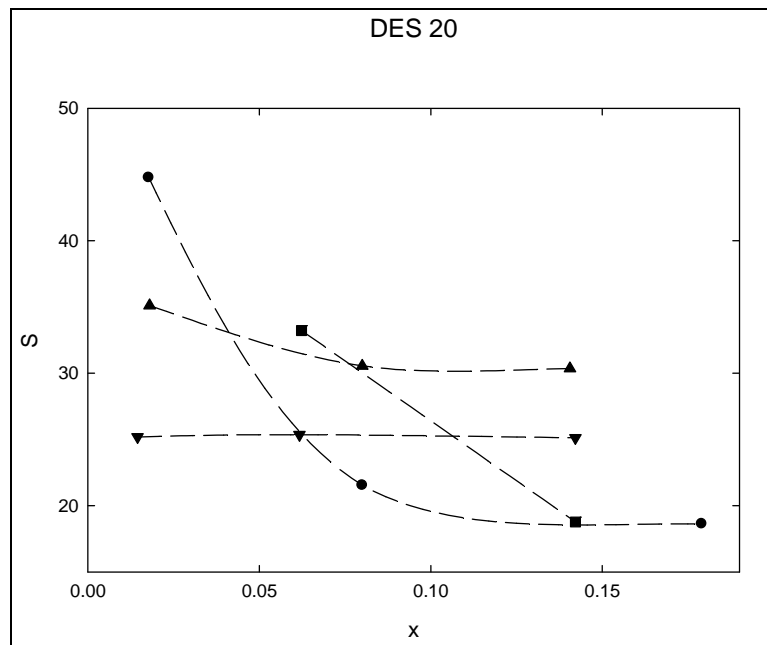


Figure 4.23: Selectivity S dependent on the composition of toluene in the raffinate layer x for DESs 16, 17, 18, 19, 20 and 21. \blacktriangledown is 30 °C, \blacktriangle is 40 °C, Δ is 50 °C and \circ is 60 °C.

c) Liquid-liquid equilibrium (LLE) data correlation

LLE calculations described in Chapter 3 were applied in Subsection 4.2.2.2.

Tables 4.26 and 4.27 illustrate the values of the binary interaction parameters. The temperature dependence is also neglected for the fitting parameters. The parameters optimized earlier using tertabutylphosphonium bromide-based DESs as solvent in Subsection 4.2.2.2 for DESs 9 and 13 are maintained for the calculations of DESs 16 – 21 here.

In the fitting step, different DESs were distinguished according to the molecules of their HBD. Those with ethylene glycol as HBD, i.e. DESs 16, 17 and 18 were assigned to the same group and the remaining DESs with sulfolane as HBD allocated to another group. The interaction between these groups of DESs with toluene or heptane was initialized according to the previous results.

As shown in Tables 4.26 and 4.27, the interaction parameters between DESs belonging to the same group with toluene (τ_{13} and τ_{31}) and heptane (τ_{23} and τ_{32}) are found to be constant. The third non-randomness parameter, i.e. α_{ij} , varies linearly with the number of moles of HBD within the same group, as shown in Figure 4.24. This variation is more significant with the ethylene glycol-based DESs than with the sulfolane-based DESs.

The parameter α in the NRTL model is a measure of the non-randomness of the mixture. When α is zero, the mixture is said to be completely random (ideal solution). This parameter gives an additional degree of freedom to the NRTL equation. It makes it applicable to a large variety of binary and ternary mixtures and allows a very good prediction of LLE.

Tassios (1976) has eliminated any physical significance attributed to α , and has stated that α is mainly an empirical parameter obtained by fitting the experimental data and may not follow the rules set out by Renon and Prausnitz (1968). Additionally, he has showed that $\alpha_{ij} = -1$ works in many cases.

However, when the NRTL equation was derived, Renon and Prausnitz have suggested a relationship between the non-randomness parameter and Guggenheim's quasichemical approximation (Renon and Prausnitz, 1968). He has shown that α is related to the inverse of the coordination number, i.e. $1/z$, that appeared in Guggenheim's expression. Since the coordination number was typically found to be within the range of 6 – 12, the non-randomness parameter was expected to vary in the range 0.1 – 0.3 (revised to 0.2 – 0.47 later on).

Here, the non-randomness parameter is subjected to optimization between 0.05 and 0.5. The results obtained in Tables 4.26, 4.27 and Figure 4.24 show that there is a relationship between the molar composition of DES and the third non-randomness parameter which implies the possibility of using the NRTL model in this case as a predictive model for interpolation and extrapolation within a certain limit.

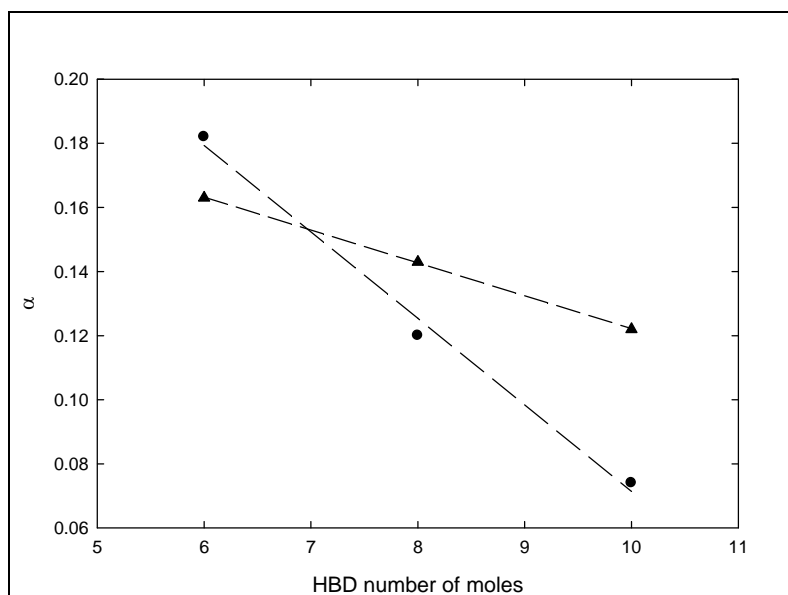
Figure 4.25 shows the ternary diagrams of both experimental and calculated tie-lines for all the 6 systems investigated at 60 °C only. It is obvious that the calculated concentrations are in a good agreement with the experimental concentrations.

Table 4.26: NRTL binary interaction parameters for the ternary system toluene (1) + heptane (2) + DES 16 or DES 17 or DES 18 (3).

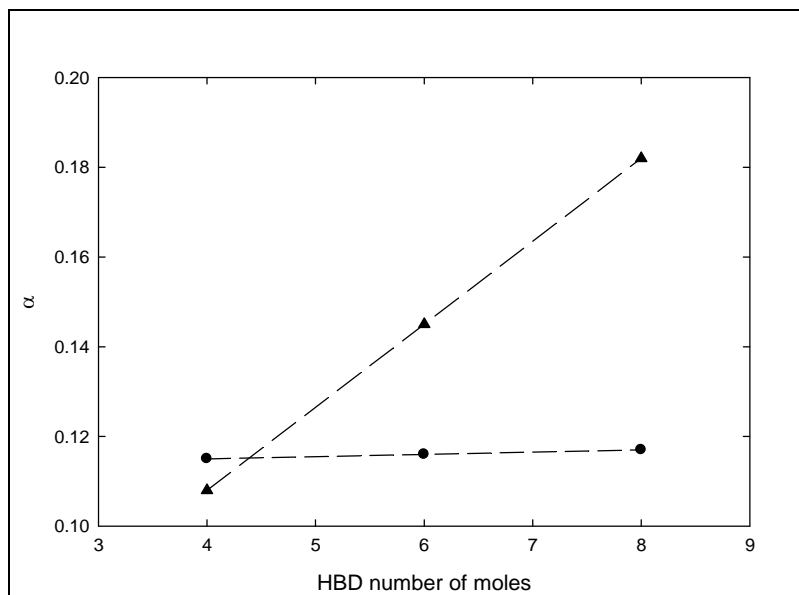
i	j	τ_{ij}	τ_{ij}	α_{ij}		
1	2	22.02	-38.84	0.39		
				3=DES 16	3=DES 17	3=DES 18
1	3	1773.85	-429.55	0.182	0.12	0.074
2	3	3134.15	802.67	0.163	0.143	0.122
Criterion				7.80E-04	6.65E-04	1.19E-05

Table 4.27: NRTL binary interaction parameters for the ternary system toluene (1) + heptane (2) + DES 19 or DES 20 or DES 21 (3).

i	j	τ_{ij}	τ_{ij}	α_{ij}		
				3 \equiv DES 19	3 \equiv DES 20	3 \equiv DES 21
1	2	22.02	-38.84	0.39		
1	3	1426.74	-578.34	0.115	0.116	0.117
2	3	3128.4	616.88	0.108	0.145	0.182
Criterion				6.59E-05	1.14E-05	2.27E-04

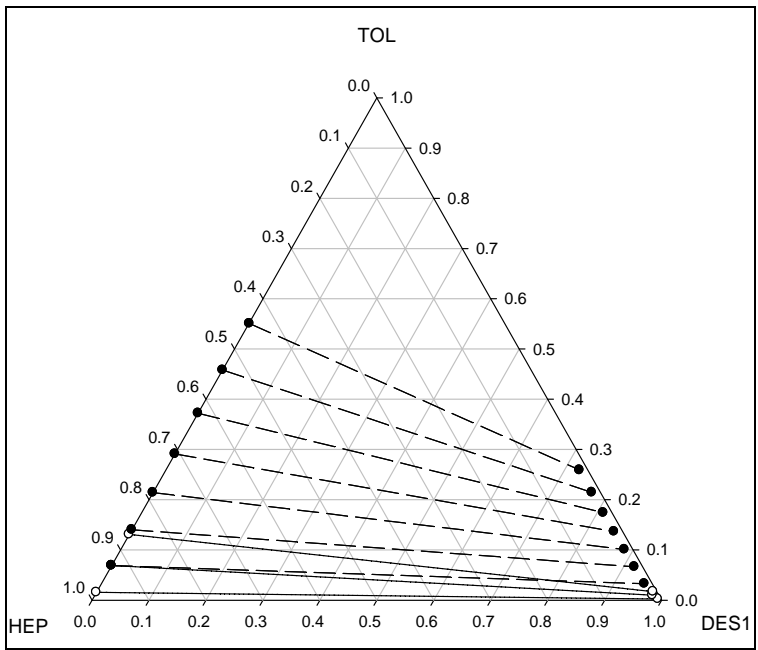


a

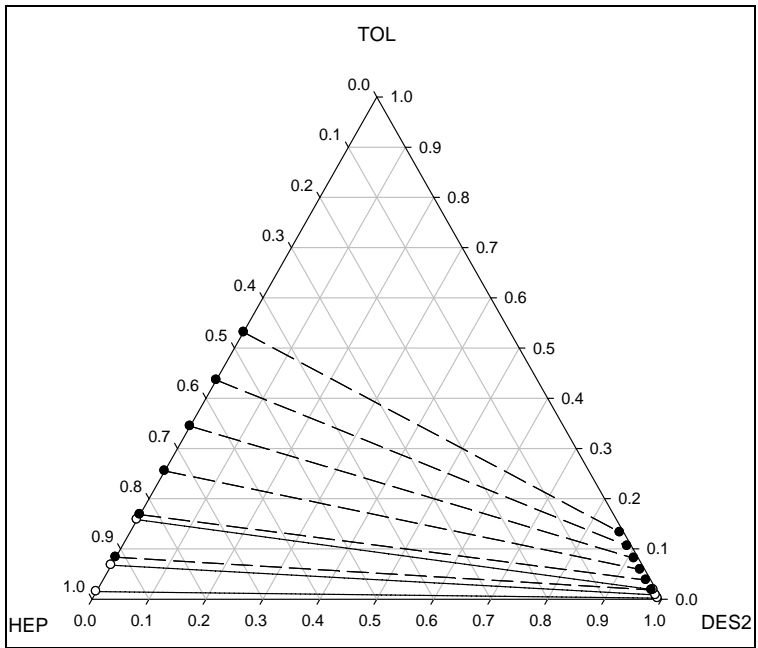


b

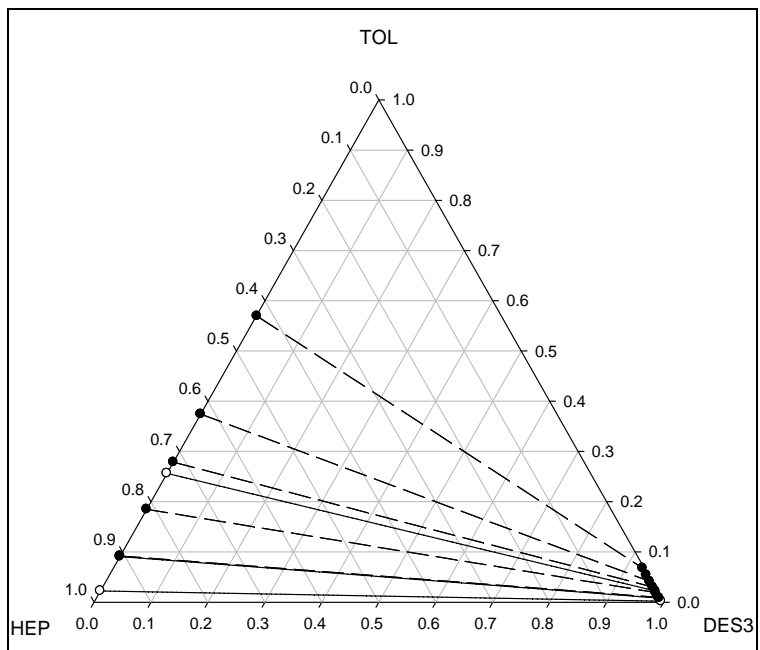
Figure 4.24: Variation of the non-randomness parameter α with the number of moles of the HBDs in DESs. a is ethylene glycol and b is sulfolane.



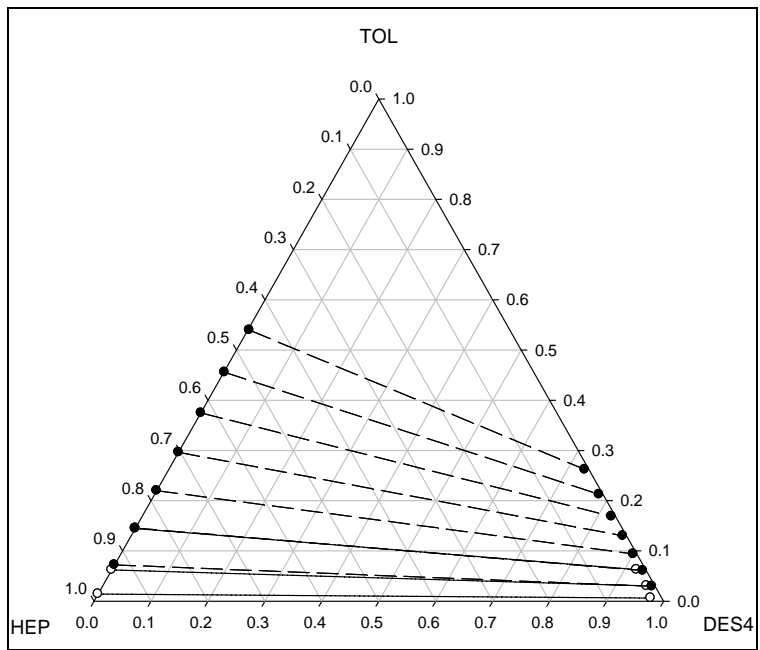
a



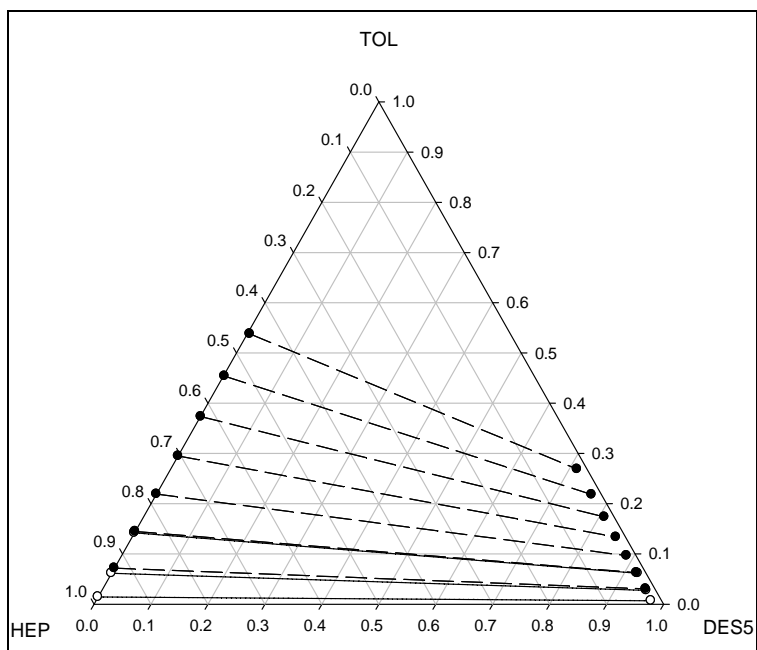
b



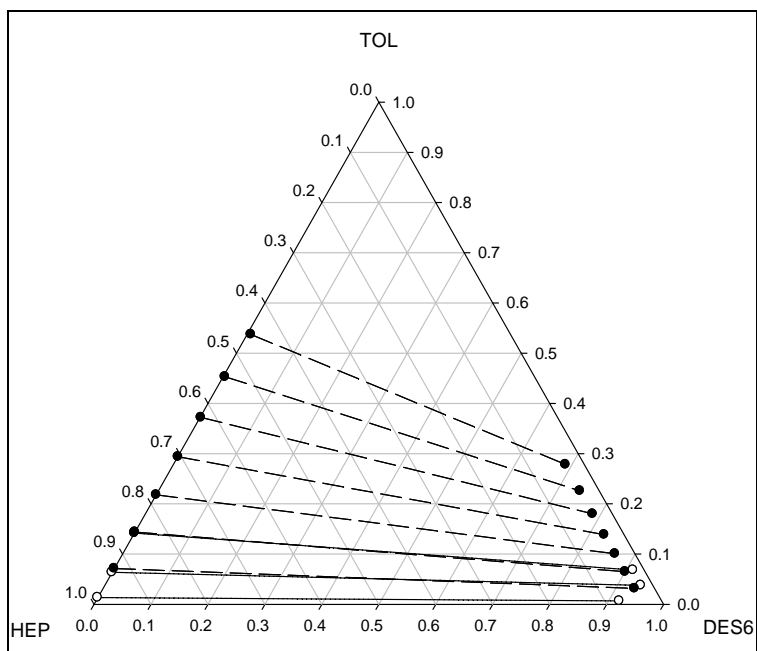
c



d



e



f

Figure 4.25: Experimental and calculated ternary compositions in mole fractions of the ternary systems of toluene + heptane + DESs 16 (a), 17 (b), 18 (c), 19 (d), 20 (e) and 21 (f) at 60 °C. Solid lines indicate experimental tie-lines and dashed lines indicate calculated data by the NRTL model.

CHAPTER V

CONCLUSIONS

Throughout the present investigation, twenty one deep eutectic solvents (DESs) were synthesized. Some of the DESs were characterized and they were employed in liquid-liquid extraction of aromatic hydrocarbons from mixtures of aromatic and aliphatic hydrocarbons. The following conclusions were drawn from the promising results of the initial investigations that were carried at at laboratory-scale experiments.

5.1 DESs were produced at high purity using simple synthesis procedure and mild conditions

DESs were easily synthesized. The synthesis procedure did not require sophisticated equipment; it only involved mixing a salt and a hydrogen-bond donor (HBD) with moderate heating. As the mixing of these two components did not involve a chemical reaction but only formation of hydrogen bonds, the purity of the produced DES was totally dependent on the purity of the salt and the HBD. For this reason, the chemicals used were all of synthesis-grade.

The DESs in the present work were considered as novel DESs as they were not synthesized, characterized or employed previously.

5.2 DESs of different phosphonium salts were synthesized at different conditions

Methyltriphenylphosphonium bromide, benzyltriphenylphosphonium chloride, tetrabutylphosphonium bromide and ethyltriphenylphosphonium iodide as phosphonium salts were utilized to synthesize different DESs by mixing with various HBDs. The salt:HBD mole ratios by which the DESs were synthesized played a major role in determining the physical properties of the synthesized DESs.

The common aspect among all of the DESs is the technique of their synthesis. Some of the synthesis required magnetic stirring with moderate heating while others required mechanical stirring and higher temperatures for preparation. Through experience in conducting the experiments, it appeared that the types of salt and HBD were the main factors that determined the optimum temperature required. For instance, the use of benzyltriphenylphosphonium chloride as a salt and 2,2,2 trifluoroacetamide as a HBD required a high temperature of 95 °C and vigorous mechanical mixing of 700 rpm to cause the formation of a DES. On the other hand, for the salt methyltriphenylphosphonium bromide and the HBD ethylene glycol, 60 °C and 200 rpm were sufficient to produce a DES.

5.3 Some DESs possess favorable physical properties

Physical properties including melting temperature, density, viscosity, electrical conductivity, pH, refractive index and dissolved oxygen content were experimentally measured for some of the synthesized DESs. Some of these DESs were characterized to be low in melting temperatures, low in viscosities and high in electrical conductivities. All these are favorable physical properties.

The physical properties were measured for some DESs within different ranges of temperatures. The type of HBD was found to significantly influence the physical behavior of the DES. It was also found that the physical behavior of the DES is a function of temperature. The relationships between the temperature and the physical properties were either linear or non-linear. A linear relationship was used to fit the profiles of density, refractive index and pH while an exponential growth and exponential decay relationships, i.e. Arrhenius-like, were used to fit both the profiles of viscosity and conductivity.

5.4 DESs are suitable solvents for aromatic hydrocarbons' extraction from naphtha

The low viscosities and melting temperatures for most of the investigated DESs suggested the possibility of applying them as solvents in liquid-liquid extraction at low temperatures. Out of the twenty one DESs, DES 2 and DESs 7 – 21 were applied in the extraction of aromatic hydrocarbons from naphtha. DESs 2, 7 and 8 were used with mixtures of benzene and hexane as a model for naphtha while DESs 9 – 21 were used with mixtures of toluene and heptane.

DESs 2, 7 and 8 showed superior results in comparison to those of sulfolane and N-formylmorpholine. Of the three, DES 7 was the best in terms of separation factors, i.e. distribution coefficient and selectivity in comparison to sulfolane. On the other hand, DES 2 was better in separation factors in comparison to N-formylmorpholine.

In a previous work, sulfolane was applied at different temperatures to extract aromatics. The lowest reported temperature was 40 °C. However, in this work, DESs were applied at lower temperatures, i.e. as low as 27 °C, and the initial results before process optimization showed a promising separation capability for these DESs.

Temperature variation clearly affected the extraction by DESs 2, 7 and 8. The extraction at 45 °C was the best in terms of distribution coefficient and selectivity in comparison to lower temperatures.

Toluene/heptane mixtures were chosen as models of naphtha in the liquid-liquid extraction of aromatics using DESs 9 – 21. The experiments were accomplished under different temperatures and different salt:HBD mole ratios. These DESs showed higher distribution coefficients and selectivities at low concentrations of toluene than at high concentrations. This implied the possibility of applying these solvents in industry to remove traces of aromatics from naphtha prior to thermal cracking to produce ethylene.

The DESs synthesized from ethyltriphenylphosphonium iodide as a salt with sulfolane as a HBD were better than those synthesized with ethylene glycol. Three

different mole ratios of salt:HBD were used for this combination to give three DESs. Among these three ratios, 1:6 was the best in terms of distribution coefficient and selectivity. The results were compared with previous results from the literature. In numerous cases, the distribution coefficients and the selectivities for DESs 16 – 21 were higher than the corresponding distribution coefficients and selectivities for sulfolane. This confirms the high potential for the utilization of these DESs as solvents for liquid-liquid extraction of aromatics from naphtha to replace conventional solvents.

Ethylene glycol and sulfolane which are the HBDs of DESs 2, 7 – 21 were not detected in the raffinate layer after the liquid-liquid extraction experiments. This led to the conclusion that when ethylene glycol or sulfolane were employed in a DES, the interaction between the salt and HBD trapped the HBD in the DES in the extract layer, preventing the transfer at low concentrations to the raffinate phase. This is an important enhancement to the extraction process.

5.5 Experimental data were ascertained by Othmer – Tobias and Hand correlations

The reliabilities of the liquid-liquid extraction data for the two ternary systems were ascertained by applying the Othmer – Tobias and Hand correlations. For heptane + toluene + DES 9 and heptane + toluene + DES 13 ternary systems, the regression coefficients R^2 were close to unity in both correlations at 50 °C and 60 °C. This indicated the high consistency of the experimental data for these systems. With the exception of the case for 40 °C, the values of R^2 were 0.9613 and 0.976 for Othmer-Tobias and Hand correlations, respectively. The results indicated the high degree of consistency of the data. For the ternary systems of toluene + heptane + DES 16, toluene + heptane + DES 17, toluene + heptane + DES 18, toluene + heptane + DES 19, toluene + heptane + DES 20 and toluene + heptane + DES 21, only Hand's correlation was used

to correlate the experimental results at different temperatures. Only one ternary system showed a poor consistency as the value of R^2 was 0.3147.

5.6 The liquid-liquid phase equilibria was successfully modelled using the Non-Random Two Liquid (NRTL) model

NRTL model was used to perform liquid-liquid equilibrium calculations. Predicted compositions by NRTL and experimental compositions were compared by plotting both compositions in ternary diagrams. The diagrams showed very good agreements between the predicted compositions and the experimental ones in ternary systems of different DESs.

CHAPTER VI

RECOMMENDATIONS FOR FUTURE WORK

The recommendations for future work are as follows:

- 1- DESs attaining moderate to high selectivities towards the aromatics can be further investigated by varying the temperature, aromatic composition in the feed, extraction time, and salt:HBD molar ratio.
- 2- Sulfolane and ethylene glycol as HBDs can be further studied by employing them in DESs with other salts which have not been investigated here.
- 3- Pilot plant-scale experiments can be carried out to assess the applicability of the studied systems in continuous extraction process.
- 4- DESs of the present work can be applied for different combinations of aromatic/aliphatic mixtures for the purpose of investigating their ability to extract other aromatic hydrocarbons such as xylene and ethylbenzene.
- 5- Ammonium salts, such as choline chloride and N,N diethylammonium chloride, can be used to synthesize DESs with ethylene glycol and sulfolane and the resulting DESs can be applied in the same process.

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Appendix A

Research outputs

Conferences

- 1- Selection of green ionic liquid analogous for the removal of aromatic compounds from the feed stream of ethylene cracker. Mukhtar A Kareem, Amir A. Masran, Mohd M. Ibrahim, Farouq S. Mjalli, Mohd Ali Hashim, Inas M. AlNashef. 2nd international conference on environmental research and technology (ICERT 2010), Penang, Malaysia.
- 2- Selected physical properties of phosphonium based ionic liquids analogous. Mukhtar A. Kareem, Farouq S. Mjalli, Mohd Ali Hashim, Inas M. AlNashef. Symposium of Malaysian Chemical Engineers (SOMCHE 2010), Kuala Lumpur, Malaysia.
- 3- Phosphonium-based ionic liquids analogue as a novel solvent for aromatic/aliphatic hydrocarbon separation. Mukhtar A. Kareem, Farouq S. Mjalli, Mohd Ali Hashim, Inas M. AlNashef. 1st international conference on ionic liquids in separation and purification technology (ILSEPT 2011), Sitges, Spain.
- 4- Reducing energy consumption in ethylene production by green solvents' utilization. Mukhtar A. Kareem, Farouq S. Mjalli, Mohd Ali Hashim, Inas M. AlNashef, Fatemeh S. Ghareh Bagh. 3rd international conference on environmental research and technology (ICERT 2012), Penang, Malaysia.
- 5- Application of deep eutectic solvents based on ethylene glycol and sulfolane for the extraction of toluene from toluene/heptane mixtures. Mukhtar A. Kareem, Farouq S. Mjalli, Mohd Ali Hashim, Inas M. AlNashef, Fatemeh S. Ghareh

Bagh. 2nd international conference on process engineering and advanced materials (ICPEAM 2012), Kuala Lumpur, Malaysia.

Journal papers

- 1- Mukhtar A. Kareem, Farouq S. Mjalli, Mohd Ali Hashim, Inas M. AlNashef. (2010). Phosphonium-based ionic liquids analogues and their physical properties. *Journal of Chemical and Engineering Data*. 55, 4632–4637.
- 2- Mukhtar A. Kareem, Farouq S. Mjalli, Mohd Ali Hashim, Inas M. AlNashef. (2012). Liquid-liquid equilibria for the ternary system (Phosphonium based deep eutectic solvent-benzene-hexane) at different temperatures: a new solvent introduced. *Fluid phase equilibria*. 314, 52–59.
- 3- Mukhtar A. Kareem, Farouq S. Mjalli, Mohd Ali Hashim, Mohamed K.O. Hadj-Kali, Fatemeh S. Ghareh Bagh, Inas M. AlNashef. (2012). Phase equilibria of toluene/heptane with tetrabutylphosphonium bromide based deep eutectic solvents for the potential use in the separation of aromatics from naphtha. *Fluid Phase Equilibria*. 333, 47–54.
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Awards

- Best participating paper. 2nd international conference on process engineering and advanced materials (ICPEAM 2012), Kuala Lumpur, Malaysia.