EXTRACTION OF AROMATIC SOLVENTS FROM REFORMATES AND PAINT SOLVENT WASTES USING IONIC LIQUIDS

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ABSTRACT

The work conducted in this study comprised three aspects: syntheses, characterizations, and multi-component liquid-liquid extractions. The main objectives of the project were: (1) to evaluate the efficacy and efficiency of ionic liquids to extract aromatic components from catalytic reformates and paint solvent wastes, and (2) to validate the method(s) used in this project to qualitatively and quantitatively analyze the aromatic molecules (BTEX) in multi-component mixtures. Therefore, this research critically investigated the major effects of the chosen ionic liquids as extractive solvents for the recovery of BTEX components from model and industrial organic mixtures. The project was concerned with the nature of solvents currently used in most industries for the separation by extraction of aromatic hydrocarbons from non-aqueous or organic mixtures. Most solvents currently employed for this purpose are highly volatile; hence they contribute significantly towards environment pollution. In addition, the extraction efficiency of these conventional solvents is limited only to mixtures containing aromatic hydrocarbons of 20% or more. Furthermore, conventional solvents are organic compounds which are generally toxic, flammable, and expensive to recover or regenerate from extract phases due to methods which involve several steps. In addition, they demand high energy input for the distillation steps.

However, the properties of ionic liquids make them suitable alternatives for these conventional extraction solvents. The choice of the ionic liquids used in this project was informed by previous work of other researchers based on the parameters such as recyclability, selectivity and distribution coefficients. Aromatic hydrocarbons were easily separated from the extract phase through evaporation at low temperature under reduced pressure using a single step procedure. Most of the results reported in this study were obtained with regenerated ionic liquids. It focused mainly on the methods used for the solvent extraction of low to high concentration (0.5 – 25 %v/v) of aromatic components from reformate petroleum fractions and paint waste solvents. In addition, the methods

used in the analysis of aromatic components were evaluated for validity. According to the literature no such work was carried out by previous researchers.

The study targeted four ionic liquids, namely, 1-ethyl-3-methylimidazolium ethyl sulphate [EMIM][ESO_4], 1-ethyl-3-methylpyridinium ethyl sulphate [EMpy][ESO_4], 1-Butyl-1-methyl-2-pyrrolidonium bromide [BNMP][Br], and 1,1-Dimethyl-2-pyrrolidonium iodide [MNMP][I] in an attempt to address this concern. These ionic liquids were synthesized and characterized in our laboratories using previously accepted methods. After synthesis and purification, they were characterized by techniques including FTIR, ^{1}H-NMR, and ^{13}C-NMR. The densities and moisture content of both the synthesized and standard ionic liquids were also determined using density meters and Karl-Fischer apparatus, respectively.

The extractions were carried out on both the model and industrial mixtures using ionic liquids. Each ionic liquid was mixed with a target mixture in a water-jacketed vessel and then stirred vigorously at constant temperature achieved by a thermostatically controlled water-bath. After a selected period of time the operation was stopped and the resulting mixture was left to stand overnight to allow phase equilibration to be reached. The two phases were then separated and analyzed for the content of individual aromatic components in each phase using GC-FID calibrated with external standards of the components present in the mixtures being investigated.

According to the results obtained from the synthesis and characterization methods the percentages yield of ionic liquids were reasonably high (> 95%). In addition, spectral studies showed high purity with fewer traces of impurities based on the observed relative intensities. Results from GC-FID indicated a relatively lower concentration of aliphatic hydrocarbons in the extract phase. On the other hand, the concentrations of aromatic

components in the extract phase were relatively higher than those of aliphatic hydrocarbons. The results obtained from the three extraction stages showed the total recovery of greater than 50% for the aromatic components. This suggests that at least six extraction stages would be required in order to achieve a total recovery of 100% aromatic components which is an indication of good efficiency. Also noticeable was that the first extraction stages for all ionic liquids recovery values were much higher than those values obtained from successive stages which showed approximately the same extraction results. In most experiments, 1-ethyl-3-methylpyridinium ethyl sulphate gave higher recovery values than the other three ionic liquids. It was also noted that the recovery values obtained from the extractions performed on model mixtures of the entire concentration range (0.5 – 25%) of individual aromatic components did not show any significant difference. Proportional difference in recoveries occurred across the entire concentration range of model mixtures. The results also indicated that the solubility of aromatic hydrocarbons in the ionic liquids decreases in the order: benzene > toluene > ethyl benzene >xylenes. This phenomenon is attributed to a decrease in π-π, cation- π, cation-anion interactions occurring between the ionic liquid and each of the aromatic molecules in this order.

The recovery values for BTEX ranged from 80 to 120 % by volume for the three extraction stages. This is in line with results previous research studies carried out on liquid-liquid extractions involving ternary systems containing only one aromatic component in each mixture. Therefore this study shows that ionic liquids are capable extraction solvents for simultaneous recovery of the aromatic components from any organic mixtures containing low to high BTEX concentrations. In addition, the outcomes of this project have proved that ionic liquids are economically viable as potential extraction solvents since they can be easily recycled and reusable many times without any noticeable degradation. The results of this study are envisaged to make significant contributions to the current research efforts aimed at achieving greener environments and

minimization of global warming. The findings of this project are also geared to boost the economy of our country through job creation using economically viable methods.

DECLARATION

This thesis is being submitted to the Durban University of Technology for the degree of Doctor of Philosophy in Chemistry. I declare that this work is my own and has not been submitted before for any degree or examination to this or any other university or institution for this or any other degree or award

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LIST OF ABBREVIATION

[BNMP][Br]	1-Butyl-1-methyl-2-pyrrolidonium bromide
[MNMP][I]	1, 1-Dimethyl-2-pyrrolidonium iodide
[EMIM][ESO_4]	1-Ethyl-3-methylimidazolium ethyl sulphate
[EMpy][ESO_4]	1-Ethyl-3-methylpyridinium ethyl sulphate
^{1}H-NMR	Proton-1 Nuclear Magnetic Resonance
ATR	Attenuated Total Reflectance
BTEX	Benzene, Toluene, Ethylbenzene, Xylene isomers
^{13}C-NMR	Carbon-13 Nuclear Magnetic Resonance
D	Distribution Coefficient
E	Extract Phase
Engen	Engen Refinery
FTIR	Fourier Transform Infrared
FTIR-ATR	Fourier Transform Infrared Attenuated Total Reflectance
GC	Gas Chromatography
GC-FID	Gas Chromatography Flame Ionization Detector
HPLC	High Performance Liquid Chromatography
ILE	Ionic-Liquid Equilibrium
IL	Ionic Liquid
ILs	Ionic Liquids
LLE	Liquid-Liquid Equilibrium
R	Raffinate Phase

RTILs	Room Temperature Ionic Liquids
S	Selectivity
SAPREF	South African Petroleum Refinery
SMME	Small, Medium, and Micro Enterprises
TEG	Tetraethylene Glycol
UV/Vis	Ultraviolet/Visible
VOCs	Volatile Organic Compounds
VOSs	Volatile Organic solvents

1 CHAPTER ONE: INTRODUCTION

1.1 Overview

The majority of industrial liquid-liquid extractions of aromatic components are performed by volatile organic solvents (VOSs) [1,2,3]. These VOSs have detrimental effects such as air pollution on the environment [4]. Currently chemical industries are under considerable and enormously increasing pressure to reduce the detrimental impacts caused by volatile organic compounds such as aromatic hydrocarbons. The non-volatile nature of ionic liquids makes them suitable for large scale extraction processes. Ionic liquids therefore show great promise as potential replacements for volatile organic solvents in liquid-liquid extraction processes.

In most petroleum refineries aromatic hydrocarbons are extracted from gasoline mixtures by using sulpholane (SAPREF) or tetraethylene glycol (Engen, South Africa) as extraction solvents [5]. Both these organic liquids have very high boiling points; hence they are relatively non-volatile. However, the regeneration methods used for their recoveries are long since they involve multiple steps which make them relatively expensive [6]. On the contrary, the methods involved for the regeneration of ionic liquids are simple and short. These methods generally use a single step such as rotary evaporation under reduced pressure in the laboratory or flash distillation in chemical industries [7]. Flash distillation is a single stage distillation process that facilitates easy removal of volatile compounds from the product. In view of the above, ionic liquids become economically affordable. Generally a good ionic liquid should meet the following criteria [8]:

- It should interact effectively with targeted molecules.
- It should have relatively high selectivity and distribution coefficients.
- It should be available in reasonably pure form with relatively low moisture content.
- It should have relatively weaker intermolecular forces with molecules of interest.
- It should be easily separable from excess reactants and solvents.

The strong interaction between ionic liquids and aromatic components promotes effective and efficient recovery of the latter from various non-aqueous mixtures. High selectivity is an important property which causes ionic liquids to extract only the species of interest. Higher distribution coefficients will promote efficacy of extraction. In this context selectivity refers to the ability of ionic liquids to extract only aromatic components with very little components of aliphatic hydrocarbons. The distribution coefficient can be described as a quantitative measure of how aromatic hydrocarbons distribute between an ionic liquid-rich phase (extract phase) and an alkane-rich phase (raffinate phase). It is equally important that ionic liquids should be pure enough to prevent any interference that might jeopardize its efficacy. The interaction between the ionic liquid and the target components should be strong enough to promote efficient extraction. The intermolecular forces between ionic liquid and BTEX (benzene, toluene, ethyl benzene, and xylenes) molecules should be relatively weaker to allow easy separation of extracted components from the respective extract phases. For example, the addition of the ionic liquid to the aromatic/aliphatic mixtures will cause the molecules of the resulting mixture to distribute themselves between the two liquid phases, namely, the extract phase and the raffinate phase, thus allowing separation of aromatic components from aliphatic components.

In order to understand how ionic liquids work in extractions involving multi-component liquid-liquid equilibrium systems, it is necessary to know the various ways in which ionic liquids differ from molten salts. The latter are solids at low temperatures and liquids at high temperatures whereas the former remain liquids even at room temperatures. It is worth noting that molten salts are symmetrical with strong electrostatic forces between their oppositely charged ions, whilst ionic liquids are asymmetrical with weaker electrostatic forces between their cations and anions. As a result of this, ionic liquids require lesser energy to break their bonds as opposed to molten salts whose bonds break at higher energies [7,8].

Most common cations for ILs are dialkylimidazolium, dialkylpridinium, and alkylpyrrolidonium; anions are halides, alkylsulphates, alkylsulphites, nitrates, carbonates, alkyl phosphates, and alkyl hydrogen carbonates [8,9]. The bulky nature of asymmetric cations and a wide variety of possible anions results in a charge distribution that causes reduction of their solidification temperatures. Ionic liquids are often referred to as "green solvents" attributed to their advantages in eliminating environmental and toxicity problems among others [10]. Ionic liquids are easily regenerated and hence reusable. This is not the case with conventional extraction solvents [11].

Ionic liquids possess important properties such as low melting points (<100 °C), low to medium viscosity, high thermal and chemical stability, solubility in both organic and inorganic substances and, negligible vapour pressures [6]. These properties make ionic liquids very useful in areas such as separation technologies for the recovery of aromatic components from petroleum mixtures by liquid-liquid extractions. They also act as ‘green solvents’ due to their non-volatile nature and negligible vapour pressure. Knowledge of these properties is important in deducing the performance characteristics of ionic liquids for industrial applications.

Most researchers synthesized their own ionic liquids in order to minimize the costs of their research. Once the ionic liquid has been synthesized it is important to measure its properties by using established and approved characterization methods. Such properties include densities, viscosities, purity, percent yield, boiling and melting points, toxicity, thermal and chemical stability. A list of these properties is crucial for the selection of an ionic liquid for a specific application. The majority of ionic liquids are highly hygroscopic and therefore they should be stored in moisture free environments such as desiccators and thermostatically controlled ovens. In most cases, high moisture content impacts negatively on the extraction ability of most ionic liquids.

1.2 Hypothesis

The hypothesis for this study is “ionic liquids are more suitable as extraction solvents for the aromatic components from industrial organic mixtures and other related mixtures containing aliphatic and aromatic hydrocarbons than conventional solvents”. The choice of this hypothesis was attributed to the variable nature of ionic liquids which made them useful in many fields of chemistry. Their abilities to dissolve a variety of both organic and inorganic materials make ionic liquids superior to conventional organic solvents. One advantage is that some components, either organic or inorganic in nature, can be separated from ionic liquids through distillation. In this way ionic liquids are capable of being recycled and reused; thus enhancing cost effectiveness.

1.3 Areas of concerns and challenges

1.3.1 Research questions

This study was undertaken to address the following questions regarding the possibility of using ionic liquids in solvent extraction processes to replace conventional solvents:

- Can the selected ionic liquids separate aromatic hydrocarbons from aliphatic hydrocarbons on a micro scale?
- Can the ionic liquids, 1-ethyl-3-methylimidazolium ethyl sulphate and 1-ethyl-3-methylpyridiniu methyl sulphate, extract components from industrial multicomponent mixtures, such as reformates and paint solvent wastes?
- Are the ionic liquids, 1-ethyl-3-methylimidazolium ethyl sulphate and 1-ethyl-3-methylpyridinium ethyl sulphate, economically viable and easy to synthesize?
- To what extent can ionic liquids, 1-ethyl-3-methylimidazolium ethyl sulphate and 1-ethyl-3-methylpyridinium ethyl sulphate, recover aromatic hydrocarbons from industrial organic multicomponent mixtures?

1.3.2 Problem statements

The research questions raised above are related to the challenges associated with conventional methods that are currently used in the separation of aromatic hydrocarbons from industrial multicomponent mixtures, in particular reformates and paint solvent wastes. These concerns and challenges entail:

- The inability of conventional solvents such as sulpholane and tetraethyl glycol to extract low concentration aromatic hydrocarbons (< 20%).
- Organic compounds used as extractants are generally toxic and flammable
- Use of expensive and tedious methods for regeneration of conventional solvents
- High energy input is needed for separating aromatic hydrocarbons by using distillation methods.

In addition, methods of analyses for determining the concentrations of aromatic components in the extract and raffinate phases have not been validated to establish their degree of precision and accuracy.

1.3.3 Aims and objectives

In order to address the problems stated above, the underlying aims and objectives need to be met:

- Investigating the efficacy of ionic liquids for the recovery of aromatic hydrocarbons from paint solvent wastes.
- Investigating the efficiency of ionic liquids in the extractions of aromatic hydrocarbons from reformate mixtures.

- Investigating the effectiveness of ionic liquids in the recovery of aromatic hydrocarbons from reformate and paint solvent waste mixtures.
- Investigating the possibility of replacing conventional solvents with ionic liquids. for the extractions of aromatic components from industrial organic mixtures.
- Pollution reduction by minimizing waste disposal generated from paint plants.

1.3.4 Future benefits

In the light of the discussions in previous sections, the envisaged benefits of this project include:

- Cost saving by using self-synthesized and characterized ionic liquids.
- Utilization of less hazardous and ‘greener’ solvents in solvent extractions.
- Cost reduction by using recycled spent paint solvents.
- Using more efficient methods in solvent extraction processes for the recovery of paint solvents.
- Enhanced research capacity in areas involving ionic liquid extractions
- Cost saving in adopting solvent extraction techniques that will use lesser energy than conventional methods.

1.4 Strategic Solutions

This investigation was undertaken in order to explore various means of exploiting ionic liquids as for extracting green solvents and recovering aromatic components from non-aqueous mixtures. Most of the ionic liquids used in this project were synthesized in our laboratories for the purpose of minimizing the cost of this study. After isolation, each ionic liquid was purified, dried, and weighed for yield. This was followed by characterizing it using various techniques such FTIR and NMR for quality and purity checks. Since ionic liquids are non-flammable and non-volatile, they are referred to as 'green' solvents in many applications. The envisaged solvents are regarded as alternatives for the recovery of aromatic components from reformates and spent solvents in oil and paint manufacturing processes. It was for this reason that an investigation on the extraction of BTEX from reformates and other related non-aqueous industrial mixtures was undertaken. It was therefore necessary to first establish the amount of each aromatic component in the reformate samples for comparison with literature values. There was also a need to establish the presence and concentration of each aromatic component in spent paint solvent organic mixtures before any extraction process was performed.

Extraction operations were firstly carried out on model mixtures of selected concentration range of aromatic components. This exercise served as a bench mark for the calibration of the instruments and external standards were exploited for this purpose. All extractions performed on the unknown organic mixtures were monitored and verified by model mixtures as quality assurance and control standards. The resultant two phases were subsequently analyzed for the content of aromatic components using a GC-FID fitted with guard column or pre-column to prevent the ionic liquid from entering the analytical column.

Reformates are organic mixtures containing approximately 38% aromatic hydrocarbons which result from catalytic processing of naphtha in oil refinery [5]. Aromatic solvents find wide application in chemical industries as solvents for various purposes. In many cases, the spent solvents are discarded as waste effluent after first use, if there was no recovery unit for recycling. This study involved the application of ionic liquids as extraction solvents for BTEX components from reformates and spent solvents. This research project involved multi-component extraction systems for the simultaneous recovery of organic solvents from mixtures of aromatic and aliphatic solvents. The majority of related studies [12,13,14,15,16,17,18,19,20] focused mainly on liquid-liquid extractions involving ternary systems and very few involved quaternary systems and there are no reports on more complex multi-component systems using ionic liquids. However, there were very few quaternary, quinary, and multi-component systems reported on liquid-liquid extractions using conventional solvents such as sulpholane [21,22,23,24,25].

1.5 Plan of the Thesis

This thesis comprises five chapters that deal with specific tasks that describe the various aspects of the study. The chapters deal with the following headings: introduction, literature review, methods and materials, results and discussion as well as conclusions and recommendations. However, due to overlapping of certain parts of the investigation, allowance was made for integrated reporting. The content of each chapter is concisely described below to highlight its structure:

Chapter Two is based on searching previous publications on ionic liquids and its applications in separation technologies as ‘green extraction solvents’. It did this by looking at previous work which involved the study of the properties of ionic liquids, liquid-liquid extractions particularly those based on industrial organic mixtures containing mainly aromatic and aliphatic hydrocarbons. It focused solely on:

- Establishing the novelty of this research in the field of ionic liquids.
- Evaluating the current state of knowledge reported in the literature so that this research work is put into context and perspective.
- Finding out if there is any gap in knowledge that needs to be filled by this research study.

Chapter Three concentrates on issues that involved experimental work under the headings methods, procedures, materials reagents, apparatus and equipment. The main parts of this chapter include preparation of solutions and mixtures for extractions, synthesis and characterization of ionic liquids; particularly 1-ethyl-3-methylimidazolium ethyl sulphate and 1-ethyl-3-methylpyridiniumethyl sulphate, development and validation of ionic multi-component liquid-aromatic extraction methods, as well as evaluation of extraction phase mixtures.

Chapter Four deals with issues pertaining to the results and their discussions; and provides explicit information with regard to:

- The significance of characterization results in the extraction processes using ionic liquids as the extracting ‘green’ solvents for aromatic components.
- The effectiveness and efficiency of ionic liquids as the alternative extraction solvents based on the extent of BTEX recovery from various multi-component non-aqueous mixtures largely containing aromatic and aliphatic hydrocarbons.

- The benefits and quality of recycled and/or regenerated ionic liquids with respect to reusability and extractability.
- The significance of BTEX recovery from various sources with regard to their uses and positive influence on environmental pollutions.

Chapter Five summarizes the overall outcomes and overview of this research project with respect to:

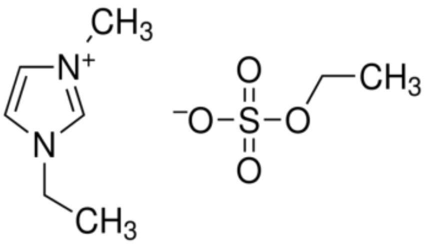
- Findings based on the primary aims and objectives relating to efficacy and efficiency of ionic liquids as extractants for aromatic hydrocarbons.
- Recommendations relating to further work that needs be carried out in future concerning this project.

2 CHAPTER TWO: LITERATURE REVIEW

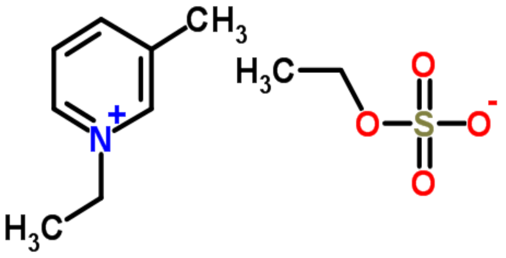
2.1 Introduction

2.1.1 Description of ionic liquids

Ionic liquids are defined as molten salts at room temperature and therefore are sometimes referred to as room temperature ionic liquids. The room temperature ionic liquids are therefore specifically described as low melting salts which represent a new class of non-molecular ionic solvents. Typically, an ionic liquid is composed of a small inorganic, weakly coordinating anion and an asymmetrically substituted bulky organic. Examples of bulky cations are dialkylimidazolium, tetraalkylphosphonium, dialkylpyridinium, N, N-pyrrolidinium, dialkylpyrrolidonium, and tetraalkylammonium. Common anions used in ionic liquids are alkylsulphates, halides, tetrafluoroborate, hexafluorophosphate, and bis-(perfluoroalkylsulphonyl) imides. The structures of the ionic liquids which were used in this study are shown in Figure 3.1.



(a)



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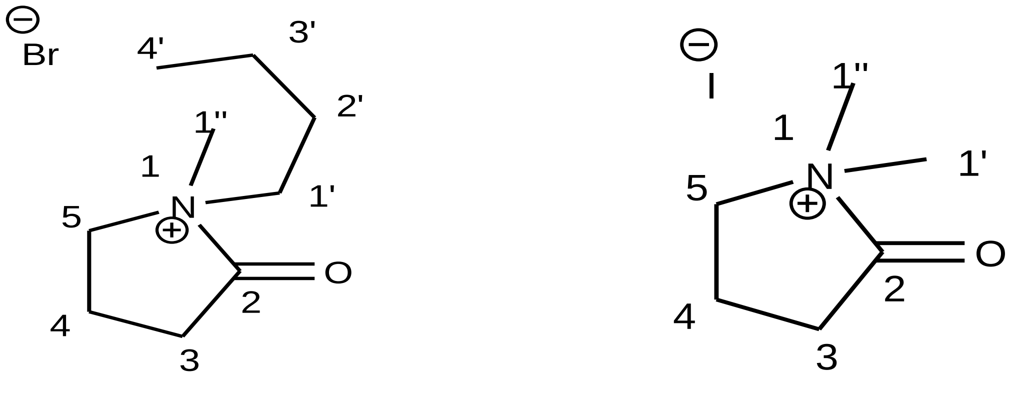


(c) (d)

Figure 2.1 Structures of ionic liquids used in the project (a) 1-ethyl-3-methylimidazolium ethyl sulphate (b) 1-ethyl-3-methylpyridinium ethyl sulphate (c) 1-butyl-1-methyl-2-pyrrolidonium bromide (c) 1,1-dimethyl-2-pyrrolidonium iodide

2.1.2 General route for the synthesis of ionic liquids

Literature review on the synthesis of ionic liquids is also important so that the researchers could make informed decisions when selecting them from available standard procedures. This could provide opportunities for making one’s own ionic liquids when and where necessary if it is economically viable to do so. However, it is a well-known fact that there are many different types of ionic liquids that have been synthesized and characterized for commercialization and other purposes. Consequently there are a vast number of methods and procedures available for the synthesis and characterization of various ionic liquids such as 1-ethyl-3-methylimidazolium ethyl sulphate, 1-ethyl-3-methylpyridium ethyl sulphate, and 1-butyl-3-methylimidazolium ethyl sulphate [26,27,28,29,30,31,32].

The first commonly used synthetic approach to the preparation of ionic liquids involves direct quaternization reaction. It proceeds through formation of the cation and anion which are weakly coordinated in the product. For example imidazole, pyridine, amine, and phosphane, are usually converted to their cations through alkylation. The respective cations (imidazolium, pyridinium, ammonium, and phosphonium) from these compounds are most common and important in the study of ionic liquids and their structures are shown in Figure 2.1. The type of the anion formed depends on the nature of the alkylating agent used which also dictates the properties of the ionic liquid produced. Many ionic liquids of different properties containing the aforementioned cations are produced by using various alkylating agents. For example, dialkylsulphate and alkylhalide produce alkylsulphate and halide, respectively, as an anion of the ionic liquid. The alkyl group forms part of the respective cation as an additional substituent.

The second method of synthesizing ionic liquids involves indirect synthesis which usually proceeds through two steps. This synthetic approach is used where the use of quaternization reaction cannot produce the desired anions by direct synthesis. In this case, the first step involves quaternization of the starting material with a suitable alkylating reagent. In the second step, the anion of the quaternized product is substituted by a desired anion from a suitable reagent, usually achieved by anion exchange called a metathesis reaction. The use of many reagents in this method put extra burden on the preparative work to produce ionic liquids of high purity. The product yield could also be affected negatively due to additive errors occurring in various synthetic steps. The presence of many unwanted species in the final product would contribute significantly to the low quality of the products, in this case, ionic liquids.

At the end of the reaction, the ionic liquid is washed with several portions of a suitable solvent to remove excess reagents. The crude ionic liquid is then dried and purified under high vacuum using rotary evaporator at 70 ºC for 5 h, followed by its characterization using appropriate equipment [33]. The finished product is kept in vessels with an inert argon atmosphere or in a moisture free environment. It is advisable to further purify the ionic liquids after long time storage prior to their applications [34].

2.1.3 Characteristics of ionic liquids

The unique properties of the ionic liquids such as negligible vapour pressure, good thermal stability, dynamic viscosity, and good extractability for various organic compounds, mainly depend on their special structures [35]. The presence of water has negative influence over the physical properties of the ionic liquids with respect to their extractability. It is therefore necessary to keep ionic liquids in bottles in a glove box under inert gas immediately after characterization and drying [36].

The availability of the different types of cations and anions enable chemists to tailor-make ionic liquids for specific applications. Due to their versatile characteristics, most ionic liquids are suitable for a wide range of applications in many fields of chemistry. They also possess important physical properties that make them suitable as potential solvents in synthesis such as:

- Ability to dissolve a wide range of inorganic and organic materials
- Non-coordinating (A weakly coordinating character)
- Not miscible with a number of organic solvents

The applications are, inter alia, catalysts in the manufacturing industries [37], extraction solvent in separation technology for the recovery of valuable solvents [38], and as stationary phase in gas chromatography [39]. Cations of ionic liquids interact strongly with π electrons of aromatic rings through cation-π interactions. There are also π-π interactions strong interactions occurring between π electrons of ionic liquids and aromatic π electrons through aromatic characters. Pyrrolidonium-based ionic liquids contain highly polarizable anions (Br^- and I^-) therefore they can interact strongly with aromatics. The presence of carbonyl groups (-C=O) in the ILs provides additional π-π interactions with aromatics.

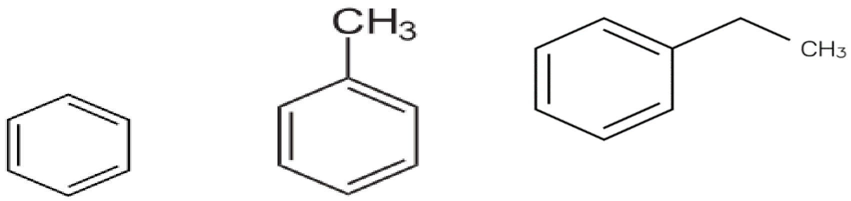
Based on their various properties, ionic liquids are capable of dissolving many organic and inorganic compounds or substances. In separation technology ionic liquids are used as replacements for traditional solvents which are environmentally unfriendly and difficulty to recover from reaction mixtures. Ionic liquids are preferred on the basis of their friendliness to environment as “green solvents” and therefore can drastically reduce waste-solvent production and hence minimize their hazardous and detrimental impact on the environment.

In industry, catalytic reformate containing 44 – 62 % (v/v) is subjected to extractive distillation in which conventional solvent is used as an extractant, resulting in the formation of aliphatic-rich phase and aromatic-rich phase. The latter phase is then processed through steam distillation to separate aromatic hydrocarbons from extracting solvent, and the solvent recycled back to the extractive distillation unit. The feed mixture is loaded to the liquid-liquid extraction tower, where aromatic hydrocarbons selectively dissolve with the solvent. The aliphatic-rich hydrocarbons (raffinate phase) coming out at the top of the column is sent to the next tower to recover the small amount of solvent from the raffinate phase. The solvent-rich extract phase exits the tower with traces of aliphatic and high quantity of aromatics. The solvent and aromatics are separated by flash distillation methods.

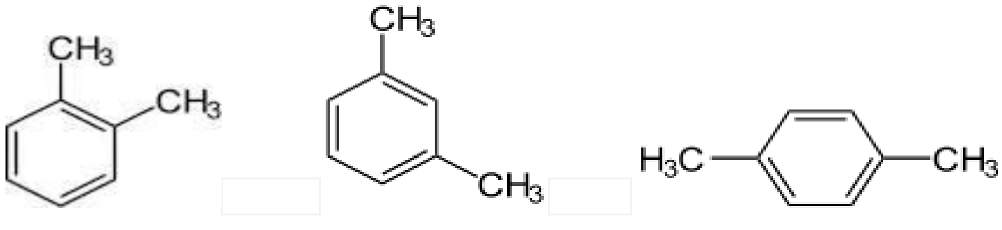
2.1.4 Application of ionic liquids for the extraction of BTEX

2.1.4.1 Description of aromatic hydrocarbons

Aromatic hydrocarbon molecules have the structures shown in Figure 2.2. These are volatile organic compounds (VOC) found in coal tar, crude petroleum, and a wide range of petroleum products. Exposure to BTEX can cause neurological, respiratory, genetic, and excretory system damage due to their toxic properties. They may be introduced into water by industrial effluents and atmospheric pollution. BTEX are extensively used as solvents and reactants in many industrial and manufacturing processes. Since they are valuable compounds, their recovery from various non-aqueous mixtures by means of solvent extraction is essential.



Benzene Toluene Ethyl benzene



o-Xylene m-Xylene p-Xylene

Figure 2.2 Structures of aromatic compounds (BTEX)

Table 2.1 Physical properties of aromatic compounds (BTEX)

Properties	**Benzene**	**Toluene**	**Ethyl Benzene**	**p-Xylene**	**m-Xylene**	**o-Xylene**
Formula	C_6H_6	C_7H_8	C_8H_{10}	C_8H_{10}	C_8H_{10}	C_8H_{10}
MM/g.mol^{-1}	78.12	92.15	106.17	106.17	106.17	106.17
Density/g.cm^{-3}	0.879	0.864	0.870	0.861	0.864	0.879
Boiling Point/°C	80.1	110.8	136.2	138.4	138.5	144.4

2.1.4.2 Extraction of aromatic hydrocarbons

Aromatic hydrocarbons are more polar in nature than aliphatic hydrocarbons, thus ionic liquids would have higher affinity for the former. Therefore, the distribution coefficients associated with them are also expected to be relatively larger as compared to aliphatic hydrocarbons. The extractions involving aromatic/aliphatic hydrocarbon mixtures involve two-phase systems which compose ionic liquid-rich phase known as extract phase and aliphatic hydrocarbon-rich phase referred to as raffinate phase. The non-volatile nature of ionic liquids facilitates the recovery of BTEX from the extract phase mixtures using simple methods such as flash distillation or stripping and/or rotary evaporation in the laboratory. As mentioned earlier, the extent of aromatic components recovery depends on the distribution coefficient or ratio. In addition, a measure of the ability of the extraction systems to separate BTEX from other components of the mixture is also important and this is referred to as the separation factor or selectivity.

Industrially used chemicals as extracting reagents are conventional polar organic solvents, like ethylene glycol, tetraethylene glycol, sulpholane, and N-methylpyrrolidone. Since these organic solvents are generally volatile, toxic, and/or flammable, it is therefore crucial to develop new extracting agents with a high distribution coefficient of aromatic hydrocarbons, high selectivity of aromatics to alkanes, and with little solvent loss [40]. In general, the characteristics of a suitable solvent for the separation of aromatic and aliphatic hydrocarbons [41] are:

- High solubility of the aromatic and low solubility of aliphatic in the solvent
- High separation factor and high distribution coefficient
- Simple recovery of the solvent from both the extract and the raffinate phases
- Fast mass transfer from the feed phase to the solvent phase
- The presence of two phases with a different density

2.1.4.3 Quantification methods of aromatic components

Analytical methods to identify and quantify individual BTEX components present in extraction phases needs sophisticated and/or complex techniques in order to achieve reliable results. Among others, Gas Chromatography (GC) was the choice in this study due to its ability to effectively resolve all six BTEX molecules (benzene, toluene, ethyl benzene, p-xylene, m-xylene, and o-xylene) in the mixture into their individual components. GC is a technique in which separation is accomplished by partitioning volatilized substances between a mobile carrier gas and a stationary phase. High

Performance Liquid Chromatography (HPLC) could have been another choice for BTEX analysis but it is slower than GC and has lower resolution due to broad peaks. In addition, most volatile compounds do not show good retention in HPLC. Moreover, mobile phases used in HPLC require preparation which involves expensive solvents. This technique is most suitable for nonvolatile and semi-volatile analytes and therefore cannot be cost effectively used for the analysis of BTEX molecules due to their high volatility.

Analysis was performed using a Shimadzu Gas Chromatograph with flame ionization detector (FID) and equipped with GC Solution software used for data analysis. The separation of BTEX components is shown in Figure 2.3 which was achieved by ZB-WAX Plus column joined to a guard column which prevents ionic liquids and other non-volatile components in the mixture from entering the analytical column.

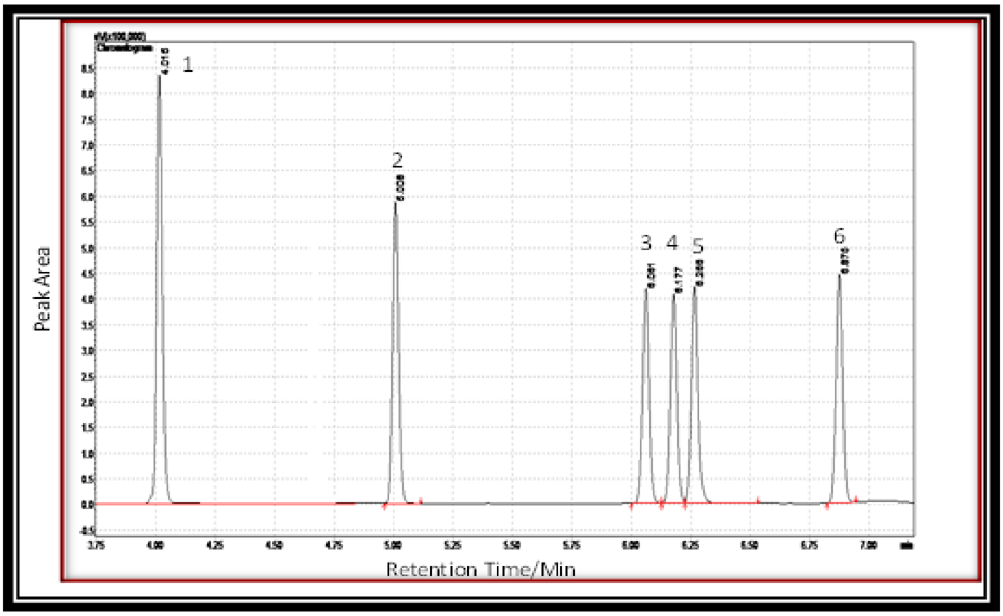


Figure 2.3 (**b)** Chromatograms for BTEX components: (1) Benzene, (2) Toluene, (3) Ethylbenzene, (4) p-Xylene, (5) m-xylene, and (6) o-Xylene

2.1.4.4 General systems using ionic liquids as solvents of extraction

Separation of organic mixtures containing ethanol and ether using ionic liquids were also investigated. Letcher et al. (2004) used two ionic liquids for the extraction of ethanol from ethyl tert-butyl ether, namely, 1-ethyl-3-methylimidazolium methanesulphonate and 1-ethyl-3-methylimidazolium trifluoromethanesulphonate [14]. Of the two, they found that the fluorinated one had high values of solute distribution ratios and selectivity except for selectivity values at high solute concentrations. They concluded that the fluorination of the anion played a negative role in the capability of the ionic liquid in ether purification by liquid extraction process.

The compositions of the sample mixtures were determined by using Nuclear Magnetic Resonance (NMR) Spectroscopy. They also found that the NRTL model was very accurate in LLE experimental data correlation for future computational simulation of liquid extractions of alcohols from ethers by means of ionic liquids. The ionic liquids 1-hexyl-3-methylimidazolium tetrafluoroborate and 1-hexyl-3-methylimidazolium hexafluorophosphate were used as extraction solvents for the liquid-liquid system of ethanol from alkenes [42]. Their study focused on investigating what effect would the variation of the anion of the environmentally friendly ionic liquid solvent have upon the separation power of the ionic liquids. They determined the tie line compositions by correlating the densities of the two immiscible liquid phases of conjugate solutions with that of a standard density curve versus composition. Their selectivity values were also determined from the tie line data to establish the usefulness of the ionic liquids in question. They concluded that 1-hexyl-3-methylimidazolium tetrafluoroborate was a suitable ionic liquid solvent for the selective extraction of alkanols from alkenes based on size of the immiscibility regions, sloping of tie lines, and selectivity data.

Deenadayalu et al. (2007) evaluated mixtures of ionic liquid (1-ethyl-3-methylimidazolium diethyleneglycolmonomethylethersulphate), methanol, and water for densities and excess molar volumes [16,69]. They used vibrating tube densitometers for the measurements of densities of pure components and ternary system and calculated excess molar volumes from experimental densities. They found that excess molar volumes became positive at higher mole fractions of ionic liquid and at a corresponding decrease in mole fraction of water.

With respect to mixtures of carboxylic acid and water, 1-octanol as an extraction solvent was used [43,44]. The carboxylic acids that were used with water include formic acid, propanoic acid, 4-oxopentanoic acid, pentanoic acid, and hexanoic acid. They determined the solubility curves by a cloud point method using a glass cell with a water jacket to maintain isothermal conditions. They analyzed for the compositions of liquid samples withdrawn from the conjugate phases using a Shimadzu GC Analyzer, equipped with flame ionization detector (FID). The former was utilized for organic components detection and the latter for water analysis. They observed from binodal curves and tie line slopes that the distribution of the carboxylic acid in a mixture of water and 1-octanol is very much dependent on the carbon number and type of the carboxylic acid.

The researchers also used isoamyl alcohol to separate butyric acid from aqueous mixtures [45]. They measured densities with an Anton Paar densitometer, refractive indexes with Abbe-Hilger refractometer, and boiling points with Fischer apparatus. They found that isoamyl alcohol might serve as an adequate solvent for butyric acid extraction for its dilute aqueous solvent and concluded that the complete break of conjugate phases was never hindered by density, viscosity, and interfacial tension related phenomena during the settling process.

Bilgin (2006) used oleyl alcohol for separation of butyric acid from its aqueous mixtures [46]. He measured water content in each phase by using a Karl Fischer method and calculated doleyl alcohol amount from the overall compositions. Butyric acid concentrations in liquid samples withdrawn from both phases were determined by titration with sodium hydroxide. They concluded that oleyl alcohol might serve as an adequate extraction solvent for butyric acid since it showed low solubility in water. Kirbaslar et al. (2006) examined liquid-liquid equilibrium data of the solubility curves and tie line end composition for the mixtures of water and propionic acid with anyone of the following alcohols as extraction solvents for the carboxylic acid from its dilute aqueous solutions: 1-octanol, nonanol, decanol, or dodecanol [47,48]. They concluded from their results that all alcohols used were suitable for carboxylic acid recovery as it was found to be more soluble in the alcohol phase than in water phase. Cehreli (2006) used cumene (isopropylbenzene, 2-phenylpropane) to extract carboxylic acid from its dilute aqueous mixtures [49,50]. The carboxylic acids investigated in his/her study include formic acid, acetic acid, and propionic acid.

The effect of different factors on the phase behaviour of imidazolium-based ionic liquids with alcohols was also studied [51]. The main focus was ionic liquids with longer alkyl chains such as hexyl and octyl on the cation. The results obtained from cloud-point curves method showed that all systems used in their investigation exhibited upper critical solution temperature (UCST) behaviour. In addition, they observed that the alcohol-rich phases contained a small amount of ionic liquid, while the IL-rich phases contained larger concentrations of alcohol. Their findings were:

- The UCST increased as the length of the alkyl chain on the alcohol increased when using different alcohols with a specific ionic liquid.
- When using specific alcohol with different ionic liquids having the same anion, the increase in alkyl chain on the cation caused a decrease in the UCST.
- For a specific alcohol with different ionic liquids having the same cation, the mutual solubility of the ionic liquid-alcohol system increased due to stronger hydrogen bonding.

The knowledge gathered in this study facilitates the development of ionic liquids as “designer solvents” for specific applications. Similar trends were also observed when a study involving alkoxyimidazolium-based ionic liquids and aromatic and aliphatic hydrocarbons [52] was done. It was reported that an increase in the alkyl chain length of n-alkane, or at benzene ring resulted in an increase in the UCST. Domanska et al. (2004) reported that although many ionic liquids had been synthesized, there is still a lack of property data on the pure fluids [53]. They concluded that ionic liquids based on the $[PF_6]^-$ and $[BF_4]^-$ anions have the tendency to decompose and the properties on the recovered materials could differ significantly from the original.

Therefore it is important to establish the standards and test systems for ionic liquids and their mixtures. The large number of possible ionic liquids is of little use for separation science if no systematic approach for the tailor-making of these substances for separation problems is provided [54]. In addition, Rey-Castro et al. conducted an investigation regarding the structure and transport properties of several ionic liquids by evaluating the cation/anion diffusion coefficients, electrical conductivity and shear viscosity [55]. Khupse and Kumar (2010) emphasized that the choice of the cation and the anion constituting an ionic liquid has a profound effect on the physical properties. Ionic liquids offer great flexibility in their properties since the high number of possible combinations of cations and anions makes ionic liquids very flexible in their properties [56]. However, the wide variety of cations and anions available makes a systematic study very difficult [57].

Traditional systems which are currently employed in separation technologies are considered as unsafe for reasons of environmental protection since the organic solvents are highly volatile and they are often used in large quantities [1]. The introduction of cleaner technologies has become a major concern throughout both academia and industry [2]. In recent years ionic liquids have attracted the attention of many researchers due to the large variety of applications of ionic liquids in industry and applied chemistry. There are very few studies in the literature which include ionic liquid equilibrium data for the quaternary systems [3].

The ionic liquids under consideration exist as liquids well below ambient temperature up to a temperature as high as 200 °C. They possess important physical and chemical characteristics since they are non-volatile, non-flammable, high thermal and chemical stability, high heat and electrical conductivities, highly soluble in both polar and non-polar organic and inorganic substances. It was suggested that ionic liquids can therefore be used to replace conventional which are toxic organic solvents, flammable, and volatile [58]. In addition, they are regarded as relatively inexpensive to manufacture.

The unusual properties associated with ionic liquids make them attractive solvents in electrochemistry, separations, chemical reactions, and synthesis [5]. However, separation and recovery of ionic liquids is one of the major challenges in future industrial applications.

The following were regarded as the most important requirements of a suitable ionic liquid for the separation of aromatic and aliphatic hydrocarbons [62]:

- High solubility of aromatic hydrocarbons in the ionic liquid
- No or low solubility of aliphatic hydrocarbons in the ionic liquid
- High separation factor or selectivity and distribution coefficient
- Easy recovery of the ionic liquid from both the extract and the raffinate phase
- Fast mass transport from the feed phase to the ionic liquid phase

Ionic liquids possess the following unique properties [59]:

- Low melting point (<100 °C)
- Suitable viscosity
- Thermal stability up to high temperatures
- High solubility for both polar and non-polar organic and inorganic substances
- Negligible vapour pressure and therefore non-flammable

A higher selectivity indicates a purer product and less extraction of aliphatic hydrocarbons. It was suggested that replacement of volatile solvents in the separation of aromatics and aliphatic hydrocarbons by non-volatile ionic liquids can offer several advantages such as less complex processes and a more simple regeneration of a solvent [7]. Ionic liquids are typically composed of a large organic cation and an inorganic polyatomic anion. Many possible ionic liquids could be made by mixing suitable cations and anions. These ionic liquids are referred to as selective solvents in separation technology [11]. Vapour pressure data indicate that the volatility of solvents can be changed dramatically by the addition of an ionic liquid, while the variation extent is different depending on the nature of both organic solvent and ionic liquid involved.

With regard to mixtures containing benzene, alkane1-methyl-3-octyl-imidazolium chloride was used as ionic liquid [60]. The compositions of the ternary mixtures by using densities and standard density calibration curves were evaluated. The findings were that the selectivity value was high which suggested that high purity benzene could readily be produced from the abovementioned mixtures. Letcher and Reddy (2005) used 1-hexyl-3-methylimidazolium tetrafluoroborate and 1-hexyl-3-methylimidazolium hexafluorophosphate as ionic liquids for the separation of the same mixtures [61]. The results obtained showed that all benzene/heptane selectivity with these ionic liquids were too low (S<10) to be of use in industrial applications. Also, 1-hexyl-3-methylimidazolium hexafluorophosphate can decompose in the presence of water and at elevated temperatures to form HF.

Meindersma et al. (2006) obtained liquid-liquid equilibria data from the mixtures of toluene (methylbenzene) and an alkane [66]. They used four ionic liquids for separation of aromatic and aliphatic hydrocarbon, namely, 1.3-dimethylimidazolium methyl sulphate, 1-ethyl-3-methylimidazolium ethyl sulphate, 4-methyl-N-butylpyridinium tetrafluoroborate, and 1-butyl-3-methylimidazolium methyl sulphate. Their study also included sulpholane concurrently with these ionic liquids as it was one of the most common solvents for extraction of aromatic hydrocarbons from mixtures of aromatic and aliphatic hydrocarbons used in industries. They found that the toluene/alkane selectivity values were higher with all four ionic liquids than with sulpholane. Of the four ionic liquids, they concluded that 4-methyl-N-butylpyridinium tetrafluoroborate was a suitable solvent to replace sulpholane for an industrial extraction process since it showed an optimal combination of a high toluene distribution coefficient and a high toluene/alkane selectivity values.

In addition, the ionic liquids could easily be regenerated by evaporating the organic compounds from the extract as well as the organic compound used in the extraction. Visible inspection of the NMR spectra of both the original ionic liquid and the regenerated product showed no significant differences between the two samples according to Meindersma et al. [62]. This off-set the cost associated with the ionic liquid as it can be reused for quite a number of separation cycles.

2.2 Extractions of BTEX from non-aqueous mixtures

It has been reported by [62,63,64,65,66] that in the petrochemical industries, liquid extraction is the most widely used process for the separation of benzene, toluene, ethyl benzene, and xylene isomers (BTEX) from aliphatic hydrocarbons because their separations cannot be carried out in an efficient and economical way by energy intensive methods due to the close proximity of the boiling points of the hydrocarbons [62].

Currently some conventional organic solvents, used by many industries for this purpose, include sulpholane, tetraethylene glycols, N-methylpyrrolidone, Nformylmorpholine, and N-methylimidazole amongst others. However, these solvents are generally toxic, flammable, and their recovery is tedious as it requires several steps [63]. Sulpholane is one of the most appropriate solvents employed for this separation due to its physical-chemical properties and much research involving its liquid-liquid equilibria in aromatic/aliphatic mixtures has been reported [67,68,69,70]. Although sulpholane is currently the most widely used solvent in the petroleum industry, its viability is limited to mixtures containing 20% and/or more of the target aromatic hydrocarbons [70]. Unless alternative techniques are developed, petroleum effluents containing less than the extractable amounts need to be treated as waste.

The search of the literature has shown that there is only one report [71] which has directly addressed the challenge of developing a method for recovering aromatic hydrocarbons from the mixtures containing less than 20% of useful components using a pilot plant. Furthermore it involved the chemical engineering aspect, namely, the design of a laboratory scale separator using ionic liquids to effect the initial separation. This study was motivated by the following observations, regarding the limitations of sulpholane as an extraction solvent, namely:

- It is only suitable for mixtures with 20-65% aromatic hydrocarbons content
- Additional separation steps are required to purify the raffinate, extract and solvent streams
- Regeneration of the spent sulpholane is very costly

On the other hand ionic liquids have many useful properties such as: zero or low solubility of aliphatic hydrocarbons in the ionic liquid, high separation factor or selectivity and distribution coefficient, easy recovery of the ionic liquid from both the extract and the raffinate phases, fast mass transport from the feed phase to the ionic liquid phase, high thermal and chemical stability, high heat and electrical conductivities, high solubility in both polar and non-polar organic and inorganic substances and high turnover frequencies [72,73]. In addition, ionic liquids have gained in appeal because traditional distillation systems are considered as unsafe for reasons of environmental protection due to high volatility of organic solvents [47]. In view of this the introduction of cleaner technologies has engaged the attention of both academics and industrialists.

It is an undisputable fact that the resources of the world are being utilized at an increasing rate by a growing population, which is expected to reach 10 billion within the next decade. Natural resources such as coal and oil are being used to produce synthetic products which are needed for industrial and domestic use. Among these synthetic by-products, aromatic and aliphatic compounds feature quite prominently [74,75]. In view of the above, it is imperative that recycling of waste be done on a significant scale to replenish the dwindling supplies. Germane to this report is the presence of aromatic solvents in mixtures with aliphatic solvents in industrial effluents. Since aromatic solvents are relatively more expensive than aliphatic ones, it is essential to find ways to beneficiate4 the aromatic component. This would entail the separation and recovery of these types of resources in a cost-effective manner [76,77].

To address this requirement, a crucial step is to develop methods for laboratory scale use of ionic liquids as suitable agents for extracting valuable organic liquids from mixtures of organic liquids. The reason why ionic liquids find favour in the extraction and separation of organic liquids is tied to the need to utilize ‘green chemistry

[78,79,80,81] to a greater extent. Ionic liquids qualify as green solvents mainly because of their property of low vapour pressure [82]. Currently organic liquids are obtained on an industrial scale, from mixtures of aromatic and aliphatic solvents, mainly by distillation and liquid-liquid extraction involving conventional solvents [83,84].

The conventional processes for the separation of these aromatic and aliphatic mixtures involve the use of extraction and extractive distillation [85]. However, distillation requires relatively high energy inputs which may prove to be expensive and therefore, there are chances of polluting the environment [86,87]. Liquid –liquid extraction would involve large volumes of extracting agents such as sulpholane and tetraethyleneglycol [88,89]. These have relatively higher vapour pressures [90] and can thus pollute the environment. Since ionic liquids have relatively low vapour pressures they can be exploited for extraction and separation as suitable ‘green solvents’ [59]. Furthermore the recyclability [91] of ionic liquids makes them eminently useful in automated multi-stage extractions needed for industrial processes.

The syntheses and uses of several types [92,93] of ionic liquids have been reported in previous studies with the same interests. They are exemplified by the cations such as alkylammonium, tetralkylammonium, tetraalkylphosphonium, N-alkylpyridinium, 1,3dialkylimidazolium, N-alkylpyridinium and pyrrolidinium. However there is a paucity of reports [94,95] on the syntheses and applications of pyrrolidonium type ionic liquids. In the light of this, the syntheses, characterization and applications of novel pyrrolidonium-based ionic liquid were undertaken. The reasons for choosing to synthesize this class of ionic liquids are inter alia:

- Superior thermal and chemical stability
- Ability to enhance separation factor in distillation processes [96]
- Useful in the trans-dermal transport of drugs [97]
- Cheaper, amenable to large scale synthesis and have low toxicity [98]

Furthermore, the importance of pyrrolidonium ionic liquids has been highlighted by the registration [99] of a patent for N-substituted pyrrolidonium ionic liquids with the United States patent office. The application involved the use of a method for separation and recovery of a ‘prepared mixture’ of aromatic and aliphatic solvents. The aromatic organic liquids were present at 0.5, 2.5, 5.0 and 10% levels (v/v) in the contrived mixtures. The reason [100] for choosing these levels is that the recovery of aromatic solvents by distillation using sulpholane is limited to mixtures containing 20% or more of aromatic liquids.

The results obtained vindicate the decision to target these ionic liquids as suitable extraction solvents for aromatic liquids from a mixture of aromatic and aliphatic liquids. This work is a continuation of our research on the synthesis [101 , 102] and thermodynamic properties and applications of new ionic liquids [103,104].

In view of the above it is apparent that very little work has been done on the extraction of aromatic liquids from mixtures of hydrocarbon waste generated by oil refineries. Furthermore, experimental data for both quaternary and quinary systems using sulpholane is rarely found in literature, especially for the latter [49]. It was for this reason that their study involved quinary systems, but only two aromatic components were present in the mixture, namely, benzene and toluene together with two alkanes and sulpholane.

This study therefore investigated the efficacy of four ionic liquids 1-ethyl-3-methylimidazolium ethyl sulphate, 1-ethyl-3-methylpyridinium ethyl sulphate, 1-butyl-1-methyl-2-pyrrolidonium bromide and 1, 1-dimethyl-2-pyrrolidonium iodide as a means of simultaneous recovery of all BTEX molecules from various organic mixtures including reformates and spent solvents. The first two ionic liquids were chosen on the basis of their properties such as low toxicity, high stability, higher selectivity, and less hygroscopic. In addition they are easy to synthesize and characterize with simple method of its regeneration after use.

The other two ionic liquids were synthesized and supplied to us by our collaborators in India. Although the certificates of analysis were given, characterization was performed on arrival to confirm their properties and purity using sophisticated equipment. These ionic liquids too were easy to recover from spent solvents and/or extract phases using simple methods. The concentrations of the aromatic individual components were varied from 2.5 to 25 % (v/v) and the targeted fractions were analyzed by GC-FID to determine the % recovery by volume.

Paint manufacturing industries are major users of aromatic and aliphatic hydrocarbons as solvents in their various processing units. Spent paint solvents in this case refer to effluent organic mixtures resulting from paint processing as waste. These effluent organic mixtures contain significant amounts of aromatic components such as toluene, ethyl benzene and xylene isomers, known by the acronym, BTEX in addition to other organic species, for example, aliphatic hydrocarbons. However, it is well known that aromatic hydrocarbons are more valuable than aliphatic ones and therefore find many uses in various chemical industries. It is for this reason that we undertook a study for their recoveries from various effluent and/or waste organic mixtures using emerging extracting liquids.

It was established in the experiments that the concentration of aromatic components in spent paint solvents vary between 4 and 13% by volume. Although aromatic solvents are generally shunned because of their classification as carcinogen [105], they do play an irreplaceable role in many chemical manufacturing processes such as paint manufacturing industries [106,107,108]. Since aromatic solvents are generally costlier to manufacture than aliphatic ones, their recoveries using economical viable methods is very important. In processes where aromatic solvents are utilized as reaction media [109], it would reduce manufacturing costs if the aromatic components could be recovered on a macro scale.

Currently, the recovery of aromatic solvents (on an industrial scale) from mixtures containing aliphatic solvents is done by distillation or by using extraction solvents such as sulpholane [110,111] It has been shown that sulpholane is not effective in cases where the concentration of the aromatic components is less than 20% [112]. Furthermore, distillation is not suitable for separating azeotropic mixtures.

In view of the important role of aromatic solvents in the chemical manufacturing industry it was decided to investigate the macro-scale recovery of these solvents from relevant organic waste mixtures using ionic liquids. To meet this aim, some of the aspects which needed to be addressed are:

- The chosen laboratory method for synthesis of the IL should be such that it can be adapted for industrial scale synthesis of the IL.
- The stability [8] of the IL is such that it can be recovered unchanged at the end of the extraction.
- The IL meets the criteria for a ‘green solvent’ [9] so that it is not hazardous to the environment.
- The ionic liquids should be selected on some established basis [113].
- The establishment of the number of extraction stages for maximum recovery.

The last two points in the above list requires some elaboration. The basis for selection could one of the several properties of ionic liquids or it could be structural feature/s believed to be involved in the interactions between the solvent and the ionic liquid. Since it has been established elsewhere that π-π interactions [114] may influence the strength of the interactions between aromatic components and ionic liquids forms the basis of this study. The structural feature to be highlighted here is the presence of π electrons in the 5-membered and 6-membered rings of imidazolium and pyridinium cations. It was also established that these ionic liquids are fairly stable to degradation by air and water vapour and that the method reported herein shows potential for industrial scale usage. Cations of ionic liquids interact strongly with pi electrons of aromatic rings through cation-π interactions. There are also π-π interactions strong interactions occurring between π electrons of ionic liquids and aromatic π electrons through aromatic characters. Pyrrolidinium-based ionic liquids contain highly polarizable anions (Br^- and I^-) therefore they can interact strongly with aromatics. The presence of a carbonyl group with π electrons in its double bond provides additional π-π interactions between the ionic liquid and aromatic molecules.

It is noted that there are several reports on the uses of ionic liquids for micro-extraction of BTEX [115,116] but none of them is associated with the extraction of aromatic components from non-aqueous mixtures. There are also several recent reports

[117,118,119,120] on the extraction of organic liquids using ionic liquids. However they are restricted to binary and ternary systems whereas this project addresses the extraction of organic liquids from multi-component systems. Furthermore this project is a continuation of our contributions [121,122,123,124,125] work on the synthesis, thermo-physical properties and use of ionic liquids for extraction of organic liquids from mixtures of organic liquids.

In this study, a number of ionic liquids were investigated as solvents for the extraction of BTEX from aliphatic hydrocarbons. Availability of experimental data is important on the effects the structures of ionic liquids have on the ability to extract organic solvents. In the light of this, the following four ionic liquids, namely; 1-methy-3-ethylimidazolium ethyl sulphate, 1-ethyl-3-methylpyridinium ethyl sulphate, 1-butyl-1-methyl-2-pyrrolidonium bromide, and 1, 1-dimethyl-2-pyrrolidonium iodide were used as extraction solvents for the recovery of organic solvents from industrial samples. The reason for choosing ionic liquids 1-methy-3-ethylimidazolium ethyl sulphate and 1-ethyl-3-methylpyridinium ethyl sulphate was based on the following characteristics investigated by other researchers:

(1) Economic viability

Commercially available ionic liquids are very expensive and they are imported. Ionic liquids that are synthesized in our laboratories are relatively cheap based on inexpensive raw materials which were also readily available from abroad suppliers. The extraction with conventional solvents is not an option since additional separation steps are required to purify the raffinate, extract, and solvent streams, which would induce high investment and energy costs. Extraction of aromatics with ILs is expected to require fewer process steps and less energy consumption than extraction with conventional solvents because ionic liquids have a negligible vapour pressure.

(2) Selectivity (S) and distribution coefficient (D)

Imidazolium- and pyridinium-based ionic liquids used in this project were chosen on the basis of their relatively higher selectivity literature values compared to most available studied ionic liquids and conventional extraction solvents [62,66,86,130]. The comparative study carried out on the ionic liquids [MMIM][Tf_2N], [EMIM][Tf_2N], [BMIM[Tf_2N], and [EMIM][ESO_4] showed that the ionic liquid 1-ethyl-3-methylpyridinium ethyl sulphate had the highest selectivity ($S = 36.4$ at 313.15 K) for toluene/n-heptane, which is higher than the selectivity of sulpholane ($S = 31$). In this work, ionic liquid [BMIM][Tf_2N] showed lower selectivity and a higher distribution coefficient than the ILs with cations $[EMIM]^+$ and $[MMIM]^+$. In addition, their synthetic methods were found to be simple and less hazardous. Literature values of ILs distribution coefficients were comparable to those regularly used in most previous and current research and also to those of conventional extraction solvents. The study found that even with a lower distribution coefficient than conventional solvents (e.g. sulpholane), extractions with ionic liquid can still be economical viable as can be seen in the following two cases [62,66]:

- Toluene/n-Heptane (10%) mixture at 40 ºC

[EMIM][ESO_4] had selectivity and distribution values of 50.5 and 0.22, respectively. Sulpholane had selectivity and distribution values of 30.9 and 0.31, respectively.

- Benzene/n-Hexane (10%) mixture at 40 ºC

[EMIM][ESO_4] had selectivity and distribution values of 66.4 and 0.59, respectively. Sulpholane had selectivity and distribution values of 28.5 and 0.58, respectively.

(3) Recovery/Regeneration of ionic liquids

Aromatic hydrocarbons were separated from extract phase through evaporation at low temperature under reduced pressure using rotary evaporator. Most of the results reported in this study were obtained with regenerated ionic liquids. NMR and FTIR were used to monitor the quality of the regenerated ILs by visual comparison of recycled ILs spectra with the spectra of the standard ILs. Conventional solvents are organic compounds which are generally toxic, flammable, and difficult to recover or regenerate from extract phases. In addition, they demand a great deal of heat for the distillation steps. The latter comprise reformates from oil refinery and spent solvents from paint manufacturing industries.

3 CHAPTER THREE: MATERIALS AND METHODS

3.1 Materials and Equipment

3.1.1 Chemicals and Reagents

The ionic liquids 1-ethyl-3-methylimidazolium ethyl sulphate [EMIM][ESO_4] and 1-ethyl-3-methylpyridinium ethyl sulphate [EMpy][E ESO_4] were synthesized in our laboratories using reported procedures described in section 3.2 below. Reference standards of these two ionic liquids were obtained from Aldrich in Germany for use as bench marks. Diethyl sulphate (≥ 99%), 1-methylimidazole (≥ 99%), and 3-methylpyridine (≥ 99%) were purchased from Fluka. Toluene (≥ 99.9%), benzene (≥ 99.9%), ethylbenzene (≥ 99.9%), m-xylene (≥ 99%), o-xylene (≥ 99%), p-xylene (≥ 99%), n-heptane (≥ 99%), n-hexane(≥ 99%), and 1-butanol (≥ 99%) were purchased from Merck. Acetone-d6 (≥ 99.5%) was purchased from Aldrich. Karl-Fischer reagents were purchased from Riedel-de-Haen. The ionic liquids 1-butyl-1-methyl-2-pyrrolidonium bromide [BNMP][Br] (≥ 98.1%)and 1, 1-dimethyl-2-pyrrolidonium iodide [MNMP][I](≥ 93.1%) were synthesized and supplied to us by researchers (Sudharsan Kumar and Prashant Singh, 2012) at Babasaheb Bhimrao Ambedker University and University of Delhi, respectively, in India with whom we collaborate.

3.1.2 Equipment

Gas Chromatography (GC) was performed on SHIMADZU GC-2010 Plus, fitted with flame ionization detector (FID) for the analysis of aromatic and aliphatic hydrocarbons. The spectra of ^{1}H-NMR and ^{13}C-NMR for ionic liquids were obtained from Bruker 400 Ultra-shield HMF Spectrophotometer. The infrared spectroscopy technique was utilized on Varian 800 FTIR-ATR spectrophotometer with the aid of Varian Resolution 4.0 software to produce the spectra of ionic liquids being investigated. Karl-Fischer auto-titrations were carried out on Metrohm 702 KF Titrino and/or 831 KF Coulometer to monitor the level of moisture in ionic liquids. The measurements of densities, refractive indices, and sound velocities were conducted on Anton Paar density and sound velocity meter DSA 5000 M. The refractive indices of the ionic liquids were measured by RFM900-T Refractometer. The removal of volatile impurities from ionic liquid (product) by rotary evaporation was performed on ROTAVAC Control Heidolph AC230V. All liquid-liquid extractions investigated in this study using ionic liquids were carried out on Heizbad WB digit AC230/240V thermostatically controlled water-bath.

3.1.3 Sample Collection

Samples of reformates (fraction after high boiling octanes have been removed) were supplied by the Engen Refinery South Africa (Durban) which is part of the Petronas group 5 [110]. Samples of spent paint solvents were obtained from Plascon Paints South Africa (Durban) which is part of the Paint Manufacturing Group. For security and safety reasons, the sampling was done by industries concerned using their respective approved procedures of obtaining representative samples. Clear glass bottles with screwed neck were employed for this purpose and all samples were stored in a cool place to avoid evaporation and hence loss of volatile constituents.

3.2 Methods and Procedures

3.2.1 Syntheses of Ionic Liquids

3.2.1.1 Introduction

In general, the ionic liquids for this project were synthesized from two reactants using a suitable solvent (usually a benzene derivative such as toluene). One of the reactants provided the cation and the other the anion. Direct syntheses without the solvent were avoided since most reactions of this type were highly exothermic hence releasing extreme heat. Special precautions were taken in the handling of the raw materials in order to avoid contaminations during synthesis. The reaction processes were carried out under nitrogen gas as inert atmosphere with reaction vessels immersed in ice water to prevent excessive heat build-up in the reaction vessel.

In most cases one of the reactants was added in a drop-wise manner to the reaction mixture, to prevent a sudden rise of temperature that might lead to explosive conditions. Once the reactants were all added in the reaction vessel the mixture was stirred vigorously for at least five hours at room temperature. The presence of the solvent in the reaction mixture facilitated effective collisions in order to speed up the rate of reaction between the reacting species. In addition the solvent also played an important role in controlling the reaction temperature by either increasing the energy of the colliding particles so that they reacted more quickly, or absorbing the heat generated during an exothermic reaction. The selection of an appropriate solvent was based on the following criteria:

- Thermal stability
- Solubility of reagents
- Chemical inertness
- Ease of separation from reaction products

The products were purified by a solvent extraction technique using appropriate apparatus such as separation funnels. In this case the solvent removed all impurities from the products. The solvent was then separated from the product by means of rotary evaporator under reduced pressure. The percentage yields of the final products were determined in order to ascertain the effectiveness of the synthetic method.

In the synthesis of 1-ethyl-3methylimidazolium ethyl sulphate and 1-ethyl-3-methylpyridinium ethyl sulphate, diethyl sulphate acted both as an alkylating agent as well as an anion provide. The reaction proceeded as follows under controlled conditions:

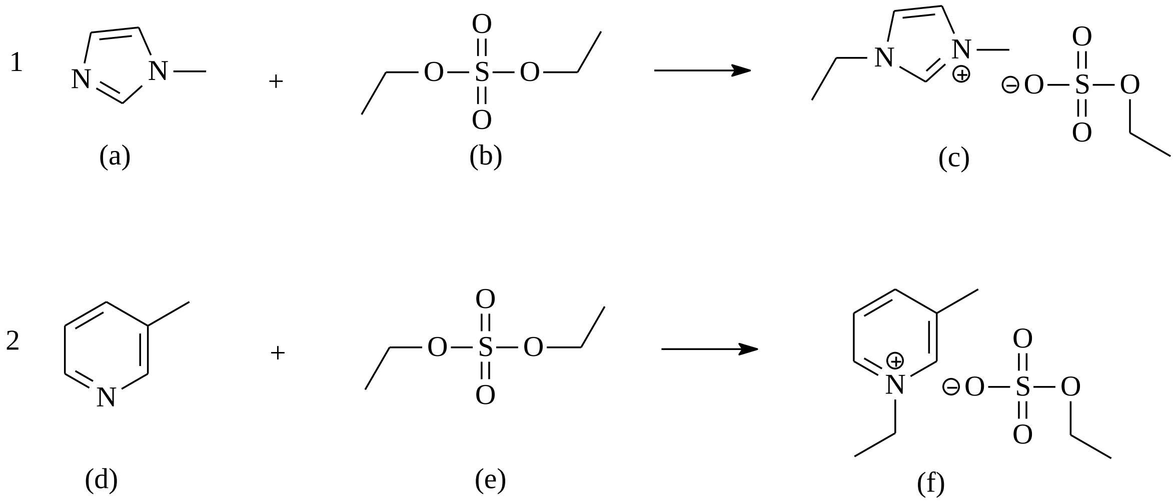


Figure 3.1 Reaction scheme for (1) Synthesis of 1-methy-3-ethylimidazolium ethyl sulphate where (a) 1-methylimidazole (b) diethyl sulphate (c) [EMIM][ESO_4] and (2) Synthesis of 1-ethyl-3-methylpyridinium ethyl sulphate where(d) 3-methylpyridine (e) diethyl sulphate (f) [EMpy][ESO_4]

The synthetic steps and apparatus involved are shown in Figure 3.2:

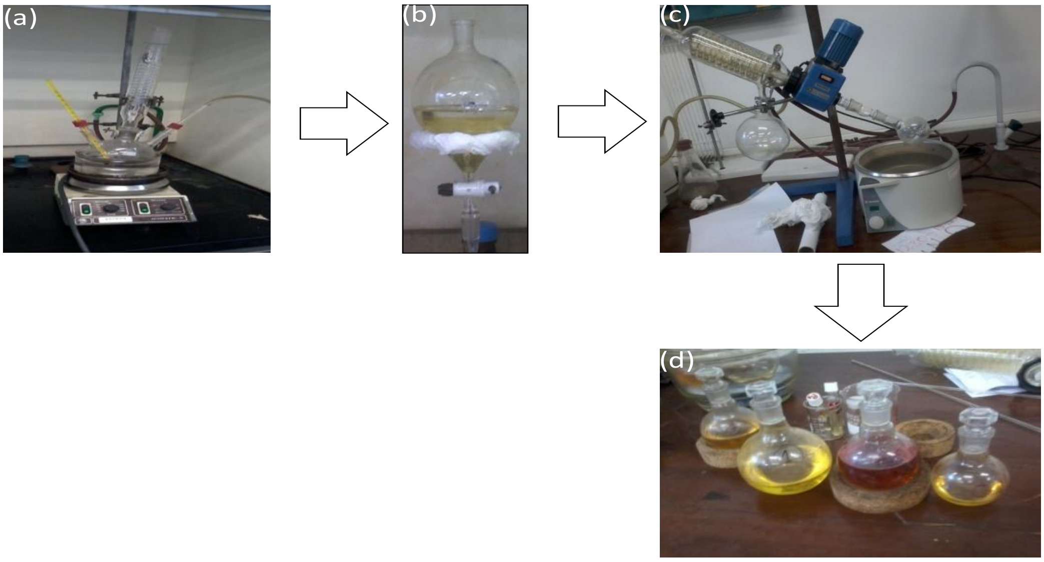


Figure 3.2 Route involved in the synthesis of ionic liquids (a) Stage 1: Synthesis process through stirring under inert atmosphere of cooled reaction mixture (b) Stage 2: Purification of crude ionic liquid by solvent extraction (c) Stage 3: Removal of volatile compounds and water by rotary evaporation (d) Stage 4: Finished products of various ionic liquids.

3.2.1.2 Synthesis of [EMIM][ESO_4] and [EMpy][ESO_4]

Ionic liquid 1-ethyl-3-methylimidazolium ethyl sulphate [EMIM][ESO_4] was synthesized according to the procedures described elsewhere [62,87,88,89] as follows: Diethyl sulphate (0.44 mol, 67.8 g or 58 mL) was slowly added drop-wise to an ice-cooled mixture of 1-methylimidazole (0.44 mol, 36.1 g or 35 mL) and toluene (200 mL) under inert atmosphere of argon. When the addition of diethyl sulphate was complete, the reaction mixture was removed from the ice bath and then stirred vigorously using a magnetic stirrer for five hours at room temperature to allow the reaction mixture to go to completion.

Ionic liquid 1-ethyl-3-methylpyridinium ethyl sulphate [EMpy][ESO_4]was synthesized following the same procedure used for the ionic liquid 1-ethyl-3-methylimidazolium ethyl sulphate [EMIM][ESO_4] above, but with its own stoichiometric quantities of reactants: Diethyl sulphate (0.44 mol, 67.9 g or 58 mL) and 3-methylpyridine (0.44 mol, 40.7 g or 43 mL) in toluene (100 mL) were treated under similar experimental conditions.

Each mixture from the synthesis which contained two layers was transferred into a clean, dry beaker of appropriate size. The top layer (toluene-rich) was separated from bottom layer (ionic liquid-rich) by decantation. The bottom layer was then transferred quantitatively into a separating funnel and washed with three portions of 50 mL toluene to remove impurities. The crude ionic liquid product was subjected to rotary evaporation at 70 ºC under reduced pressure for three hours in order to remove volatile impurities and moisture. Pure ionic liquid products were then stored in the desiccators to prevent them from absorbing moisture from the surroundings.

3.2.1.3 Determination of Moisture

The amount of moisture in the ionic liquids was determined by auto-titration method using Karl-Fischer Metrohm 702 KF Titrino. Hydranal composite 5 was used as a titrant and methanol (>99.9 %) as solvent. The titrant was always standardized before using it for the analysis of ionic liquid samples to ensure validity of measurements. A blank determination was carried out in order to check the amount of moisture in the solvent using the same procedure used for the samples. The moisture content was reported in percent mass and the model used for its determination in this study is shown in Figure 3.3 illustrating the apparatus used.

Figure 3.3: Karl-Fischer Metrohm 702 KF Titrino

3.2.1.4 Percentage Yields

The percent yield of each synthesized ionic liquid was determined from the accurately measured masses to the nearest 0.0001 g of reactants and the product except the solvents as they were used in excess. From these measurements, theoretical yield was determined and then used with the actual or experimental yield in order to calculate the percent yield of the product.

$$\%\text{Yield} = \frac{\text{Actual Yield}}{\text{Expected Yield}} \times 100 \qquad 3.1$$

The stoichiometric quantities of the reactants required for the synthesis were measured according to the desired amount of the ionic liquid. Table 3.1 indicates some of the quantities used in this study and any other desired quantity were proportionally based on these values.

Table 3.1 Stoichiometric quantities of reactants required for the synthesis of 1-ethyl-3-methylimidazolium ethyl sulphate [EMIM][ESO_4] and 1-ethyl-3-methylpyrdinium ethyl sulphate [EMpy][ESO_4], where ρ = density, n = number of moles, MM = molecular mass, m = mass, v = volume

Synthesis reactants	MM/g mol^{-1}	ρ/g mL^{-1}	n/mol	m/g	v/mL
	1-ethyl-3-methylimidazolium ethyl sulphate [EMIM][ESO_4]				
1-Methylimidazole	82.10	1.03	0.44	36.12	35.1
Diethyl sulphate	154.2	1.18	0.44	67.85	57.5
	1-ethyl-3-methylpyrdinium ethyl sulphate [EMpy][ESO_4]				
Diethyl sulphate	154.2	1.18	0.44	67.85	57.5
3-Methylpyridine	93.13	0.96	0.44	40.98	42.7

The percentage yields obtained for [EMIM][ESO_4] and [EMpy][ESO_4] were all greater than 97.5 %. The calculation details were shown in section 3.2.5. An example of how the percentage yields of each ionic liquid produced were calculated from the masses of the reactants in Table 3.2 below using equation 3.1 in section 3.2.5 is given below:

Product 1 [EMIM][ESO_4]: %Yield = $\frac{102.8933}{105.4921} \times 100 = 97.6\ \%$

Product 1 [EMpy][ESO_4]: %Yield = $\frac{105.9906}{108.0205} \times 100 = 98.1\ \%$

The percentage yields of eight products for each ionic liquid are shown in Table 3.2 below. The yield for 1-ethyl-3-methylimidazolium ethyl sulphate ranges from 97.6 – 99.3 % and 97.3 – 99.1 % for 1-ethyl-3-methylpyridinium ethyl sulphate. It can therefore be said that the minimum percentage yield for these ionic liquids is not less than 97 %.

Table 3.2 Percentage yield of the synthesized ionic liquids

Ionic Liquid	1-ethyl-3-methylimidazolium ethyl sulphate [EMIM][ESO_4]						
Expected Mass	105.4921	106.0102	103.4164	104.1154	105.2143	104.1015	105.7605
Actual Mass	102.8933	103.8900	102.6925	102.7619	103.0048	102.8523	103.0107
Yield/%	97.6	98.0	99.3	98.7	97.9	98.8	97.4
Ionic Liquid	1-ethyl-3-methylpyrdinium ethyl sulphate [EMpy][ESO_4]						
Expected Mass	108.0205	107.9545	107.6756	108.1724	107.1321	107.4994	108.7312
Actual Mass	105.9906	105.6875	105.8451	105.7926	105.9537	105.8869	105.7955
% Yield	98.1	97.9	98.3	97.8	98.9	98.5	97.3

3.2.2 Characterization of Ionic Liquids

After purification, the ionic liquids were characterized using FTIR-ATR and NMR spectroscopy to ascertain their structures. Other properties that were measured are refractive indices, densities, and sound velocities including moisture content using appropriate equipment. The analytical techniques employed for these purposes were viscometers, densitometers, Fourier Transform Infrared fitted with Attenuated Total Reflectance (FTIR-ATR), Nuclear Magnetic Resonance (^{1}H-NMR and ^{13}C-NMR), and Gas Chromatography fitted with Flame Ionization Detector (GC-FID). All instruments used were calibrated by using standards of high purity before any work was done. The spectra obtained from FTIR and NMR gave qualitative information on the structure of the ionic liquids while GC-FID chromatogram indicated the presence or absence of excess reactants and/or solvent in the product. The latter forms the basis of blank determination when using ionic liquids for the extraction of aromatic components (BTEX) from organic mixtures.

3.2.3 Instrumental Techniques

3.2.3.1 Gas Chromatography

Gas chromatography was employed in this study on the basis of separating and identifying aromatic components (BTEX) present in the petroleum reformates and paint waste solvents for the purpose of their individual quantification. The flame ionization detector (FID) was used in conjunction with Gas Chromatograph (GC) for the detection of eluted components. The instrument was operated at a programmed temperature (40 –

115 °C) to achieve optimal running time. The gaseous components being analyzed interacted with the walls of the capillary column (30 m x 0.25 mm x 0.25 µm) coated with a stationary phase ZB-Wax-Plus, causing each BTEX component to elute at a different retention time. The retention times obtained were used to identify each component in a mixture before any quantitative analysis could be performed. Throughout the analysis, the guard column (5 m x 0.25 m) was always used to prevent non-volatiles including ionic liquids from entering the analytical column.

The choice of the analytical column for this study was informed by the nature of aromatic components to be separated in terms of their physical and chemical properties. Since ZB-Wax-Plus is a polar substance it was therefore chosen as a suitable stationery phase for the separation of BTEX components. The elution time was dependent on both the boiling points and the polarity of the individual components being analyzed. The peak areas were used to quantify the concentration of each aromatic component in the mixture or sample. The external standards of appropriate concentration range were used for the instrument calibration and the determination of the BTEX components in the mixtures.

3.2.3.2 NMR Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy is generally a technique used to determine the structure of a compound. It identifies the carbon hydrogen framework of an organic compound and is often used with other instrumental methods including infrared and mass spectrometry to enable determination of the entire structure of a molecule. In this study, the focus is on both ^{1}H-NMRand ^{13}C-NMR as the most commonly used techniques together with other instrumental techniques to determine the structures of synthesized and recycled ionic liquids.

^{1}H-NMR measures chemically equivalent protons which are described as protons that are in the same environment. During measurement, each group of chemically equivalent protons gives rise to a signal. Therefore, the number of sets of chemically equivalent protons can be determined from the number of signals in its ^{1}H-NMR spectrum. Proton NMR spectra of most organic compounds are characterized by chemical shifts in the range 0 to 15 ppm and by spin-spin coupling between protons. Chemical shift can be described as a measure of how far the signal produced from the proton is from the reference compound signal whereas spin-spin coupling arises when different kinds of protons are close enough such that the spin of one nucleus influences the spin of another adjacent nucleus with respect to their magnetic fields. Only non-equivalent protons couple and therefore cause a split in their signals. The (N+1) rule determines the type of spin signals as singlet, doublet, triplet, quartet, or multiplet caused by adjacent H atoms. For example, ethyl acetate, CH_3-COO-CH_2-CH_3, has three different types of H atoms. H atoms on ethyl acetate CH_3-COO are not coupling with other H atoms, thus appear as a singlet. But -CH_2- and -CH_3 hydrogen atoms of the ethyl group (CH_3-CH_2-) are coupling with each other, resulting in a quartet and triplet respectively.

The purity of the synthesized ionic liquids was determined by both proton-nuclear magnetic resonance (^{1}H-NMR) and carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrophotometers in order to confirm the quality of the product. The most common solvents used for this purpose were chloroform-d ($CDCl_3$) and acetone-d6 due to their volatility nature which facilitates easy recovery of the samples after analysis. Proton nuclear magnetic resonance is associated with measurements with respect to hydrogen-1 nuclei within the molecules of the compound under investigation in order to determine its structure. ^{1}H-NMR spectra produced from ionic liquids were characterized by chemical shifts in the range 0 – 10 ppm. ^{13}C-NMR is analogous to ^{1}H-NMR and allows the identification of carbon atoms in an organic molecule the same way the proton NMR identifies hydrogen atoms. However, the ^{13}C NMR spectra of ionic liquids determined were in the range 0 – 150 ppm.

Approximately 5 – 8 mg of the synthesized ionic liquid was accurately measured and dissolved in chloroform-d. The solution was then transferred into a clean and dry NMR sample tube. The sample in the tube was adjusted to give the length of 4.5 to 5 cm. After wiping the sample tube clean and dry, it was put onto the carousel and then placed into spinner turbine for scanning.

3.2.3.3 FTIR-ATR Spectroscopy

Infrared spectroscopy is a useful technique to characterize compounds by determining their structures using the mid-infrared region. The infrared spectra are interpreted in terms of wave-numbers which indicate the position of the absorption bands of the compounds being investigated. Mid-infrared comprises group frequency region (4000 – 1500 cm^{-1}) in which the functional groups absorb, and fingerprint region (1500 – 500 cm^{-1}) in which the bending vibrations absorb. The former region has fewer absorption bands in the infrared spectrum and therefore makes it easy to identify the functional groups associated with the compound using frequency data sheets. Fingerprint region, on the other hand, usually contains a very complicated series of absorption bands due to many number of bending vibrations within the molecule. However, each different compound produces a different pattern of frequency absorption bands in this part of the infrared spectrum. Therefore, a compound can be identified in this region by comparing its spectrum with the reference spectra.

One of the most noticeable strengths of infrared spectroscopy as an analytical technique is its ability to obtain spectra from a very wide range of solids, liquids, and gases. However, in many cases some form of sample preparation is required in order to obtain a good quality spectrum. Sample preparation can be very challenging and time consuming and is further complicated by difficulties in getting sample to matrix ratios correct and homogeneous throughout the sample. To address these issues the technique of Attenuated Total Reflectance (ATR) was used in this study since it allows both qualitative and quantitative analysis with little or no sample preparation hence it is relatively fast. ATR is better described as an FTIR sampling technique that provides excellent quality data in conjunction with the best possible reproducibility of any FTIR sampling technique. The main benefit of ATR sampling comes from the very thin sampling path-length and depth of penetration of the IR beam into the sample. In qualitative analysis, sample is directly attached to an ATR crystal that has a high refractive index. Most importantly, the improved spectral acquisition and reproducibility associated with this technique leads to better quality database building for more precise material verification and identification. ATR is clearly an extremely robust and reliable technique suitable for use in research studies involving liquids.

The structures of ionic liquids were checked by analyzing the samples with Varian 800 FTIR-ATR spectrophotometer with the aid of Varian Resolution 4.0 software. The standards and samples were scanned between 4000 and 400 cm^{-1} frequency mid-infrared region which encompasses both the group-frequency (4000 – 1300 cm^{-1}) and finger-print (1300 – 600 cm^{-1}) regions. All the spectra obtained from scanning standards and samples were visually inspected to check the absence or presence of impurities in the ionic liquids.

3.2.4 Determination of Density

The DSA 5000 M instrument simultaneously determines three independent physical properties using one sample. The two in one instrument is equipped with a density cell and a sound velocity cell thus combining the Anton Paar oscillating U-tube method with a highly accurate measurement of sound velocity. The temperature of both cells is controlled by a built-in Peltier thermostat. The densitometer model used in this study is shown in Figure 3.4 from which the densities of most ionic liquids were obtained.

Figure 3.4 Densitometer model DSA 5000M fitted with RXA 156 and X-sample 452

The sample was introduced into a U-shape borosilicate glass tube that is excited to vibrate at its characteristic frequency electronically. The characteristic frequency change depends on the density of a sample. Through a precise determination of the characteristic frequency and mathematical conversion, the density of the sample can be measured. The density was calculated using equation 3.2 as follows:

$$\text{Density} = KA \text{ x } Q2 \text{ x } f1 - KB \text{ x } f2 \qquad (3.2)$$

Where KA and KB are instrument constants, Q is the quotient of the period of oscillation of the U-tube divided by the period of oscillation of the reference oscillator and f1and f2 are correlation terms for temperature, viscosity and non-linearity.

3.2.5 Sound Velocity Measurement

The sample is introduced into a sound velocity measuring cell that is bordered by an ultrasonic transmitter on the one side and a receiver on the other side. The transmitter sends sound waves of known period through the sample. The velocity of the sound can be measured by determining the period of received sound waves and by considering the distance between the transmitter and receiver. Due to the high temperature dependency of the density and sound velocity, the measuring cell has to be precisely thermostatically controlled. The velocity of sound was calculated using equation as follows:

$$u = \frac{l \times (1 + 1.6 \times 10^{-5} \times \Delta T)}{\frac{P_s}{512} - A \times f_3} \qquad (3.3)$$

Where l is the original path length of sound waves, ΔT is temperature deviation, P_s is the oscillation period of the received sound waves, A is the constant for sound velocity, and f_3 is the correction term for temperature.

3.3 Extraction of BTEX using ionic liquids

3.3.1 Introduction

Extraction of BTEX from aromatic/aliphatic mixtures involves liquid-liquid extraction procedures. It is a separation technique that takes advantage of the difference solubility of components of a homogeneous mixture in a suitable solvent. The addition of the solvent to the mixture causes the appearance of a second liquid phase which selectively transfers to the most soluble components. Solvent extraction is used when distillation alone cannot provide a good separation and a good economic solution. The two phases formed from extractions are referred to as extract phase and raffinate phase. The extract phase contains mainly the solutes of interest and the solvent (extractant).

In industry, catalytic reformate containing 44 – 62 % (v/v) is subjected to extractive distillation in which conventional solvent is used as an extractant, resulting in the formation of aliphatic-rich phase and aromatic-rich phase. The latter phase is then processed through steam distillation to separate aromatic hydrocarbons from extraction solvent, and the solvent recycled back to the extractive distillation unit. The feed mixture is fed to the liquid-liquid extraction tower, where aromatic hydrocarbons selectively dissolve with the solvent. The aliphatic-rich hydrocarbons (raffinate phase) coming out at the top of the column is sent to the next tower to recover the small amount of solvent from the raffinate phase. The solvent-rich extract phase exits the tower with traces of aliphatic and high quantity of aromatics. The solvent and aromatics are separated by flash distillation methods.

In the laboratory, a series of liquid-liquid multi-component extraction experiments were carried out using the synthesized ionic liquids. Further extractions were performed using regenerated ionic liquids which were characterized before reuse. During extraction the mixtures under investigation were vigorously stirred in a constant temperature thermostatically controlled water-bath and water-jacketed vessels. The following experimental procedure was adopted and followed for the extraction processes:

- All ionic liquids were synthesized under inert atmosphere of nitrogen using toluene as a reaction solvent.
- After synthesis ionic liquids were dried under reduced pressure to remove volatile by-products/reactants and moisture prior to using them in extractions.
- After each extraction, the ionic liquid was regenerated under reduced pressure and then reuse for further extractions after re-characterization.
- A known volume of a selected ionic liquid and a sample (organic mixture containing aromatic hydrocarbons) were transferred into water-jacketed vessels.
- Each mixture was stirred vigorously at constant temperature using a thermostatically controlled water-bath until equilibrium was reached.
- At the end of the extraction process, the resultant mixtures were left to stand overnight in order to allow the two conjugate layers to reach equilibrium.
- After separation each phase was analyzed for individual concentration % (v/v) of aromatic components using GC-FID fitted with ZB-WAX plus analytical column as well as a guard column.
- Peak areas from chromatograms and linear regression equations from calibration curves were used for the calculation of percentages of aromatic components.

- Lastly the recovery values of individual aromatic components present in each phase were calculated from the original concentrations of the sample mixtures.

For the purpose of this study, three categories of organic mixtures were investigated, namely; prepared or model mixtures, reformates, and spent solvents. Model mixtures refer to the solutions of known concentrations containing BTEX components mixed with either n-hexane or n-heptane as an aliphatic hydrocarbon. Reformates and spent solvents were non-aqueous mixtures serving as samples for this research obtained from local petroleum and paint manufacturing industries.

Model mixtures were used in various liquid-liquid extractions before any industrial related mixtures were investigated under similar conditions. Such mixtures paved the way for multi-component systems of liquid-liquid equilibria for the extraction of benzene, toluene, ethylbenzene, and isomers of xylenes (BTEX) from the mixtures containing aliphatic and aromatic hydrocarbons. Each mixture was made to contain at least one n-alkane and the targeted aromatic components in varying concentrations. The prepared mixtures were then subjected to a five-hour long extraction at 40 ºC with ionic liquids. The schematic cross-section diagram of the water-bath used is shown in Fig. 3.5

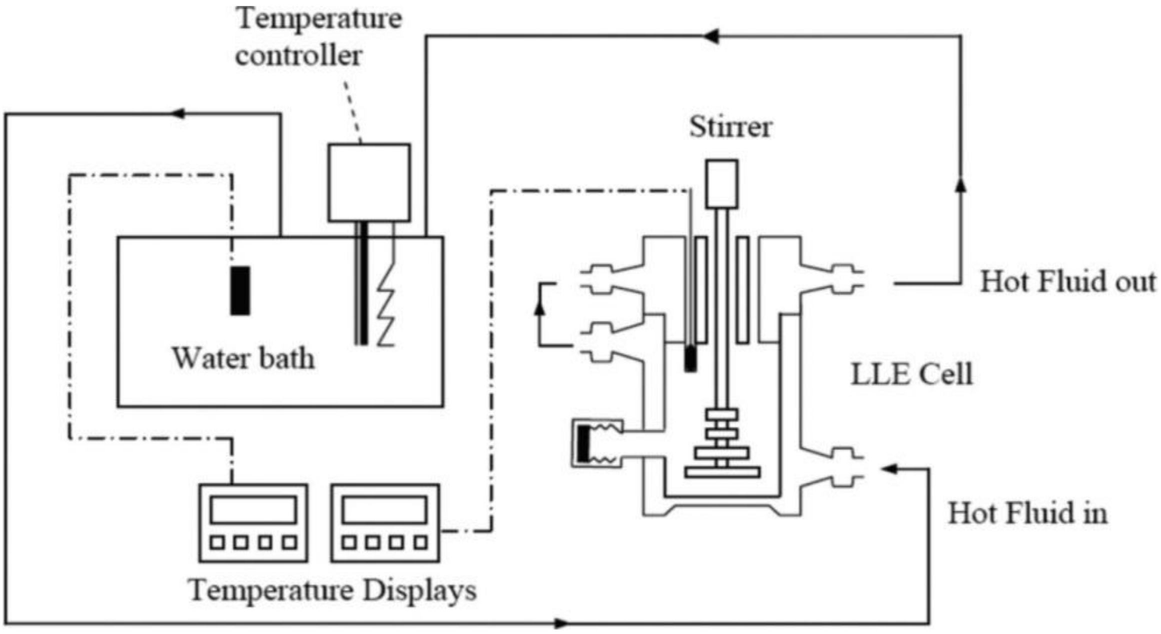


Figure 3.5 Cross-section schematic diagram of a thermostatically controlled water-bath

The two-phase mixtures were then left overnight at room temperature to ensure complete equilibration. The extract and raffinate phases were then carefully separated using separating funnels of appropriate size and then stored in suitable viable for GC-FID analysis.

3.3.2 General Extraction Procedure

Before each experiment, the ionic liquids were dried at 80°C under reduced pressure in a rotary evaporator since all ionic liquids are hygroscopic and the presence of water can change their properties [66].

- Liquid-liquid extraction experiments were carried out in jacketed vessels. The vessels were jacketed to circulate water from a water bath in order to keep the temperature constant inside the vessels at 40°C.

- Ratio of 2:1 (ionic liquid: reformate mixture, 20:10 mL) was placed into the vessel and stirred for four hours using a magnetic stirrer to reach equilibrium.
- After stirring, the two phases were allowed to settle for 24 hours

In general, extraction processes do not give complete extraction in a single step or stage [86]. It was therefore necessary to conduct several extractions for each test sample in order to establish the number of stages required for the complete recovery of BTEX from various aromatic/aliphatic and other related organic mixtures. The successive extractions using regenerated ionic liquids were performed on a number of raffinate phases after each extraction, followed by analysis of the resulting phases by GC-FID, that is, both the extract and raffinate phases were analyzed. This exercise is important in that it provides valuable information with regard to the extraction efficiency and effectiveness of ionic liquids for the total recovery of all aromatic components. In addition, the time required for the equilibrium to be reached in each stage of extraction was noted. In this way, the optimum conditions of the processes for the recovery of aromatic components from aromatic/aliphatic mixtures were optimized.

3.3.3 Preparation of model mixtures

An appropriate aliquot of each aromatic component was quantitatively transferred into a 100 mL volumetric flask, followed by adding n-alkane to mark. The following aromatic/aliphatic model mixtures of varying composition and concentrations were prepared in volumetric flasks (100 mL) where n-alkanes were used as solvents or diluents:

- Benzene and toluene in the concentration range 0.5 – 25 % (v/v) each.
- Benzene, toluene, ethylbenzene, and o-xylene in the concentration range 2.5 – 10 % (v/v) each.
- Benzene, toluene, ethylbenzene, p-xylene, m-xylene, and o-xylene in the concentration range 2.5 – 10 % (v/v) each.

These mixtures were kept well sealed in the refrigerators to prevent loss of volatile components through evaporation. Each mixture was used for the calibration of GC-FID as well as in the liquid-liquid extractions using different ionic liquids. All samples and standards were analyzed under the same experimental conditions which were detailed in previous sections. However, the experiments were specifically devised to investigate the effects of:

- Varying the concentrations of BTEX components
- Using regenerated or recycled ionic liquids
- Varying the phase settling periods
- Varying the nature of n-alkanes
- Varying the nature of cations in the ionic liquids
- Varying the nature anions in the ionic liquids
- Increasing the number of extraction stages

3.3.4 Extractions Involving Model Mixtures

Aromatic components present in each model mixture described in section 3.3.2 were extracted using different ionic liquids at 40 ºC. The purpose of using the wide concentration range of model mixtures was to test the accuracy and validity as well as the precision of the experimental methods and procedures. The nature of the multi-component systems involving BTEX extractions using ionic liquids in this study range from quaternary to multi-component mixtures as summarized in the following mixtures:

- Benzene + toluene + n-heptane + [EMIM][ESO_4]
- Benzene + toluene + ethylbenzene + o-xylene + n-heptane + [EMIM][ESO_4]
- Benzene + toluene + ethylbenzene + o-xylene + n-hexane + [EMIM][ESO_4]
- Benzene + toluene + ethylbenzene + o-xylene + n-hexane + [EMpy][ESO_4]
- Benzene + toluene + ethylbenzene + xylene isomers + n-hexane + [EMIM][ESO_4]
- Benzene + toluene + ethylbenzene + xylene isomers + n-hexane + [EMpy][ESO_4]
- Benzene + toluene + ethylbenzene + xylene isomers + n-hexane + [BNMP][Br]
- Benzene + toluene + ethylbenzene + xylene isomers + n-hexane + [MNMP][I]

The common extraction procedures were carried out as follows:

Each experimental mixture (10 mL) was placed in a jacketed vessel (100 mL) connected to a thermostatically controlled water-bath set at 40 0C, followed by addition of the chosen ionic liquid (20 mL) [90]. Maximum of four extraction operations were effectively carried out simultaneously without any noticeable fluctuations on the desired fixed temperatures. The mixtures were then agitated vigorously using magnetic stirrers for 3 hours in order to allow intimate contact between the two phases (ionic liquid-rich phase and aliphatic hydrocarbon-rich phase) in each mixture. The respective equilibrium mixtures were then transferred into separating funnels and allowed to settle for at least 12 hours at room temperature to ensure complete phase separation [90,94,95,96,97]

The resulting two phases of each mixture were separated and quantitatively transferred into suitable sample vials and then sealed with silicon caps. The samples were then retained for GC analysis in a cool place to prevent loss of volatile components. The ionic liquid-rich phase and the aliphatic hydrocarbon-rich phase were referred to as extract phase and raffinate phase, respectively. The ionic liquids were recovered from the mixtures by using a rotary evaporator under reduced pressure to remove organic solvents and other volatile substances as well as water.

Each phase was then analyzed by GC-FID under optimal experimental conditions in order to determine:

- The extent of percentage recovery for each aromatic component from model mixtures.
- The selectivity of each ionic liquid for individual aromatic components.
- The nature of distribution pattern of aromatic components on each ionic liquid.
- The recyclability of each ionic liquid for further reuse in the extraction processes.

3.3.5 Extractions Involving Reformates

In the section, the extraction capacity of the four ionic liquids (1-ethyl-3-methylimidazolium ethyl sulphate [EMIM][ESO$_4$], 1-ethyl-3-methylpyridinium ethyl sulphate [EMpy][ESO$_4$], 1-butyl-1-methyl-2-pyrrolidonium bromide [BNMP][Br], and 1, 1-dimethyl-2-pyrrolidonium iodide [[MNMP][I]), were investigated. The extraction of various reformate samples of known BTEX concentrations obtained from Oil Refineries (Engen SA) were used for this purpose. However, reformate samples were first directly analyzed for the content of aromatic hydrocarbons (BTEX) by percent volume using GC-FID before being extracted by the four afore-mentioned ionic liquids. The same procedure and experimental conditions used in the analysis of model mixtures were followed for the determination of aromatic hydrocarbons in the original reformate samples. The extractability of each ionic liquid was to be determined based on the original concentrations of aromatic components present. It also aimed to provide valuable information on how the experimental values compared with the literature values as far as this study is concerned.

Reformate samples were extracted by the four afore-mentioned ionic liquids under similar experimental conditions that were used for the model mixtures. Aliquots (10 mL) of the reformate samples were placed in jacketed vessels at 40 ºC, followed by addition of the respective ionic liquid (20 mL). The mixture was agitated vigorously using a magnetic stirrer for 3 hours in order to allow for intimate contact between the two phases. When the equilibration time for the settling of phases was reached, the two phases were separated and then analyzed for BTEX content using GC-FID.

3.3.6 Extractions Involving Spent Solvents

The effective number of extraction stages required for the total recovery of aromatic components, were investigated using extractions involving spent solvent samples obtained from Paint Manufacturing Industries. The two ionic liquids (1-ethyl-3-methylimidazolium ethyl sulphate [EMIM][ESO_4] and 1-ethyl-3-methylpyridinium ethyl sulphate [EMpy][ESO_4]) were used for the purpose of this study. In this investigation, these ionic liquids were involved in a series of three stages as extraction solvents for the recovery of aromatic components present in the spent solvents. As it was the case with reformate samples, the concentrations of individual aromatic components present in the spent solvent were first determined.

To achieve this objective, the multi-component system experiments were carried out at 40 ºC and atmospheric pressure to simultaneously extract toluene, ethyl benzene, and xylene isomers (TEX) using the two afore-mentioned ionic liquids. These ionic liquids were used in order to compare their strengths in the extraction of aromatic hydrocarbons from paints effluent organic mixtures in terms of their extractabilities. The concentrations of each aromatic component in the extract and raffinate phases were measured by GC-FID as % volume to determine extraction capacity of the ionic liquids under investigation.

Mixtures of original spent solvents from paint manufacturers were extracted by the afore-mentioned ionic liquids under controlled conditions using appropriate apparatus and equipment. The procedure used for the extraction of aromatic components from the spent solvent samples was the same as the one followed in reformates investigation. Aliquots (10 mL) of the spent solvent were directly placed in jacketed vessels at 40 ºC, followed by addition of the respective ionic liquid (20 mL). The mixture was agitated vigorously using a magnetic stirrer for 3 hours in order to allow for intimate contact between the two phases. When the equilibration time for the settling of phases was reached, the two phases were separated and then analyzed by GC-FID for the concentrations of individual aromatic components present.

3.4 Analysis of Mixtures by GC-FID

3.4.1 Introduction

The percentages of each aromatic component in model mixtures, reformate samples, spent solvents, extraction phase mixtures (extract phase and raffinate phase) were analyzed by GC-FID under the same instrument conditions shown in 3.2.5.2 section. The GC instrument was fitted with ZB-Wax-Plus capillary column (30m x 0.25mm x 0.25µm) and a guard column (5m x 0.25mm). The latter protected the analytical column by trapping the ionic liquids thus avoiding disruptions of the analysis. The instruments were calibrated by using external standards covering the concentration range of all determinations in this study. A portion of each sample mixture or standard solution was transferred into a suitable sample vial for GC analysis. The vials were sealed with silicon septa through which a micro syringe needle was used to draw 1 µL of each sample for GC analysis. Peak areas and linear regression equations from calibrations curves were used for the calculation of concentrations in all cases. Furthermore, since the ionic liquids contained small amount of toluene from the synthesis stage, a blank analysis was done to adjust the results with respect to toluene, if necessary.

The analysis of the blank was also administered on the recycled ionic liquids to determine residual BTEX components before any further extraction operations were performed. This study focused on GC-FID analysis that involved model mixtures, reformate samples, spent solvent samples, and extraction phase mixtures as well as ionic liquids as blank samples all performed under similar experimental conditions.

3.4.2 Instrument conditions and parameters

The Gas chromatography parameters were first investigated in order to identify the best conditions for the separation of BTEX components in terms of peaks for the purpose of identification and quantification. On completion of the optimization of the instrument, it was therefore possible to measure the retention times and peak areas corresponding to all of the targeted individual components, in this case, benzene, toluene, ethylbenzene, p-xylene, m-xylene, and o-xylene. The following instrument optimal conditions and parameters were therefore finalized and used for the analysis of all the mixtures containing BTEX experimented in this study:

Column oven : 40 ºC (2 min → 115 ºC at 20 ºC/min)
Carrier gas : nitrogen; column flow
Injector : 250 ºC; split ratios were 1:100 for the standards and Raffinate phase, 1:100 for the extract phase
Detector : FID; 250 ºC
Injector : 250 ºC
Split ratio : 1:100
Carrier gas : nitrogen/ air
Flow control mode : linear velocity
Linear velocity : 25.6 cm/sec
Flow rate : 1.00 mL/min
Analytical column : ZB-Wax-Plus (30m × 0.25mm ×0.25µm)
Guard column : 5m × 0.25mm
Program : 400C [2min to 115 ºC] at 10 ºC/min

Detector (FID) : 250 ºC

3.4.3 Analysis of Model Mixtures

3.4.3.1 Analytical Method Validation

Method validation was performed in order to justify the selection of the analytical method that was used in this project. The parameters evaluated for this purpose included limit of detection (LOD), limit of quantification (LOQ), selectivity, specificity, sensitivity, signal-to-noise (S/N), precision, accuracy, percent recovery, linear calibration range and method linearity which are briefly described below. The limit of quantification (LOQ) is described as the lowest concentration of an analyte in the sample that can be determined with acceptable precision and accuracy under the stated experimental conditions. Linearity refers to the ability of an analytical procedure to produce experimental results that are proportional to the concentration of the analyte in the samples within a given concentration range. For a linear calibration curve, it is assumed that the instrument response y is linearly related to the standard concentration x for a limited range of concentration.

The working range of an analytical procedure is the interval of analyte concentrations in the samples for which it has been demonstrated that the analytical method has suitable levels of precision, accuracy, and linearity. The linear range is measured by the coefficient of determination (R^2) for a calibration curve which must be $\geq$ 0.995 [126]. Selectivity is the ability of an analytical method to accurately determine the analyte and specifically determine the analyte of interest in the presence of other compounds in a sample matrix under the stated conditions of the experiment. In all cases, sufficient analyte concentration must be present to produce an analytical signal that can reliably be distinguished from analytical noise which is the signal produced in the absence of analyte. The accuracy was determined by percent recovery of each aromatic component in the model mixtures under investigation which must be within the acceptable range 80 – 120%. The precision was measured and expressed as relative standard deviation which must be < 20%. If the injection volume is identical for every standard and sample, then instrument calibration using external standards provides both accurate and precise results. However, for quantitative work requiring high accuracy and precision, the use of internal standards is recommended.

In this project, the characteristics of the method performance were estimated statistically as follows:

- Limit of detection, limit of quantification, linearity, linearity range, coefficient of determination (R^2), and analytical method error were all determined using BTEX model mixtures (solutions of known concentrations) of the concentration range 0.5 – 25 % (v/v) by means of LINEST function in the MS Excel.

  From the calibration curves, LOD and LOQ are estimated by using the formula:

  $$\text{DOL/LOQ} \quad = \quad F \times S_y/m$$

  Where

  F: factor of 3 for LOD and 10 for LOQ

  S_y: Standard deviation of the y-intercept

  m: Slope of the regression line

  The values of S_y and m were obtained from the LINEST function when creating the calibration curves in the MS Excel.

- The accuracy was determined by extracting various model mixtures of concentrations ranging from 0.5 to 25 % (v/v) containing two to six aromatic components. The recovery values were calculated from extract and raffinate phases.
- The precision was estimated from the replicates of the reformate samples all analyzed under similar conditions. Standard deviations and relative standard deviations were calculated from the data obtained from the analysis.

- Selectivity and specificity were determined by retention times of the individual aromatic components appearing on the chromatograms.
- Signal-to-noise ratio could not be accurately measured due to the absence of pronounced noise on the base-line of the peaks.

The results obtained from this investigation are shown in Chapter 4 where the discussion of the effects of new ionic liquids in extracting 0.5 – 25 % (v/v) model mixtures is done.

The extent of accuracy and precision was estimated by means of standard deviations, and the linearity was determined by the values of the correlation coefficient (R^2) for each BTEX component [126]. The data for these measurements are dealt with in Chapter 4 using statistical methods to ensure sustained reliability of measurements. In this study, this was done by using replicates of four reformate samples for which their BTEX concentrations were known from suppliers [5] and have been verified by independent users [102]. This was done in order to evaluate the analytical methods and techniques employed in this study were within the acceptable limits in terms of statistical evaluation. The instruments were always first calibrated before carrying out any analysis of the real samples using model or standard solutions covering the concentration range of the unknowns.

3.4.3.2 Preparation of Calibration Standards

Model mixtures of varying concentration range and composition of aromatic components (BTEX) in either n-heptane or n-hexane were accurately prepared from standards of high purity (> 99.9 %). The solutions investigated in this study covered the concentration range 2.5 – 25.0 % (v/v), 2.5 – 10 % (v/v), and 0.5 – 10 % (v/v) of each selected aromatic component. All standard solutions were stored in a cool place to prevent loss of volatile components through evaporation and were used one at a time at room temperature when needed. These solutions were also used as model mixtures in the extractions of BTEX using ionic liquids. Their recovery values were also used to validate the analytical methods used in this investigation.

The chromatograms were produced and its peak areas used to construct calibration curves from the afore-prepared model mixtures. The results obtained from the analysis of BTEX in model mixtures were tabled in Chapter 4 and also in Appendix section. The chromatograms and calibration curves and other type of graphs were also recorded in Chapter 4 for the purpose of treatment and interpretation.

3.4.4 Analysis of Reformates

Replicates of reformate samples were analyzed in order to validate the results obtained from the methods used in this study. This was done by repeating the measurements on replicate samples to estimate the precision of results and hence the reliability of the method. Eight replicates were analyzed on each of the four reformate samples from which the standard deviations and relative standard deviations were determined.

3.4.5 Analysis of Spent Solvent Wastes

A number of distillates were obtained from spent solvent samples using rotary evaporator distillation method. A known volume of spent solvent mixture was distilled 0using rotary evaporator to collect all volatile organic components including aromatic and aliphatic hydrocarbons as the most important ones. The volume of the distilled liquid was measured to 0.1 mL accuracy and then analyzed for the percentage by volume of each aromatic component present in the distillate using GC-FID fitted with capillary column. The concentrations of individual aromatic hydrocarbons present in the spent solvents were calculated using the original volume of the sample.

Each phase from extraction mixtures was prepared and analyzed according to the standard procedure outlined in 3.2.5.1 and the instrument conditions in 3.2.5.2 above. Chromatograms obtained from these measurements are given in Chapter 4 and also in Appendices section.

4 CHAPTER FOUR: RESULTS AND DISCUSSIONS

4.1 Characterization of Ionic Liquids

4.1.1 Density, moisture, sound velocity, and refractive index

The characterization results obtained from measuring density, moisture content, sound velocity, and refractive index of 1-ethyl-3-methylimidazolium ethyl sulphate [EMIM][ESO_4] and 1-ethyl-3-methylpyridinium ethyl sulphate [EMpy][ESO_4] are shown in Table 4.1. The average experimental density for 1-ethyl-3-methylimidazolium ethyl sulphate is 1.2289 $g.cm^{-3}$ measured at 25 °C and the literature value is 1.2376 $g.cm^{-3}$ at 25 °C [127]. For the ionic liquid 1-ethyl-3-methylpyridinium ethyl sulphate, the average experimental density is 1.2149 $g.cm^{-3}$ measured at 25 °C and the literature value is 1.2223 $g.cm^{-3}$ at 25 °C [128]. For both ionic liquids, the experimental density values measured are slightly lower than that reported in the literature.

The average moisture content was computed to be 0.21 % for 1-ethyl-3-methylimidazolium ethyl sulphate and 0.10 % for 1-ethyl-3-methylpyridinium ethyl sulphate. These results indicate that 1-ethyl-3-methylimidazolium ethyl sulphate has higher density and more hygroscopic than 1-ethyl-3-methylpyridinium ethyl sulphate. Table 4.1 also reveals that the refractive index and sound velocity values for the respective unused and recycled ionic liquids do not differ significantly. The average experimental refractive index values for [EMIM][ESO4] and [EMpy][ESO_4] were calculated to be 1.4788 and 1.5054 and the literature values are 1.4794 and 1.5067, respectively [127, 128]. For respective ionic liquids, the experimental average values of sound velocity were found to be 1679.4 and 1677.6 $m.s^{-1}$ and the literature values are 1679.0 and 1678.1 $m.s^{-1}$ [127,128].

The summary of results for density, sound velocity, and refractive index in Table 4.1 indicates that the experimental values are in excellent agreement with the literature values in both ionic liquids 1-ethyl-3-methylimidazolium ethyl sulphate and 1-ethyl-3-methylpyridinium ethyl sulphate.

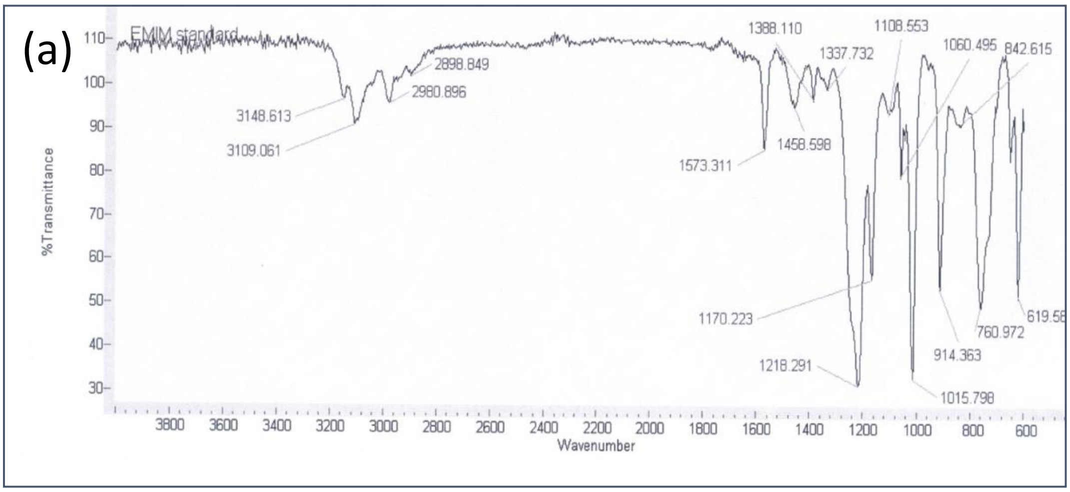
In general, the values for all the properties measured for the new and recycled ionic liquids show small changes to the freshly prepared product. This is taken to indicate that the ionic liquids retain their qualities even after they have been used several times after regeneration. Another observation is that the results in Table 4.1 also show a gradual increase in the density of 1-ethyl-3-methylimidazolium ethyl sulphate with increasing number recycling times whilst the 1-ethyl-3-methylpyridinium ethyl sulphate show no significant changes in its densities.

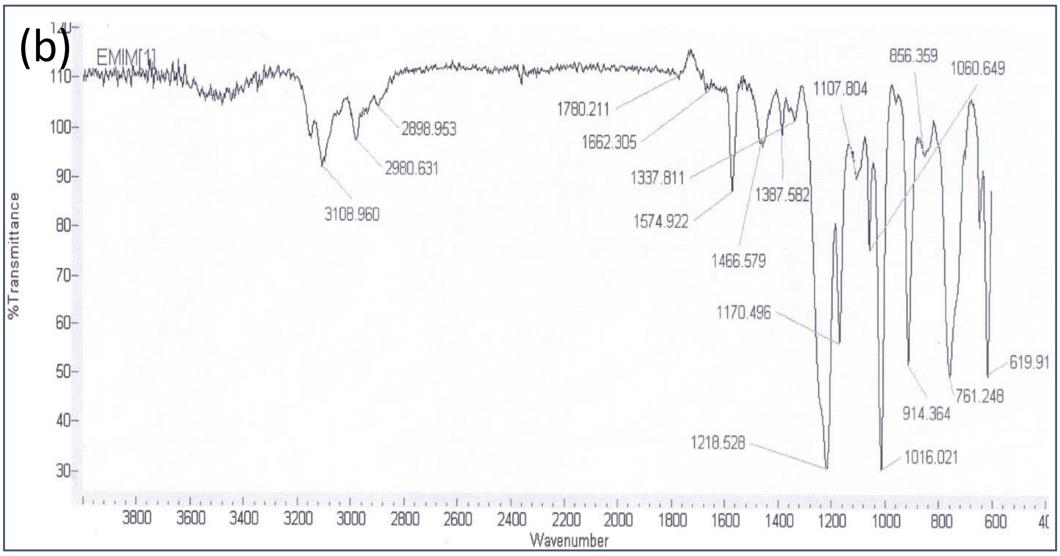
Table 4.1 Density ρ, sound velocity n, refractive index μ, and moisture content of [EMIM][ESO_4] and [EMpy][ESO_4] measured at 25 °C

Recycles	None	One	Two	Three	Four	Five	Six	Average	Lit.
Ionic Liquid: 1-ethyl-3-methylimidazolium ethyl sulphate [EMIM][ESO_4]									
ρ/g.cm^{-3}	1.2265	1.2275	1.2255	1.2282	1.2297	1.2334	1.2318	1.2289	1.2376
H_2O/%	0.30	0.21	0.18	0.15	0.13	0.25	0.23	0.21	0.08
μ/m.s^{-1}	1677.8	1682.1	1682.0	1670.0	1680.2	1674.5	1689.4	1679.4	1678.2
n_D	1.4779	1.4773	1.4791	1.4809	1.4782	1.4811	1.4771	1.4788	1.4794
Ionic Liquid: 1-ethyl-3-methylpyridinium ethyl sulphate [EMpy][ESO_4]									
ρ/g.cm^{-3}	1.2138	1.2120	1.2152	1.2161	1.2172	1.2157	1.2149	1.2150	1.2223
H_2O/%	0.05	0.06	0.03	0.05	0.15	0.18	0.21	0.10	0.05
μ/m.s^{-1}	1676.06	1678.9	1677.4	1678.0	1676.9	1678.3	1677.3	1677.6	1681.2
n	1.5051	1.5055	1.5046	1.5065	1.5041	1.5058	1.5062	1.5054	1.5067

4.1.2 Structural determination by FTIR Spectroscopy

The infrared spectra for the ionic liquid 1-ethyl-3-methylimidazolium ethyl sulphate [EMIM][ESO_4] are all depicted in Figure 4.1, illustrated with letters a, b, c, and d. (See Appendix 1, Figures A7.1 – A7.8 for individual spectra.) All four spectra show similar pattern thus indicating that this ionic liquid retains its structure shown in Figure 4.3 after several times of recycling.





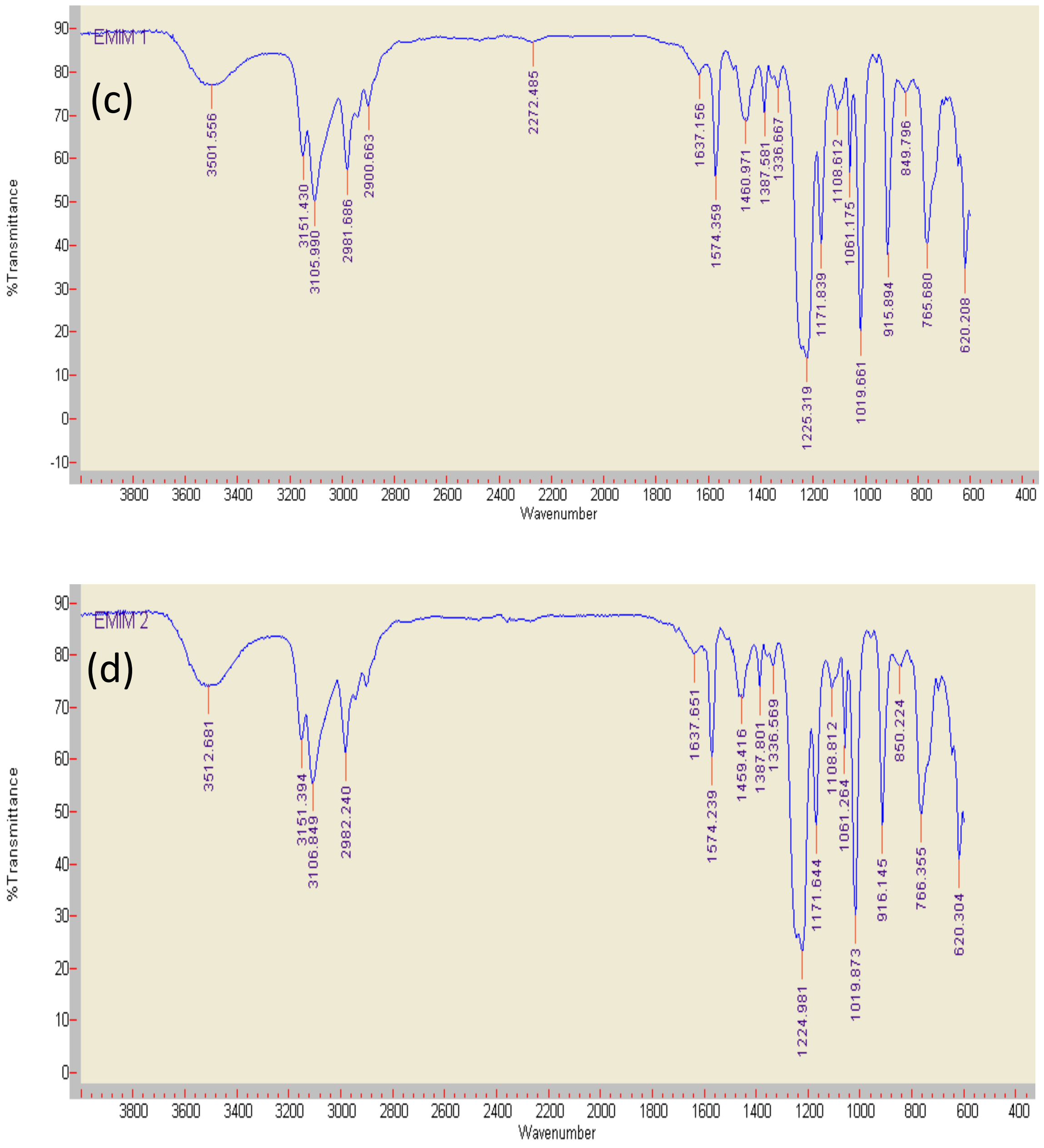
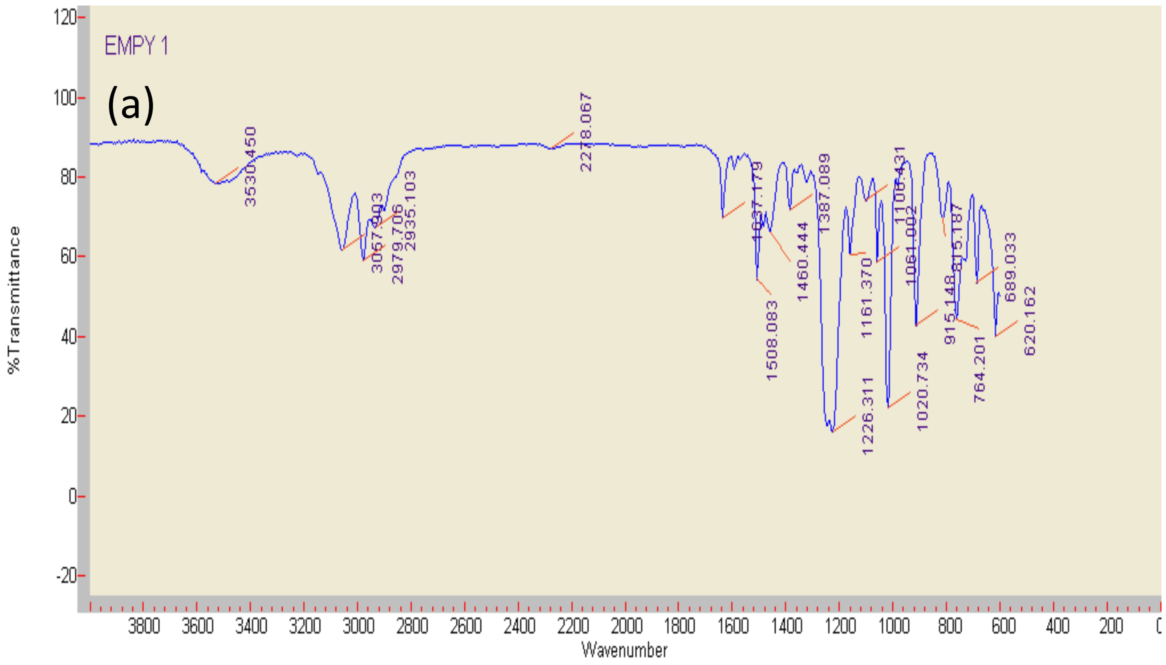
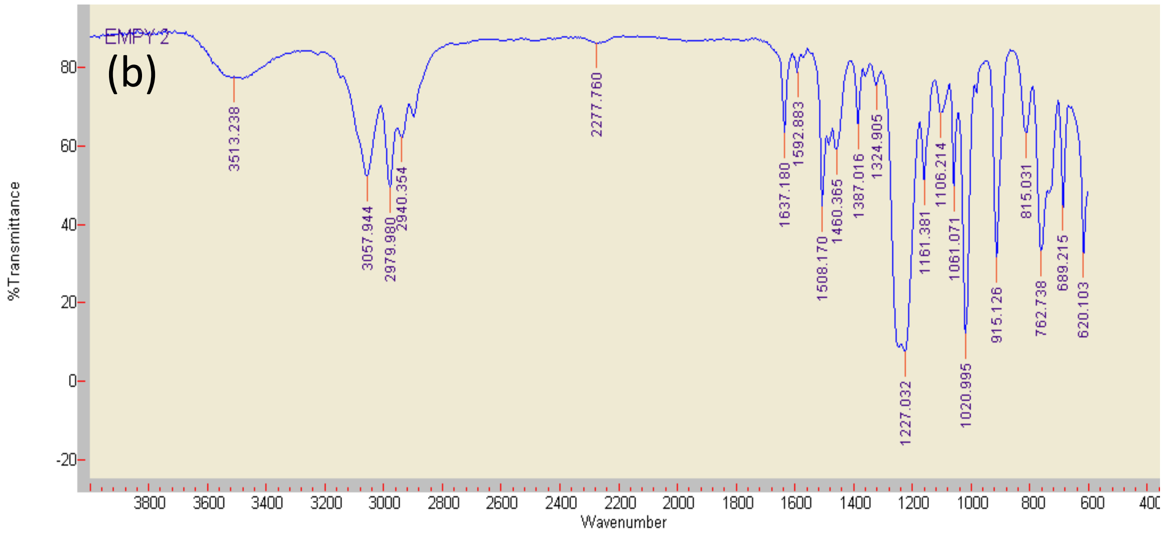


Figure 4.1 Infrared spectra for the ionic liquid [EMIM][ESO_4] where (a) Standard IL (b) Synthesized IL (c) Regenerated twice IL (d) Regenerated thrice

The infrared spectra for the ionic liquid 1-ethyl-3-methylpyridinium ethyl sulphate [EMpy][ESO_4] are all depicted in Figure 4.2 illustrated with letters a, b, and c. (See Appendix 1, Figures A7.9 – A7.11 for individual spectra.) The spectra show similar pattern thus indicating that this ionic liquid retains its structure shown in Figure 4.4 after regeneration.





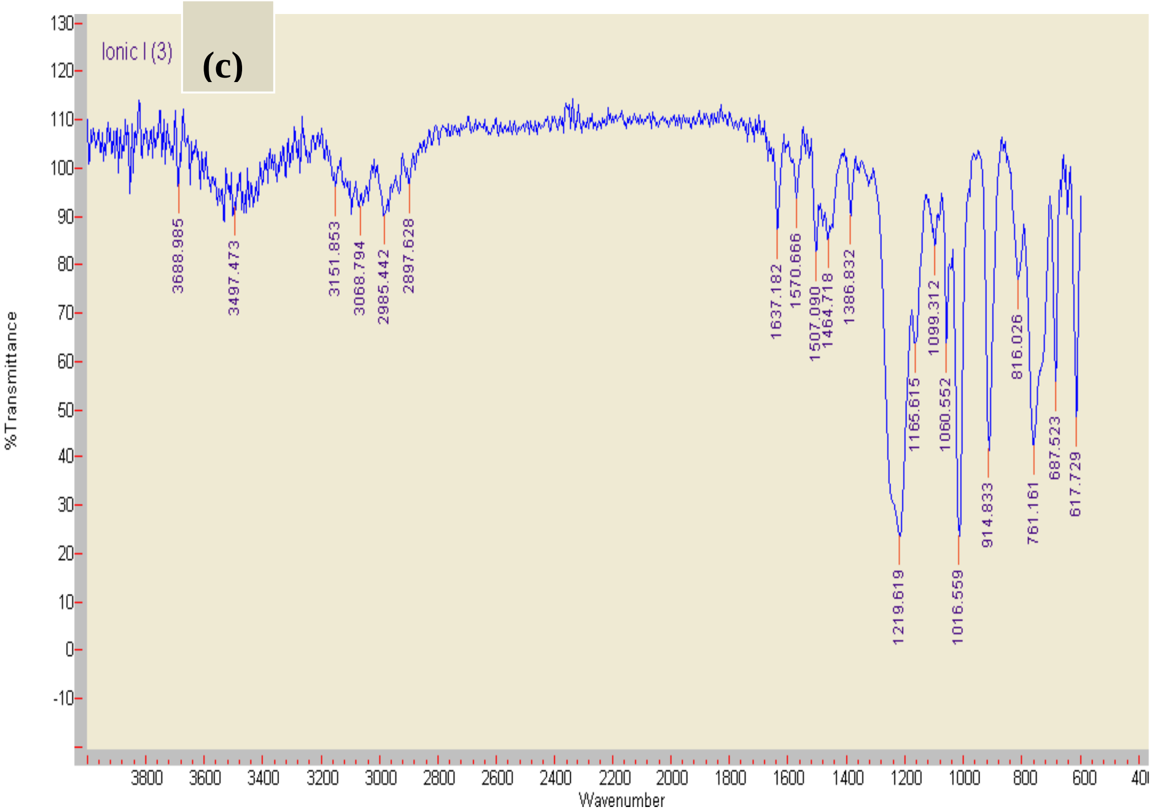


Figure 4.2 Infrared spectra for the ionic liquid [EMpy][ESO_4] where (a) Standard IL (b) Synthesized IL (c) Regenerated IL

The spectra of the ionic liquid 1-ethyl-3-methylimidazolium ethyl sulphate [EMIM][ESO_4] showed the following typical bond stretches:

C – H stretch of alkyl group at 2980 – 2985 cm^{-1}

C – H stretch of aromatic amine at 3100 – 3150 cm^{-1}

C – C stretch of aromatic at 3100 – 3150 cm^{-1}

C – N stretch of aromatic amine at 1250 – 1330 cm^{-1}

C – N stretch of alkyl amine at 1015 – 1219 cm^{-1}

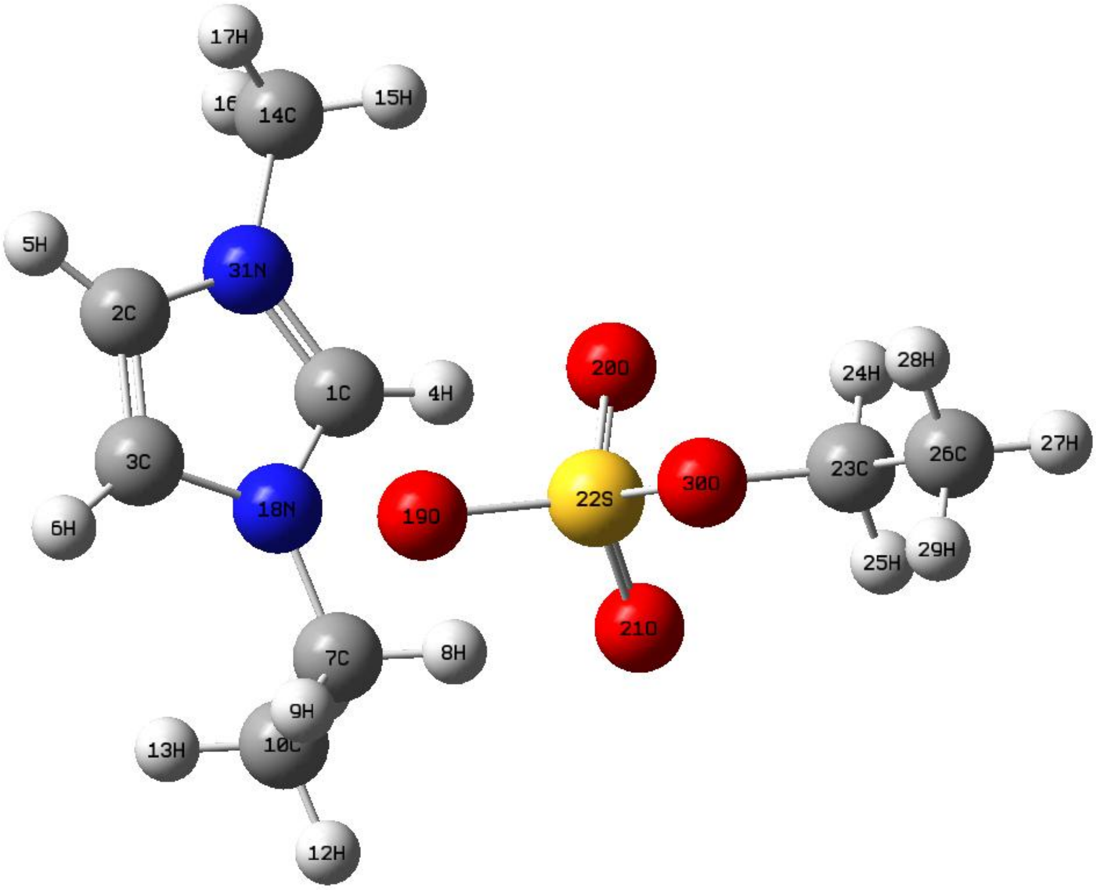


Figure 4.3 Structure of 1-ethyl-3-methylimidazolium ethyl sulphate [EMIM][ESO$_4$]

All infrared spectra of ionic liquid 1-ethyl-3-methylpyridinium ethyl sulphate [EMpy][ESO$_4$] showed the following common bond stretches:

Standard ionic liquid: [EMpy][ESO$_4$]

O – H stretch of water or moisture at 3500 – 3513 cm^{-1}

C – H stretch of alkyl group at 2980 – 2985 cm^{-1}

C – H stretch of aromatic amine at 3110 – 3160 cm^{-1}

C – C stretch of aromatic at 3100 – 3150 cm^{-1}

C – N stretch of aromatic amine at 1250 – 1330 cm^{-1}

C – N stretch of alkyl amine at 1019 – 1225 cm^{-1}

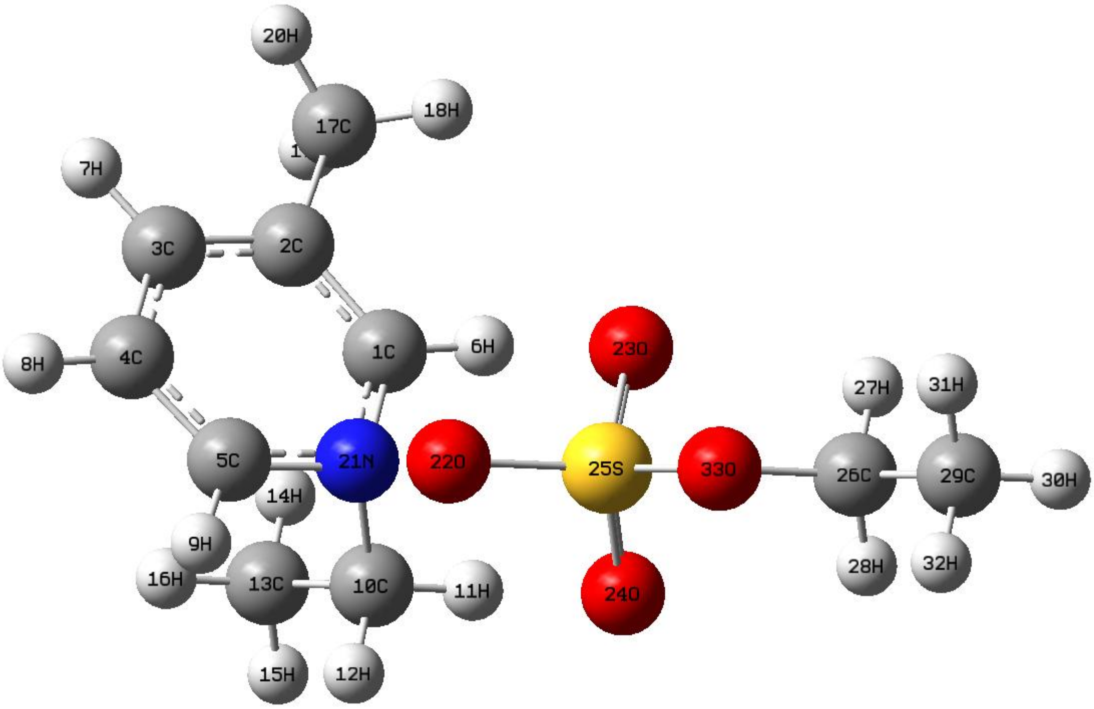


Figure 4.4 Structure of 1-ethyl-3-methylpyridinium ethyl sulphate [EMpy][ESO$_4$]

Table 4.2 FT-IR wave-numbers from the spectra of synthesized ionic liquids

IL	1-ethyl-3-methylimidazolium ethyl sulphate/Wave-Numbers (cm^{-1})									
1	3109	2981	1573	1459	1218	1170	1016	914	760	620
2	3105	2981	1574	1456	1216	1170	1015	913	759	618
3	3105	2982	1574	1453	1215	1169	1015	913	761	619
4	3104	2981	1573	1452	1216	1170	1015	913	759	618
5	3109	2983	1576	1458	1218	1170	1016	915	763	622
6	3107	2981	1574	1460	1215	1170	1015	913	761	620
7	3103	2979	1574	1461	1215	1170	1015	913	758	619
8	3102	2981	1574	1454	1218	1170	1016	913	760	619
9	3110	2981	1575	1465	1217	1170	1018	915	762	623
10	3105	2982	1574	1461	1225	1172	1020	916	766	620
IL	1-ethyl-3-methylpyridinium ethyl sulphate/Wave-Numbers (cm^{-1})									
1	3059	2978	1637	1508	1219	1162	1017	914	760	620
2	3058	2980	1637	1506	1217	1161	1017	913	757	619
3	3055	2981	1637	1508	1220	1162	1017	914	761	620
4	3059	2978	1637	1508	1218	1161	1016	913	757	618
5	3059	2980	1637	1507	1219	1161	1017	913	760	620
6	3058	2978	1638	1507	1219	1161	1016	913	760	619
7	3069	2985	1637	1507	1220	1166	1017	915	761	618
8	3058	2980	1637	1506	1217	1161	1016	913	758	620
9	3058	2980	1637	1508	1227	1161	1021	915	753	620
10	3057	2980	1637	1508	1226	1171	1021	915	764	620

Table 4.2 shows that the wave-numbers of both ionic liquids fall in the mid-infrared region range of 4000 – 400 cm^{-1}. For the ionic liquid 1-ethyl-3-methylimidazolium ethyl sulphate the range is 3110 – 618 cm-1, and 3059 – 618 cm^{-1} for 1-ethyl-3-methylpyridinium ethyl sulphate. Most absorption bands appear in the fingerprint region (1300 – 600 cm^{-1}) with fewer bands falling in the group frequency region (4000 – 1300 cm^{-1}). According to the values in the tables it can be seen that the spectra for the synthesized ionic liquids match very well with each other and also with those of standard or reference ionic liquids. This confirms that the recycled ionic liquids retain their structures after several recycles. Hence they meet the required level of purity based on their IR spectra obtained from frequency absorption bands. It can be seen from the spectra in Figures 4.1 and 4.2 that there are very little or no impurities present in the synthesized and regenerated ionic liquids based on the standard and reference spectra.

4.1.3 Structural determination by NMR Spectroscopy

The spectra obtained from ^{1}H-NMR- and ^{13}C-NMR for the ionic liquid 1-ethyl-3-methylpyridinium ethyl sulphate [EMpy][ESO_4] are depicted in Figure 4.5. (Refer to Appendix 2, Figures A7.12 – A7.13, A7.20 – A7.21, A7.28 – A7.29 for more NMR spectra.) The spectra given by the ionic liquid 1-ethyl-3-methylimidazolium ethyl sulphate [EMIM][ESO_4] from ^{1}H-NMR- and ^{13}C-NMR are depicted in Figure 4.6. (See also Appendix 2, Figures A7.12 – A7.17)

It can be noticed in Figures 4.5 and 4.6 that all ^{1}H-NMR- and ^{13}C-NMR spectra produced from respective ionic liquids match each other very well. This serves to confirm the structures of ionic liquids being investigated. The spectra which were given by ionic liquids [EMIM][ESO$_4$] and [EMpy][ESO$_4$] from NMR (^{1}H and ^{13}C) gave the following data in terms of frequency assignments:

Standard ionic liquid: [EMIM][ESO$_4$]

Aliphatic protons from ^{1}H-NMR (400 MHz, d$_6$-acetone) were assigned as:

δ (ppm) = 9.10 (s, 1H, H-2), 7.36 (d, 1H, H-4), 7.33 (d, 1H, H-5), 4.07 (q, 2H, N-CH$_2$), 3.79 (s, 3H, N-CH$_3$), 1.28 (t, 3H, N- CH$_2$CH$_3$), 0.98 (t, 3H, O$_3$SO-CH$_2$CH$_3$), 0.94 (s, 3H, C-CH$_3$)

Aliphatic carbons from ^{13}C-NMR (75 MHz, d$_6$-acetone) were assigned as:

δ (ppm) = 14.99, 15.29, 35.98, 44.76, 62.90, 77.23, 77.55, 77.87, 122.09, 123.70, 136.44

Synthesized ionic liquid: [EMIM][ESO$_4$]

Aliphatic protons from ^{1}H-NMR (400 MHz, d$_6$-acetone) spectra were assigned as:

δ (ppm) = 9.18 (s, 1H, H-2), 7.40 (d, 1H, H-4), 7.39 (d, 1H, H-5), 4.13 (q, 2H, N-CH$_2$), 3.86 (s, 3H, N-CH$_3$), 1.30 (t, 3H, N- CH$_2$CH$_3$), 1.05 (t, 3H, O$_3$SO-CH$_2$CH$_3$), 1.01 (s, 3H, C-CH$_3$).

Aliphatic carbons from ^{13}C-NMR (75 MHz, d_6-acetone) were assigned as:

δ (ppm) = 15.05, 15.34, 36.06, 44.84, 62.99, 77.13, 77.44, 77.77, 122.11, 123.75, 136.55

Standard ionic liquid: [EMpy][ESO$_4$]

Aliphatic protons from ^{1}H-NMR (400 MHz, d_6-acetone) were assigned as:

δ (ppm) = 9.00 (s, 1H, H-2), 8.11 (d, 1H, H-6), 7.80 (d, 1H, H-4), 7.68 (t, 1H, H-5), 4.58 (q, 2H, N-CH$_2$), 3.86 (s, 3H, N-CH$_3$), 2.41 (d, 2H, C-CH$_2$), 1.45 (t, 3H, N- CH$_2$CH$_3$), 1.05 (t, 3H, O$_3$SO-CH$_2$CH$_3$), 1.01 (s, 3H, C-CH$_3$).

Aliphatic carbons from ^{13}C-NMR (75 MHz, d_6-acetone) were assigned as:

δ (ppm) = 15.11, 16.94, 18.31, 56.96, 62.93, 77.12, 77.44, 77.76, 127.84, 137.63, 139.76, 141.96, 144.51, 145.53

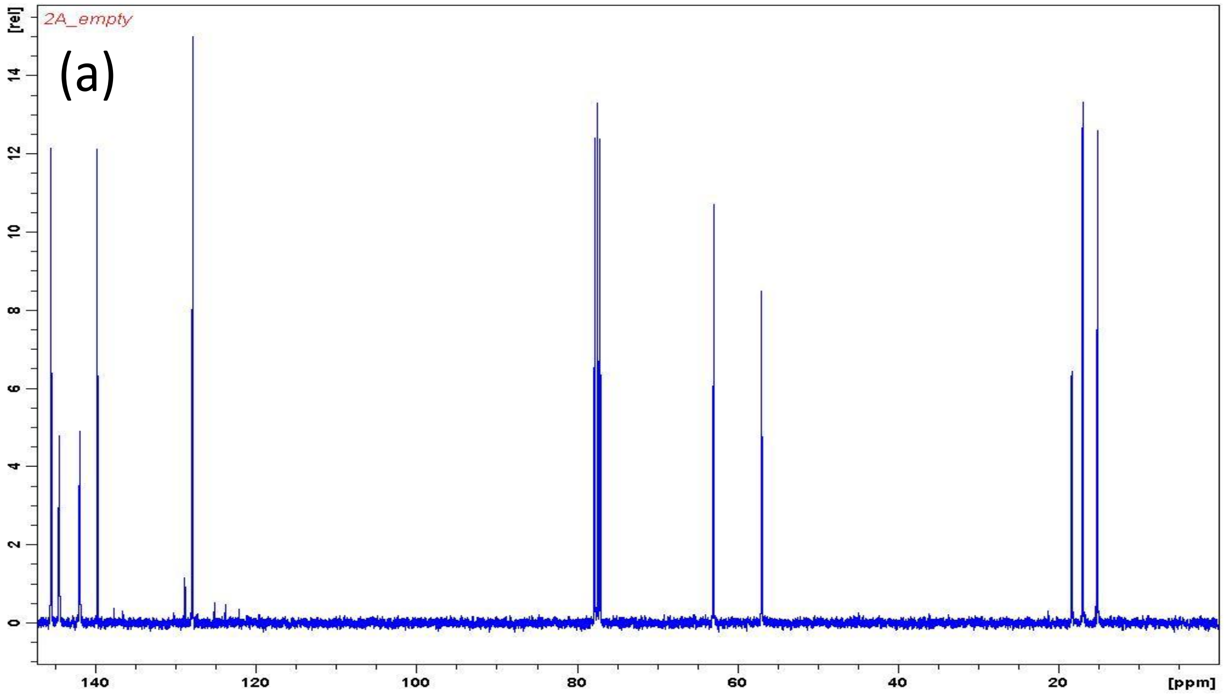
Synthesized ionic liquid: [EMpy][ESO$_4$]

Aliphatic protons from ^{1}H-NMR (400 MHz, d_6-acetone) were assigned as:

δ (ppm) = 9.27 (s, 1H, H-2), 7.45 (d, 1H, H-6), 7.44 (d, 1H, H-4), 7.35 (t, 1H, H-5), 4.19 (q, 2H, N-CH$_2$), 3.93 (s, 3H, N-CH$_3$), 2.19 (q, 2H, C-CH$_2$), 1.42 (t, 3H, N- CH$_2$CH$_3$), 1.13 (t, 3H, O$_3$SO-CH$_2$CH$_3$), 1.09 (s, 3H, C-CH$_3$).

Aliphatic carbons from ^{13}C-NMR (75 MHz, d_6-acetone) were assigned as:

δ (ppm) = 15.13, 16.94, 18.35, 57.07, 63.07, 77.02, 77.34, 77.66, 127.92, 137.71, 139.78, 141.98, 144.45, 145.55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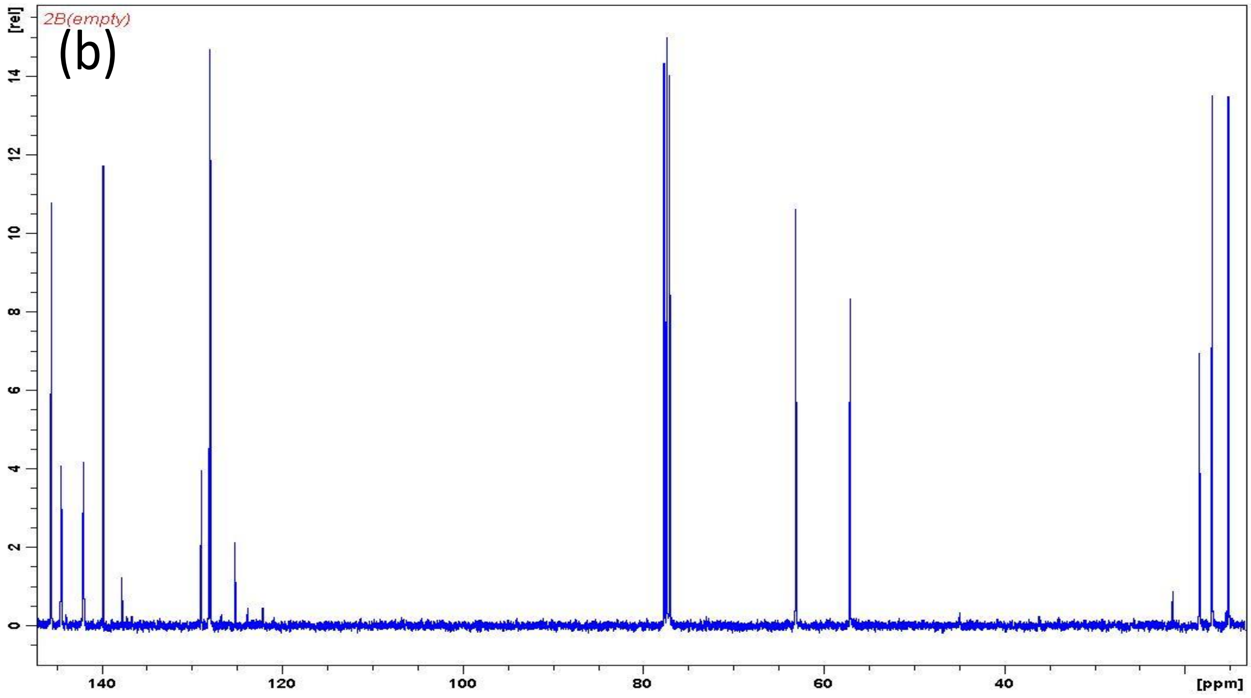
140
120
100
80
60
40
20
[ppm]


[rel]
2B(empty)
(b)
14
12
10
8
6
4
2
0
140
120
100
80
60
40
[ppm]

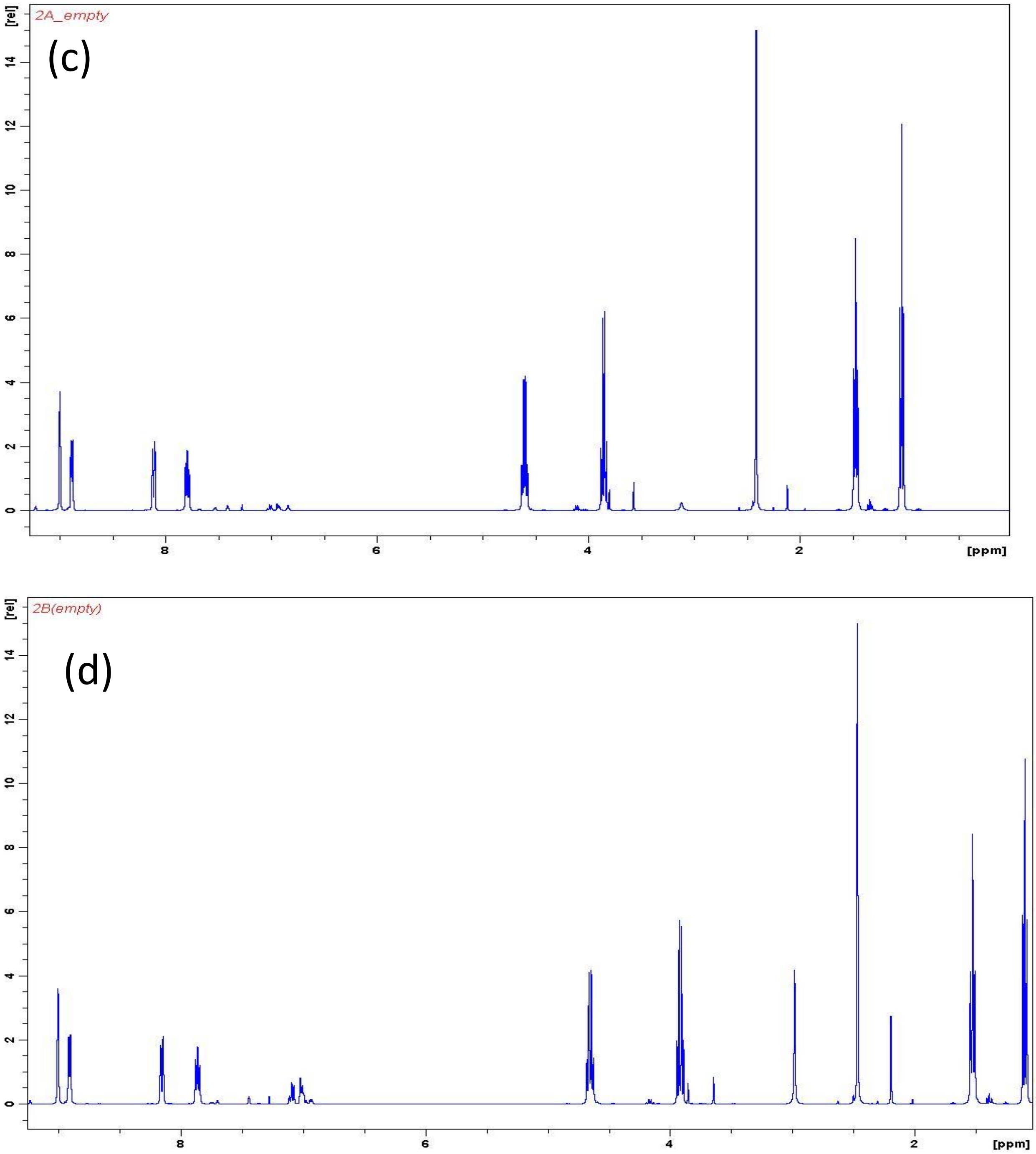
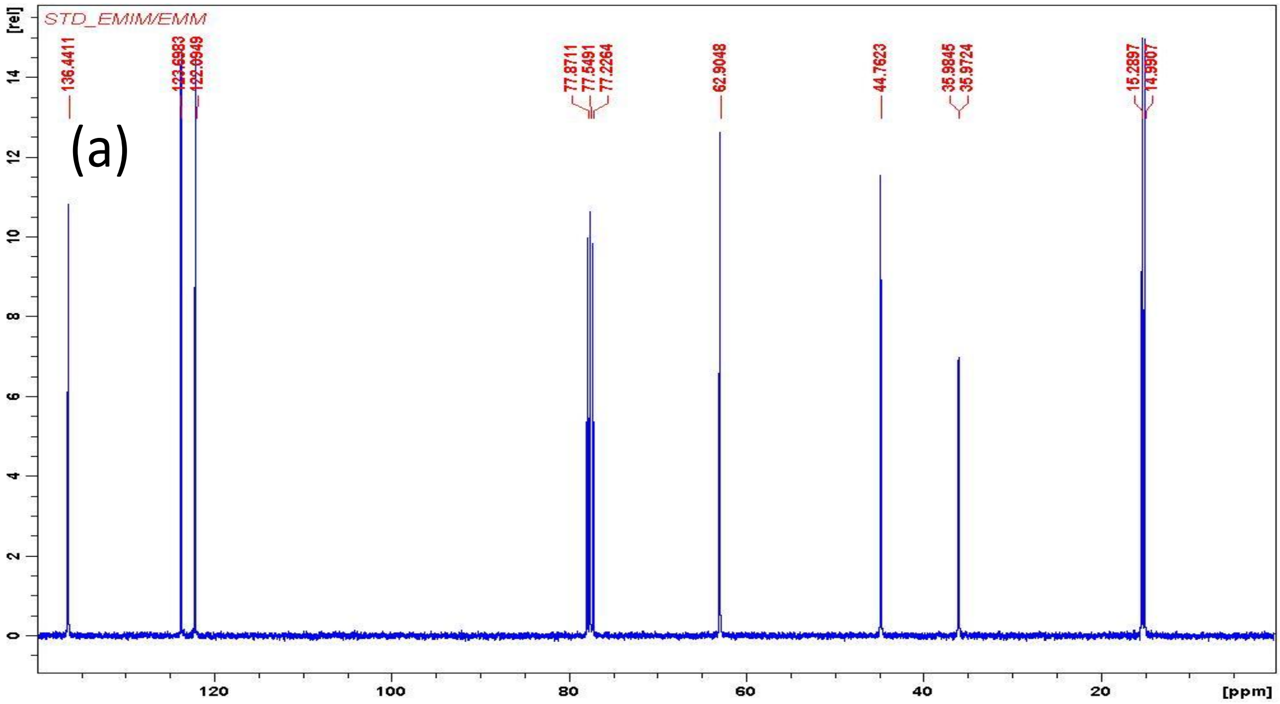
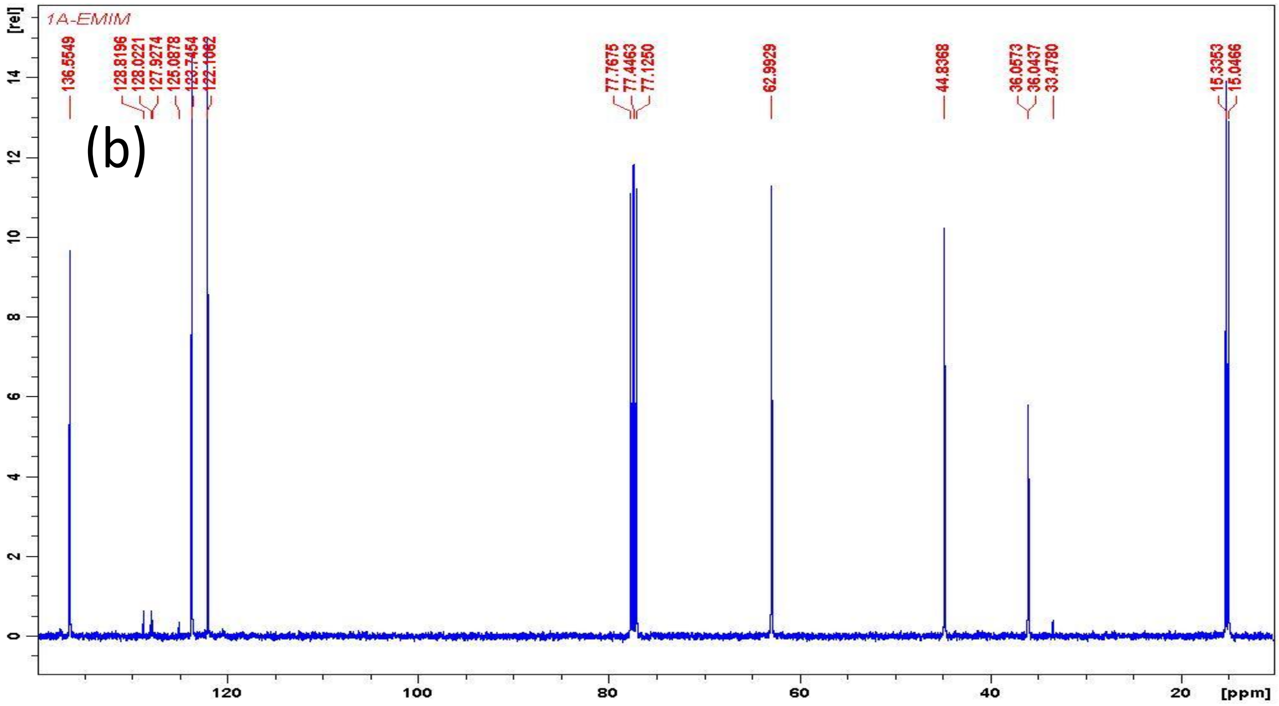


Figure 4.5 ^{13}C NMR spectra: (a) Standard [EMpy][ESO$_4$] (b) Synthesized [EMpy][ESO$_4$] ^{1}H NMR Spectra: (c) Standard [EMpy][ESO$_4$] (d) Synthesized [EMpy][ESO$_4$]


STD_EMIM/EMM
(a)
[rel]
136.4411
123.6983
122.0949
77.8711
77.5491
77.2264
62.9048
44.7623
35.9845
35.9724
15.2897
14.9907
0
2
4
6
8
10
12
14
120
100
80
60
40
20
[ppm]


1A-EMIM
(b)
[rel]
136.5549
128.8196
128.0221
127.9274
125.0878
123.7454
122.1062
77.7675
77.4463
77.1250
62.9929
44.8368
36.0573
36.0437
33.4780
15.3353
15.0466
0
2
4
6
8
10
12
14
120
100
80
60
40
20
[ppm]

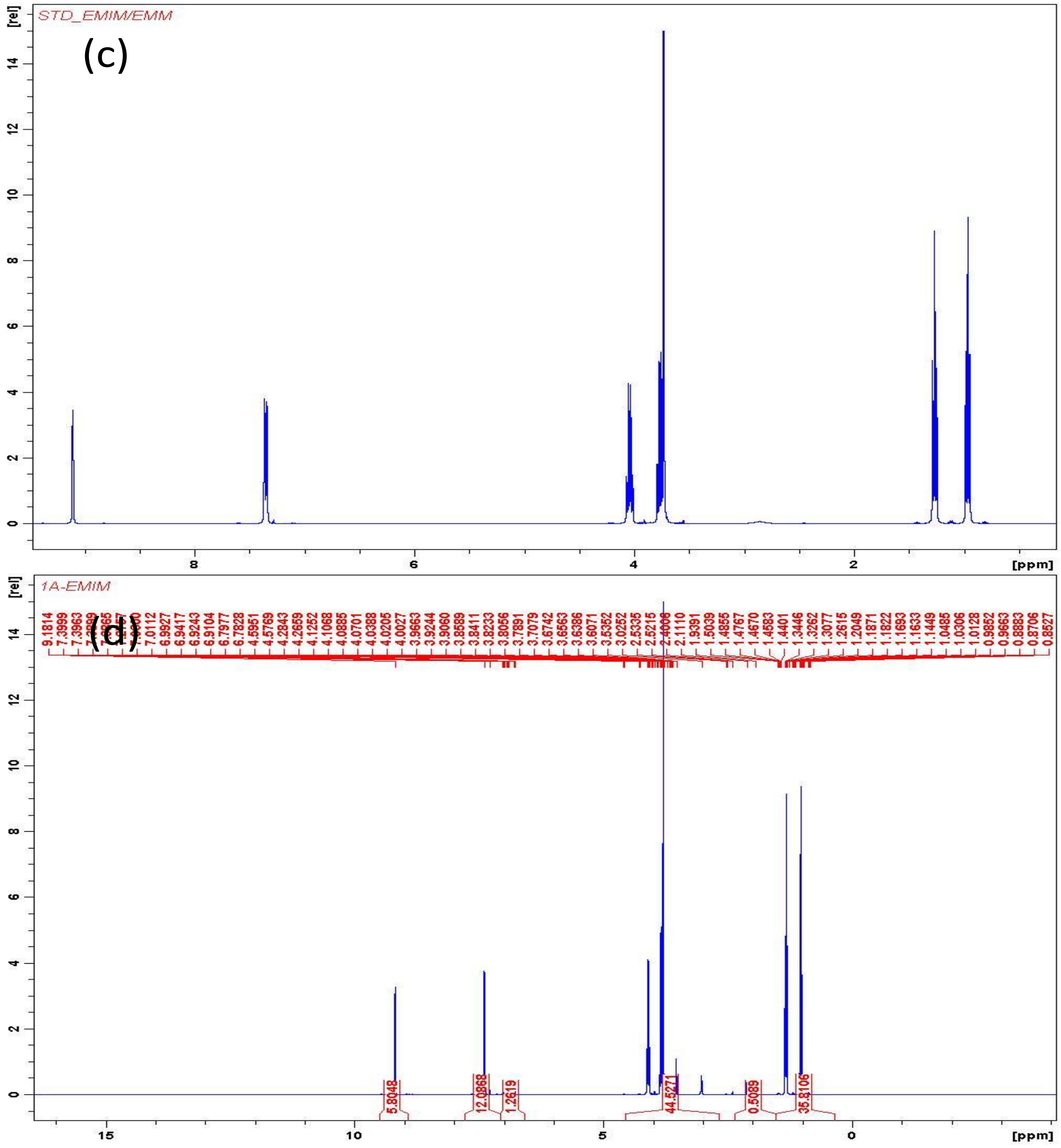


Figure 4.6 ^{13}C NMR Spectra: (a) Standard [EMIM][ESO$_4$] (b) Synthesized [EMIM][ESO$_4$] ^{1}H-NMRSpectra: (c) Standard [EMIM][ESO$_4$] (d) Synthesized [EMIM][ESO$_4$]

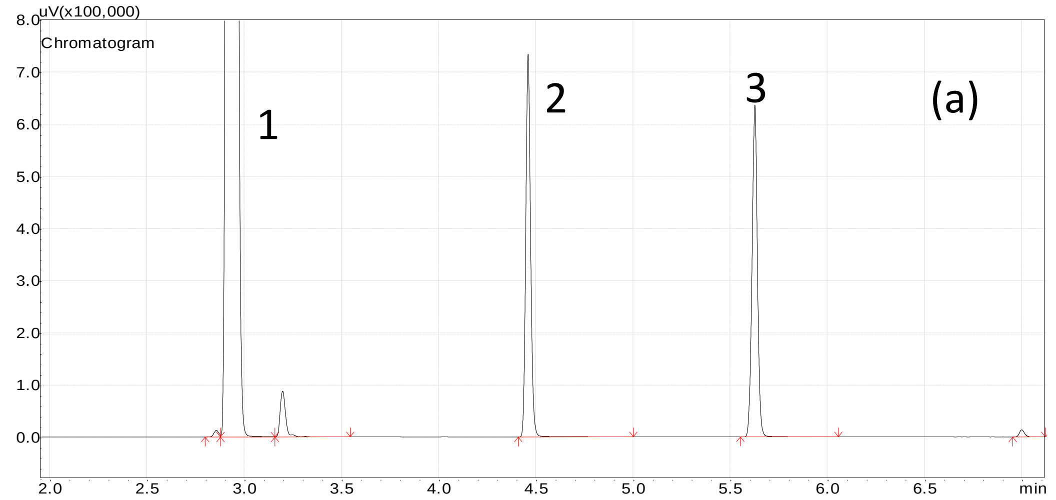
4.2 Extraction of BTEX from Model Mixtures

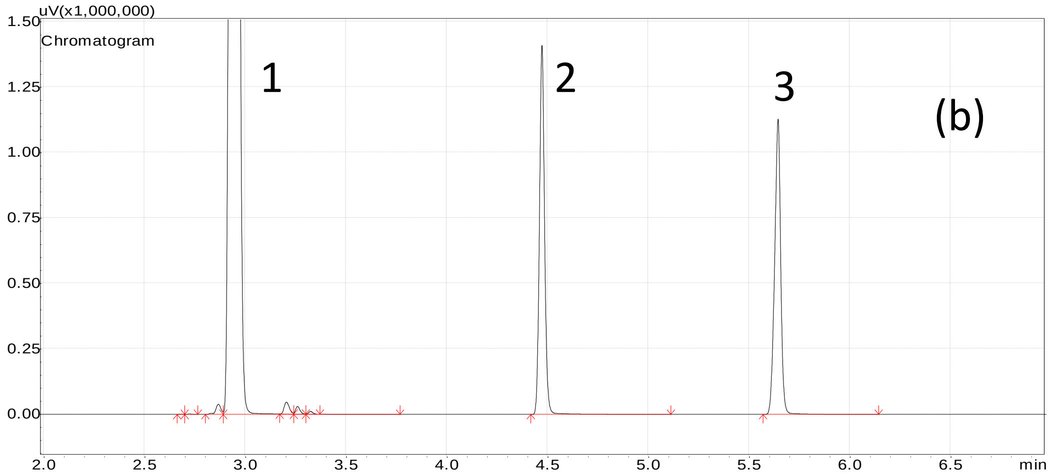
4.2.1 The effects of varying the concentrations of BTEX components

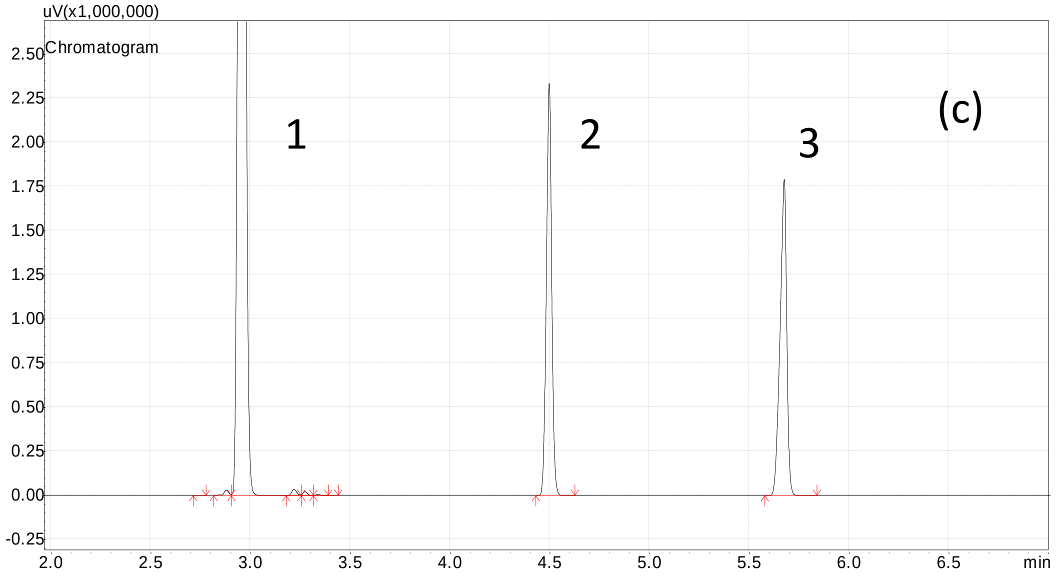
Quaternary: Benzene + Toluene + n-Heptane + [EMIM][ESO$_4$]

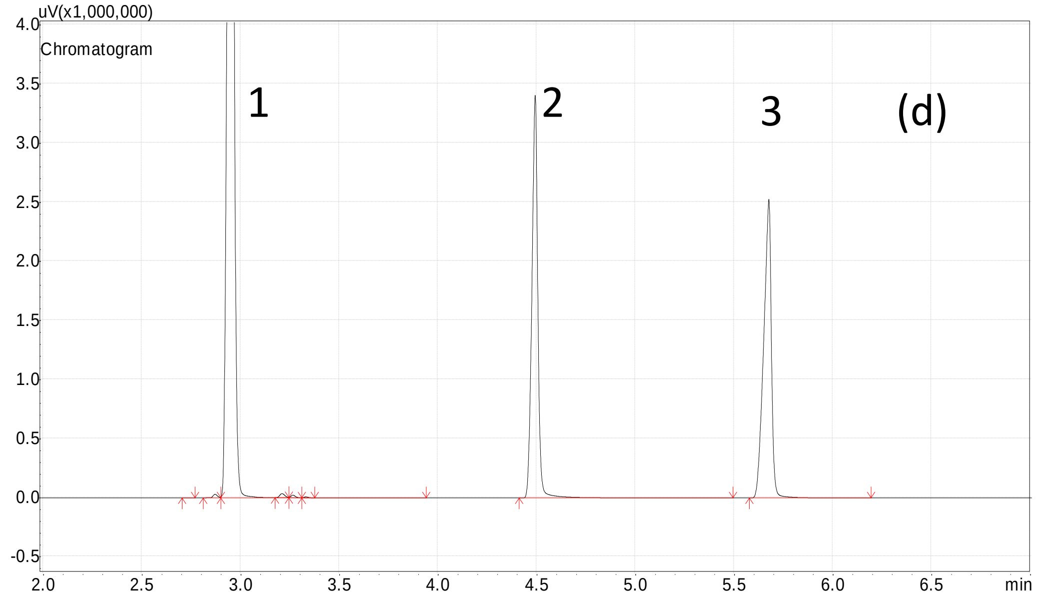
These model mixtures for the calibration of the instrument (used also in the extraction processes with ionic liquids) were made up of benzene and toluene in the range 2.5 – 25 % (v/v) each using n-heptane as an alkane. The GC-FID chromatograms obtained from these solutions are depicted in Figure 4.7. The respective calibration curves constructed from the concentration versus peak areas are shown in Figure 4.8. It can be seen that both curves indicate linear relationship between two variables across the measured concentration range. In addition, this relationship is confirmed by the coefficients of determination (R^2) which appear very close to unity which is 0.998 for both components.

These trends provide good evidence of high reliability of the instrument that was used in measuring the concentrations of the samples. This is also a strong indication of good performance characteristics of gas chromatography used in this study. Therefore, all calculations involving these measurements were performed by direct use of linear regression equations from the calibration curves of respective standards.


uV(x100,000)
Chromatogram
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
min
1
2
3
(a)


uV(x1,000,000)
Chromatogram
1.50
1.25
1.00
0.75
0.50
0.25
0.00
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
min
1
2
3
(b)


uV(x1,000,000)
Chromatogram
2.50
2.25
2.00
1.75
1.50
1.25
1.00
0.75
0.50
0.25
0.00
-0.25
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
min
1
2
3
(c)


uV(x1,000,000)
Chromatogram
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
min
1
2
3
(d)

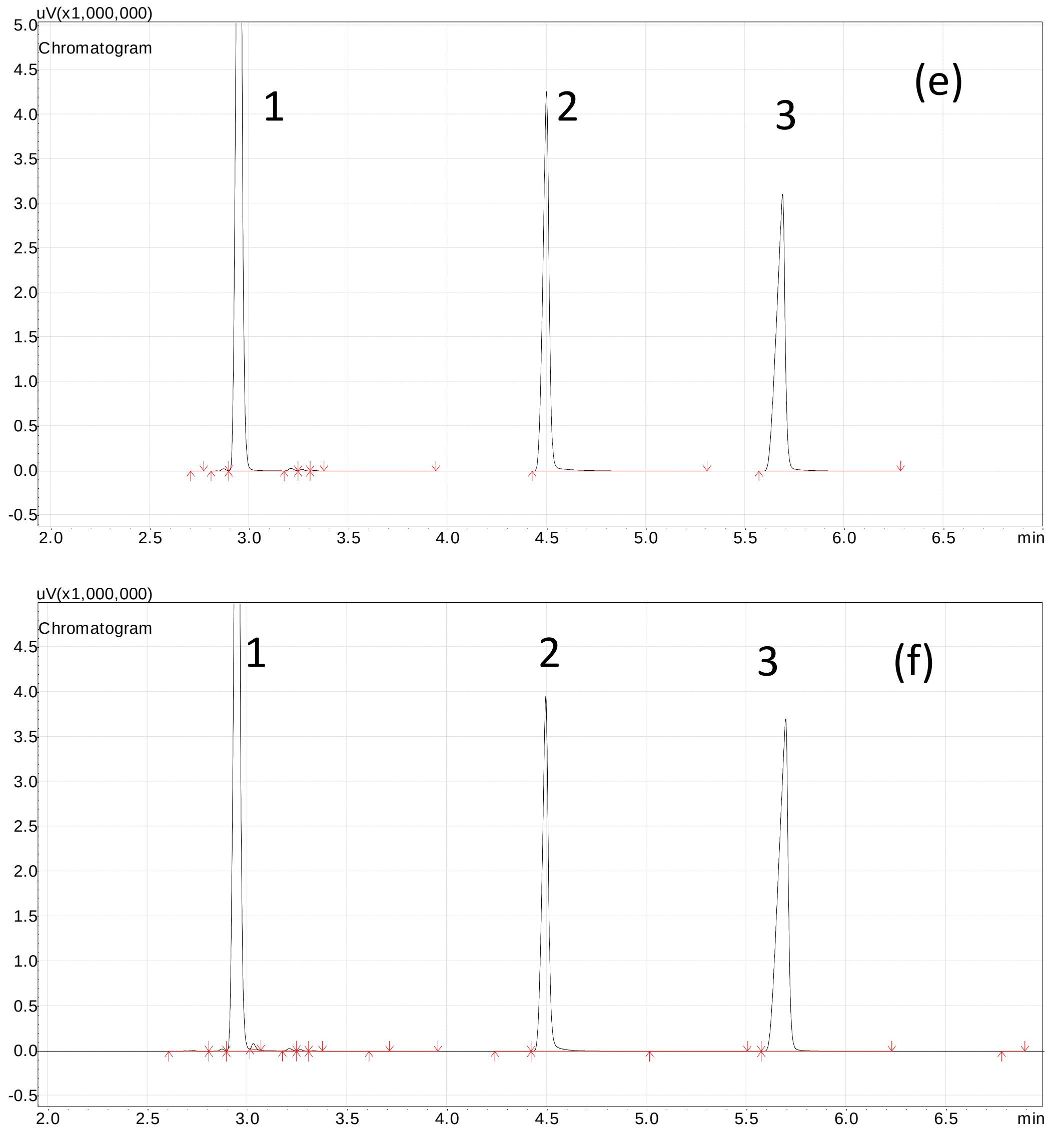
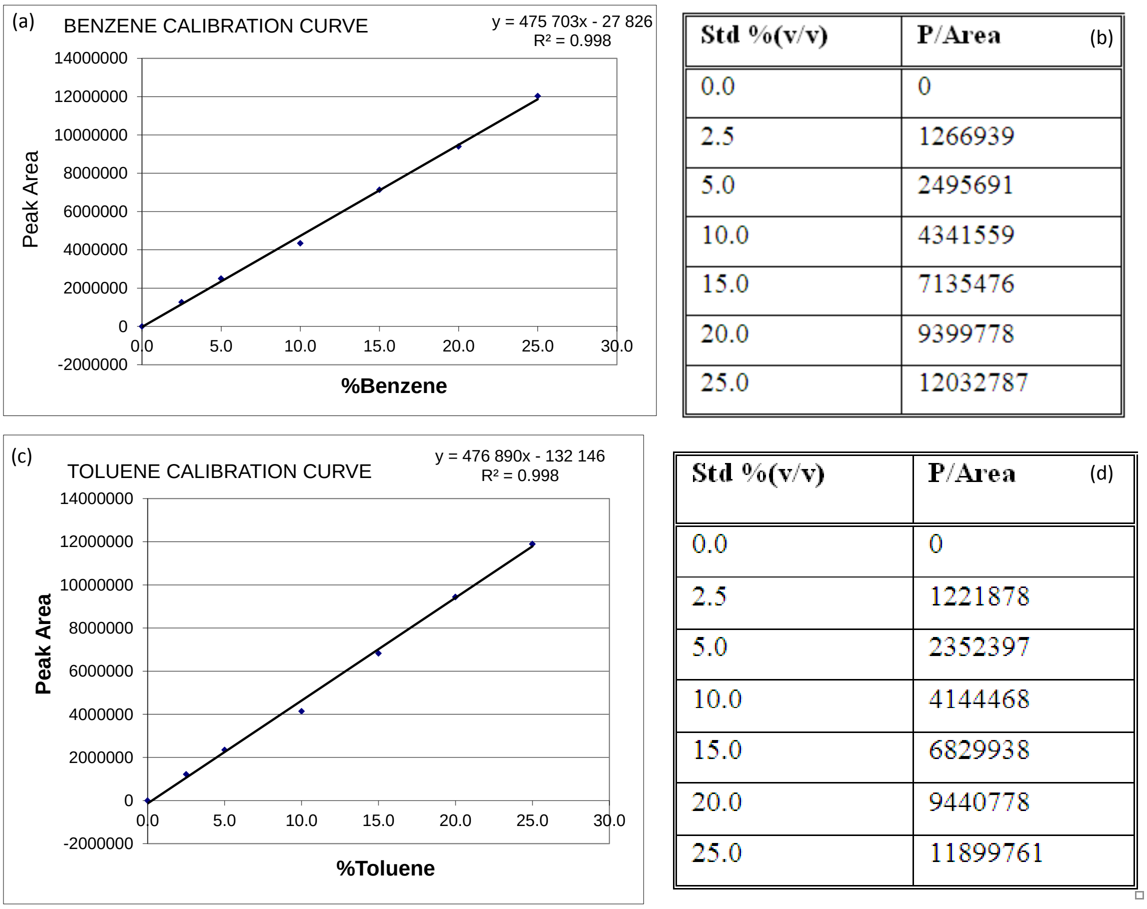


Figure 4.7 GC Chromatograms for the calibration model mixtures: (a) 2.5 % (v/v) (b) 5 % (v/v) (c) 10 % (v/v) (d) 15 % (v/v); (e) 20 % (v/v); (f) 25 % (v/v) where 1 = n-Heptane 2 = Benzene 3 = Toluene



(b)

Std %(v/v)	P/Area
0.0	0
2.5	1266939
5.0	2495691
10.0	4341559
15.0	7135476
20.0	9399778
25.0	12032787

(d)

Std %(v/v)	P/Area
0.0	0
2.5	1221878
5.0	2352397
10.0	4144468
15.0	6829938
20.0	9440778
25.0	11899761

Figure 4.8 Model mixtures 2.5 – 25 % (v/v): (a) Benzene curve (b) Benzene peak areas (c) Toluene curve (d) Toluene peak areas

The linear equation is given by:

$$y = mx + c \qquad 4.1$$

Therefore, for benzene calculations, the equation from its calibration curve was used:

$$y = 475703x - 27826 \qquad 4.2$$

Thus: $$x = \frac{y+27826}{475703} \qquad 4.3$$

Where y = Peak Area of the sample, x = Concentration of the sample.

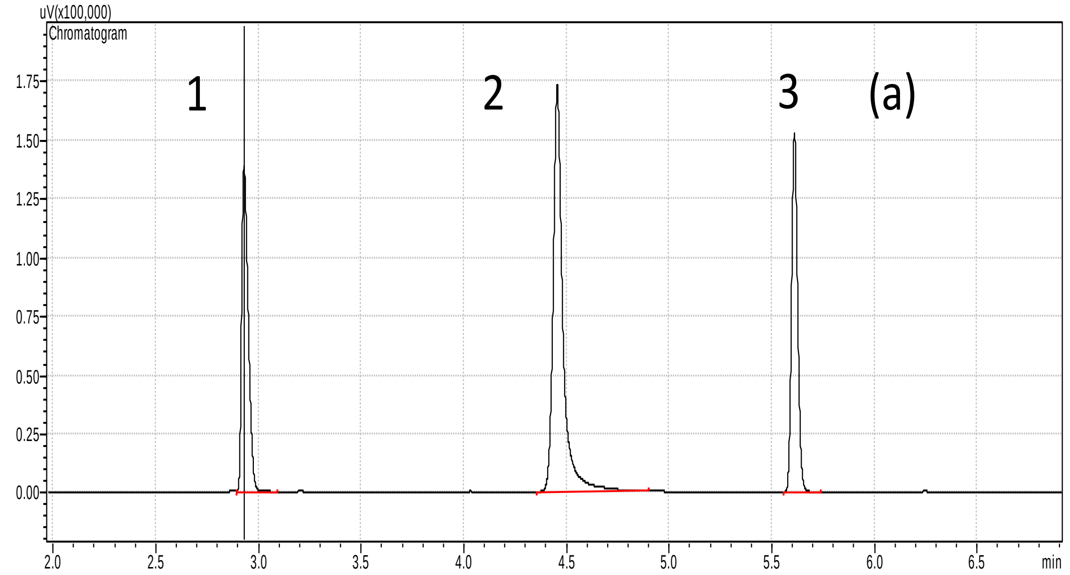
Similarly, all calculations associated with toluene analysis, the equation given for the toluene calibration curve was used:

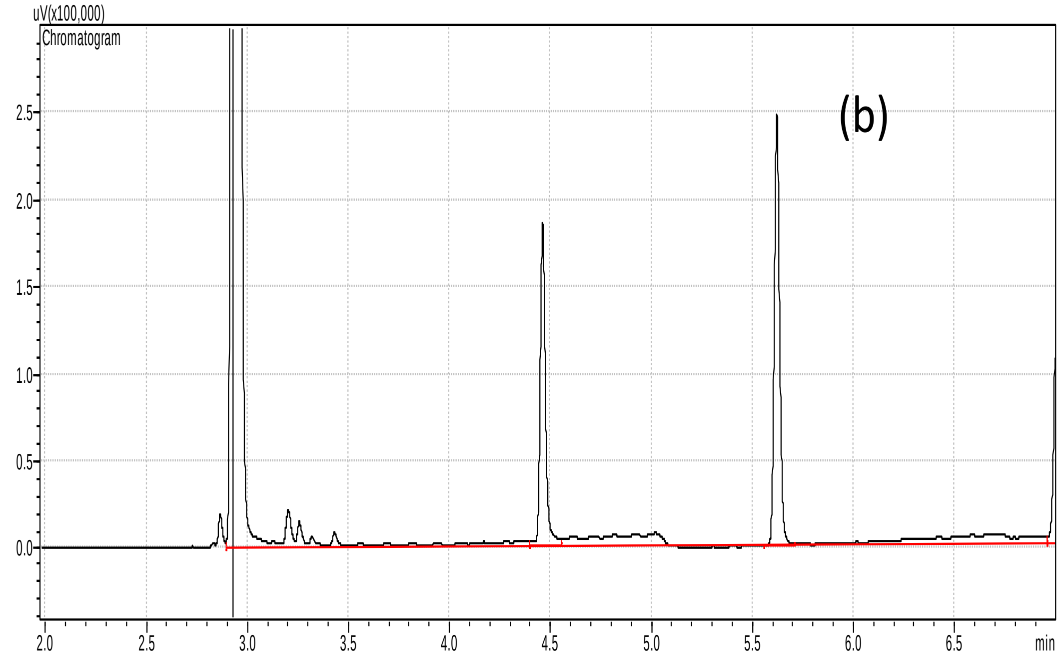
$$y = 476890x - 132146 \tag{4.4}$$

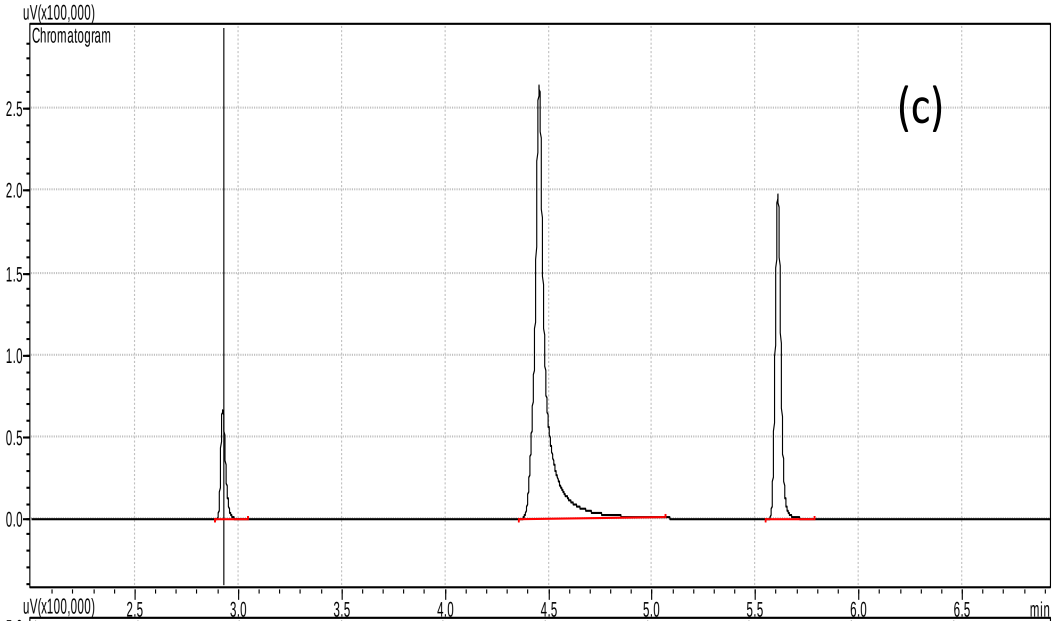
Thus: $$x = \frac{y+132146}{476890} \tag{4.5}$$

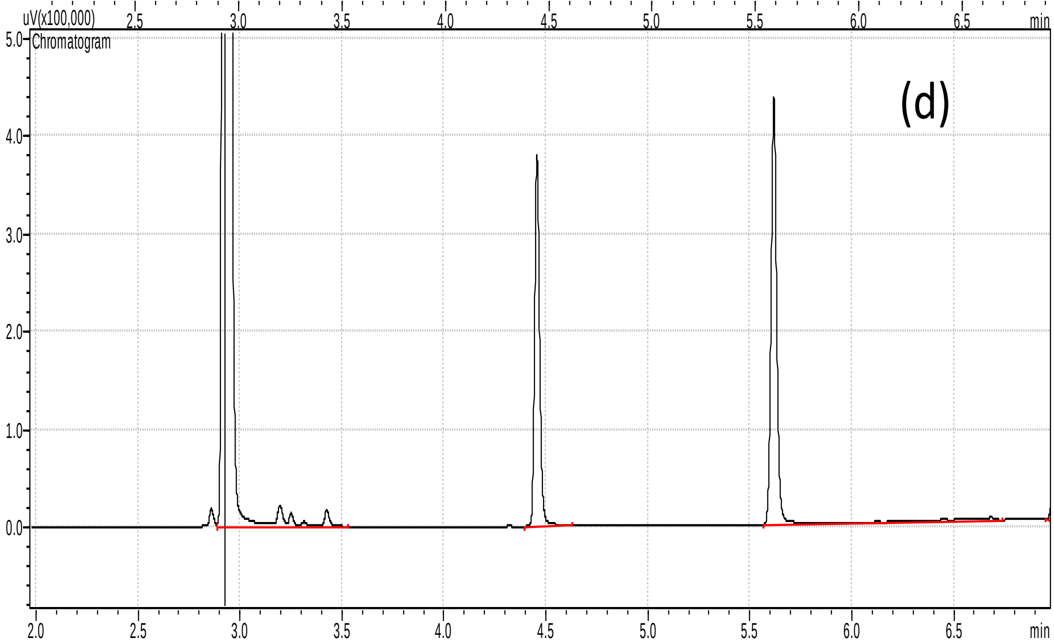
The GC chromatograms for benzene and toluene in the extract and raffinate phases for the concentration range 2.5 – 25 % (v/v) are depicted in Figures 4.9. The chromatograms in Figures 4.9 show relatively much lower concentrations of n-heptane (< 0.5%) in the extract phases than the concentration of aromatic hydrocarbons across the concentration range. (Also refer to Appendix 6, Table A7.4). This indicates that aromatic molecules are more soluble in the ionic liquid than the aliphatic hydrocarbons, which also suggests a relatively higher selectivity of ionic liquid for aromatic components. On the other hand, peak heights of chromatograms in Figure 4.9 shows very high concentrations of n-heptane in all raffinate phases relative to that of aromatic components. It can also be seen in Figure 4.9 that the concentration of n-heptane in the extract phases decreases steadily as the concentration of the mixtures increases.

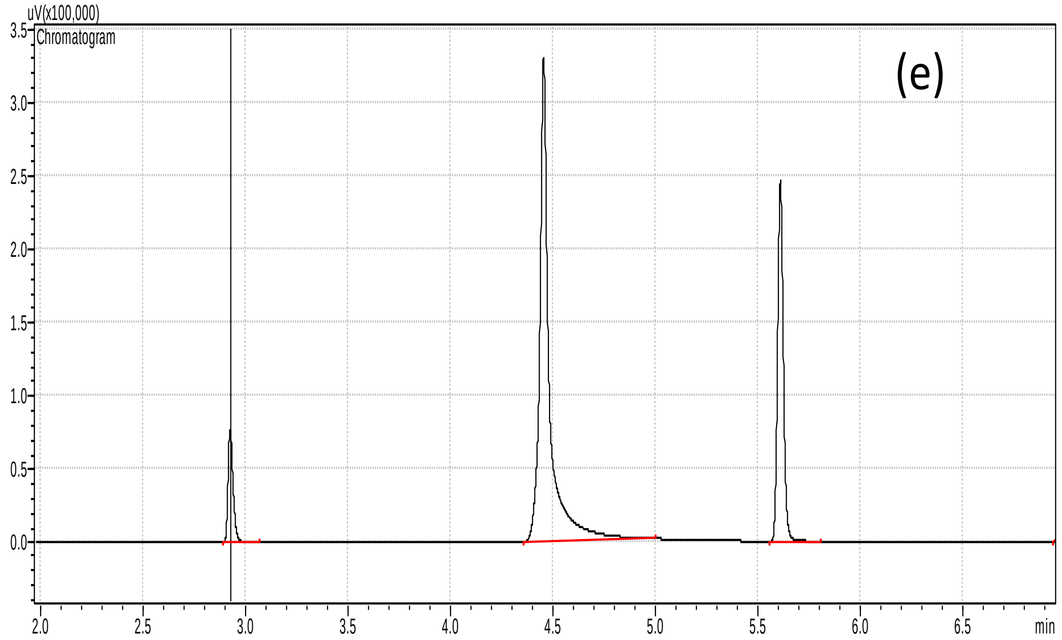
This trend is indeed expected since the concentration of heptane in the original model mixtures decreases with increasing concentration of aromatic components, in this case, benzene and toluene. In all chromatograms the concentration of benzene in the extract phases is relatively higher than the concentration of toluene. This observation suggests that the ionic liquid interacts strongly with benzene than it does with toluene. This could be due to the presence of methyl substituent in toluene which may slightly hinder its interaction with the ionic liquid.

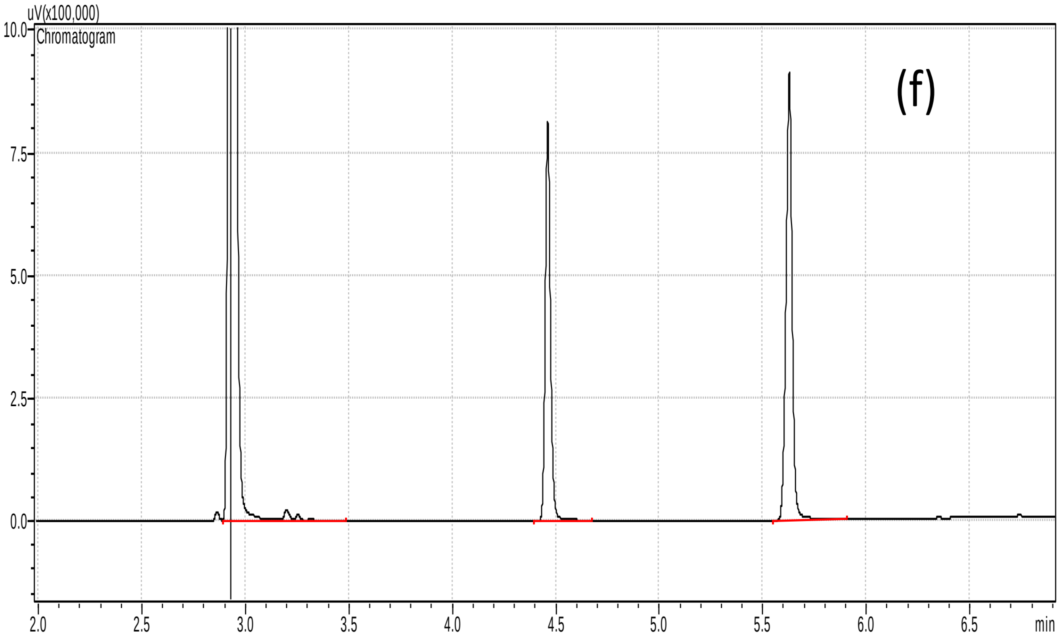

uV(x100,000)
Chromatogram
1
2
3
(a)
1.75
1.50
1.25
1.00
0.75
0.50
0.25
0.00
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
min

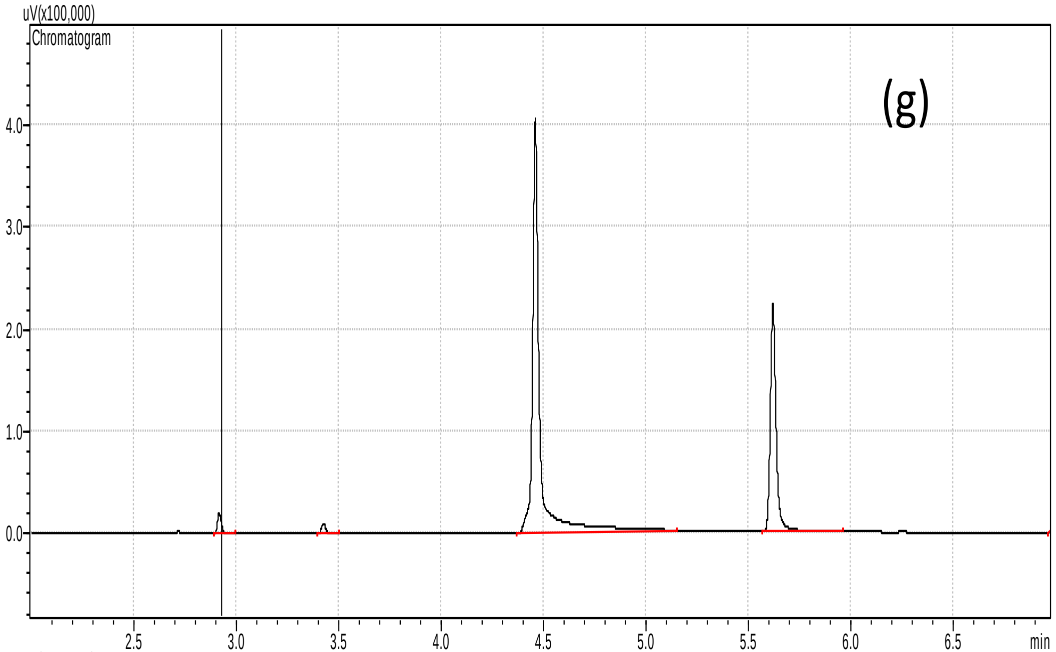

uV(x100,000)
Chromatogram
(b)
2.5
2.0
1.5
1.0
0.5
0.0
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
min

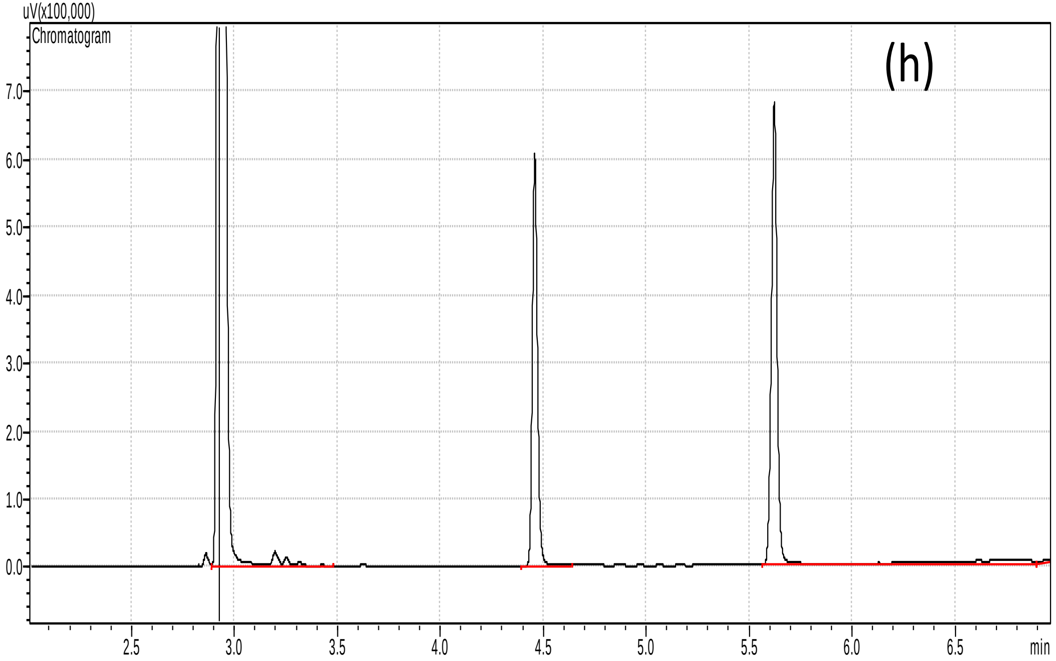

uV(x100,000)
Chromatogram
(c)
2.5
2.0
1.5
1.0
0.5
0.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
min

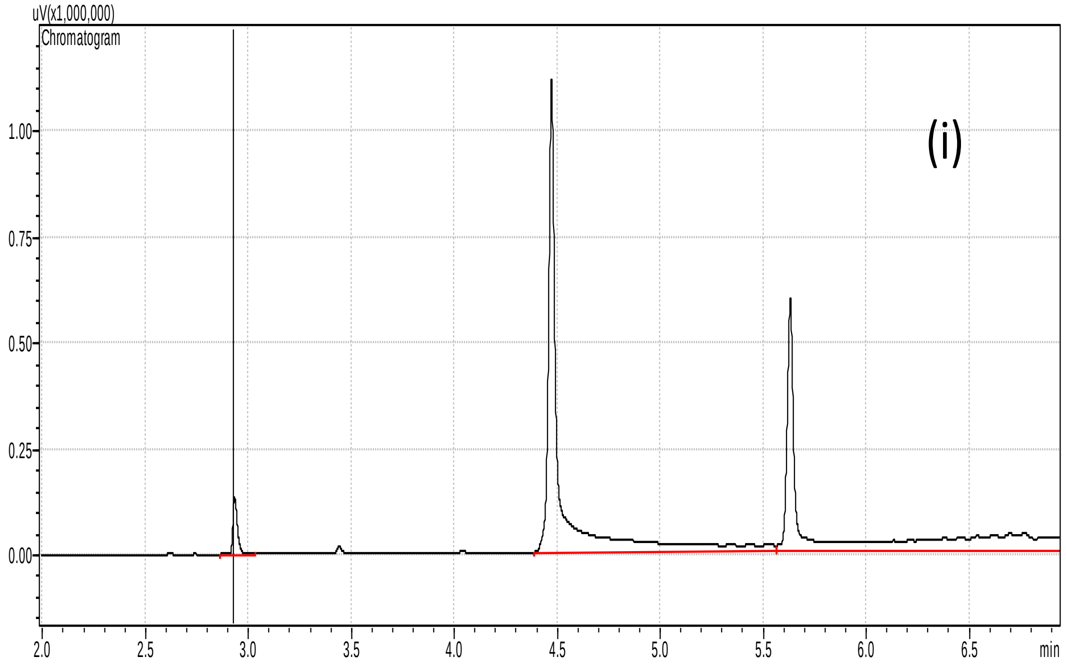

uV(x100,000)
Chromatogram
(d)
5.0
4.0
3.0
2.0
1.0
0.0
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
min

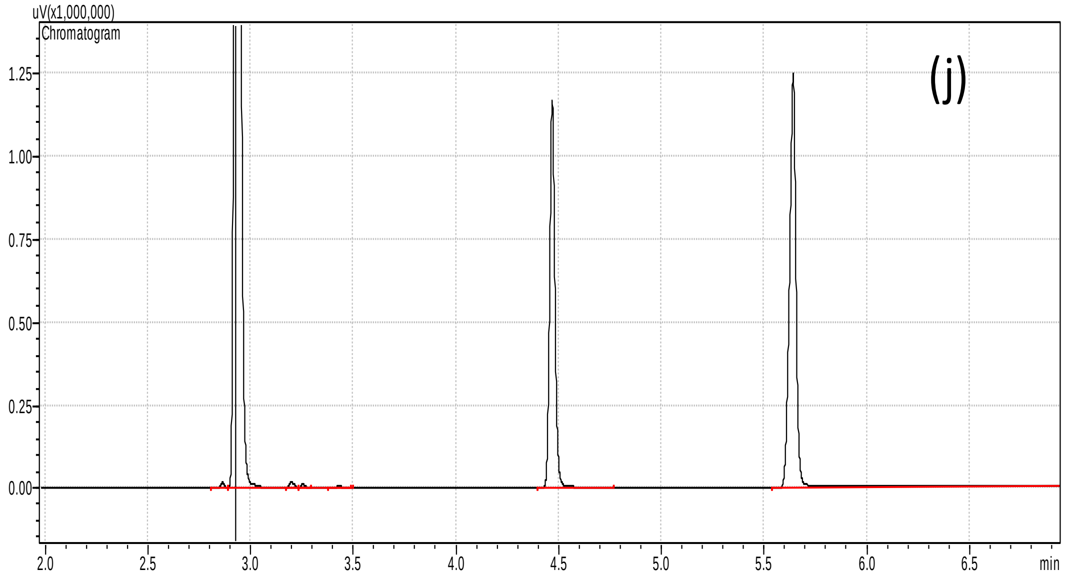

uV(x100,000)
Chromatogram
(e)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
min

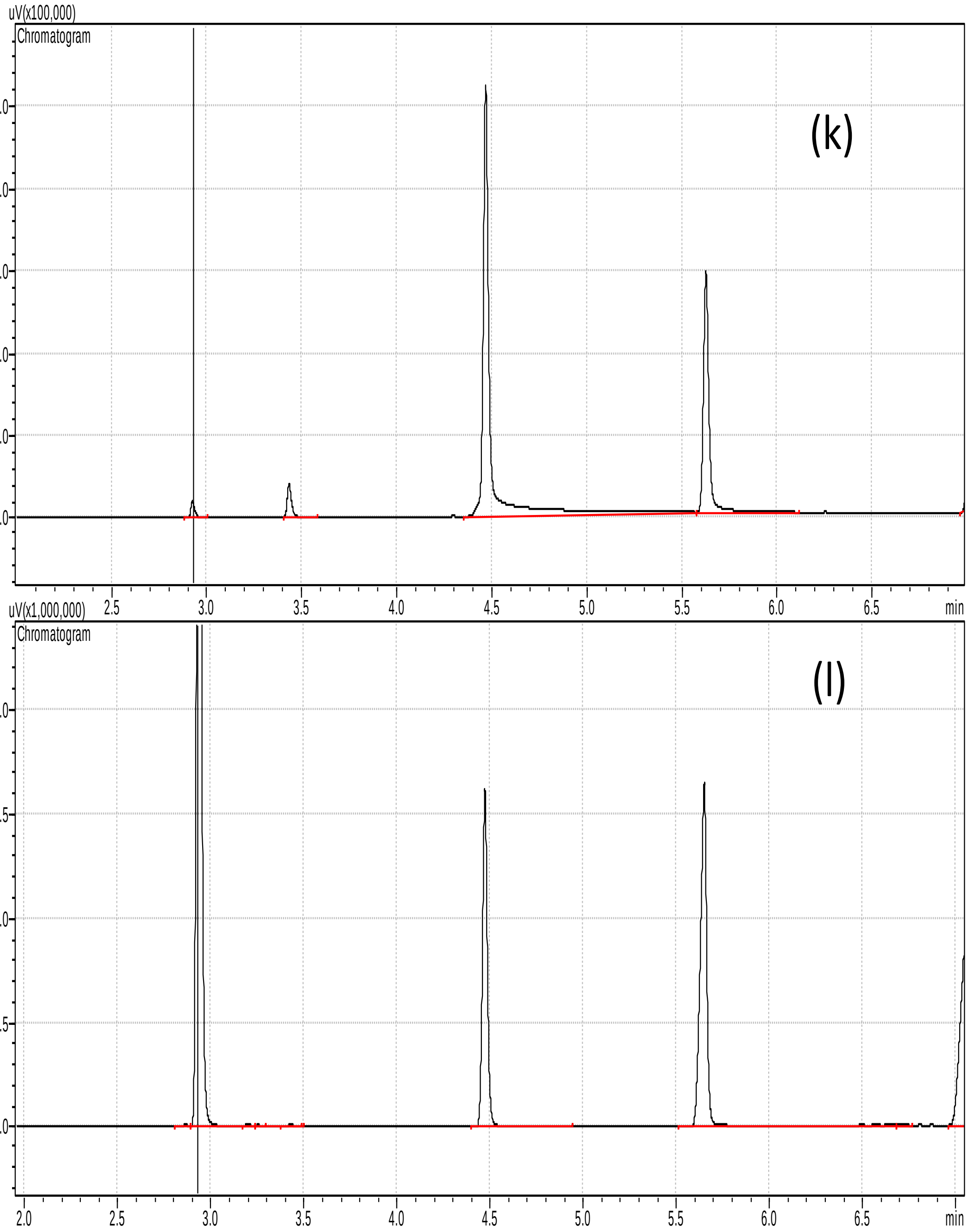

uV(x100,000)
Chromatogram
(f)
10.0
7.5
5.0
2.5
0.0
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
min


uV(x100,000)
Chromatogram
(g)
4.0
3.0
2.0
1.0
0.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
min


uV(x100,000)
Chromatogram
(h)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
min


uV(x1,000,000)
Chromatogram
(i)
1.00
0.75
0.50
0.25
0.00
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
min


uV(x1,000,000)
Chromatogram
(j)
1.25
1.00
0.75
0.50
0.25
0.00
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
min


uV(x100,000)
Chromatogram
(k)
5.0
4.0
3.0
2.0
1.0
0.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
min
uV(x1,000,000)
Chromatogram
(l)
2.0
1.5
1.0
0.5
0.0
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
min

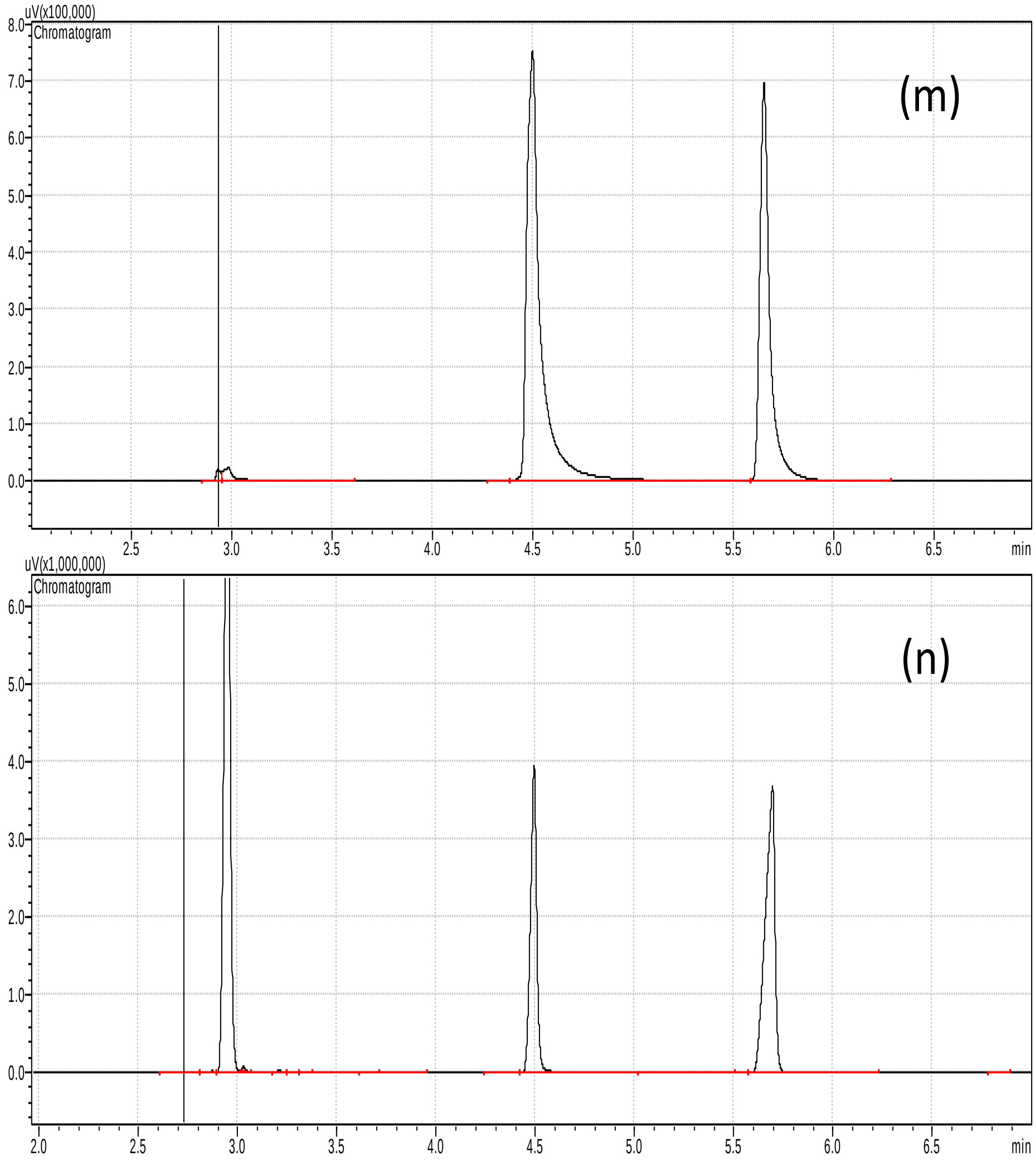
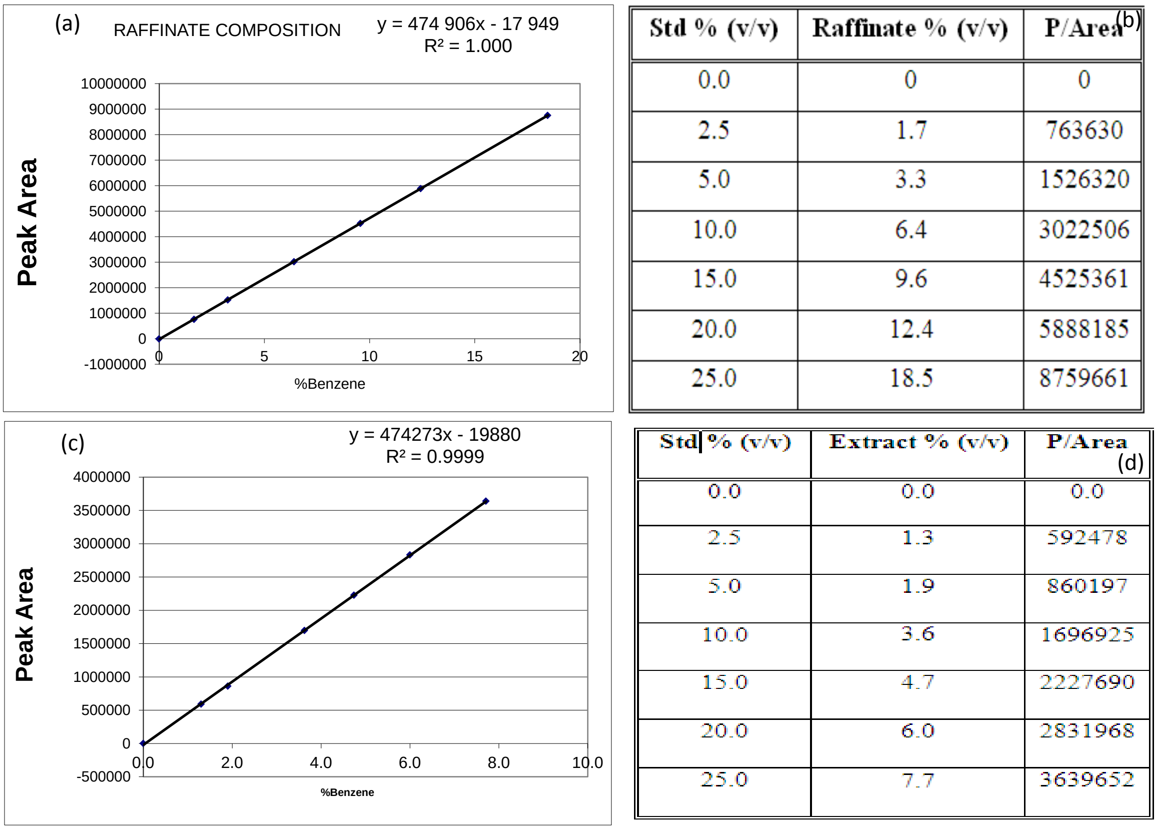


Figure 4.9: Chromatograms showing the component peaks in the extract and raffinate phases of model mixtures containing aromatics in the concentration range 2.5 – 25 % (v/v) where 1 = n-Heptane 2 = Benzene 3 = Toluene

Extract chromatograms: (a) 2.5 % (c) 5 % (e) 7.5% (g) 10 % (i) 15 % (k) 20 % (m) 25 %

Raffinate chromatograms: (b) 2.5 % (d) 5 % (f) 7.5% (h) 10 % (j) 15 % (l) 20 % (n) 25 %

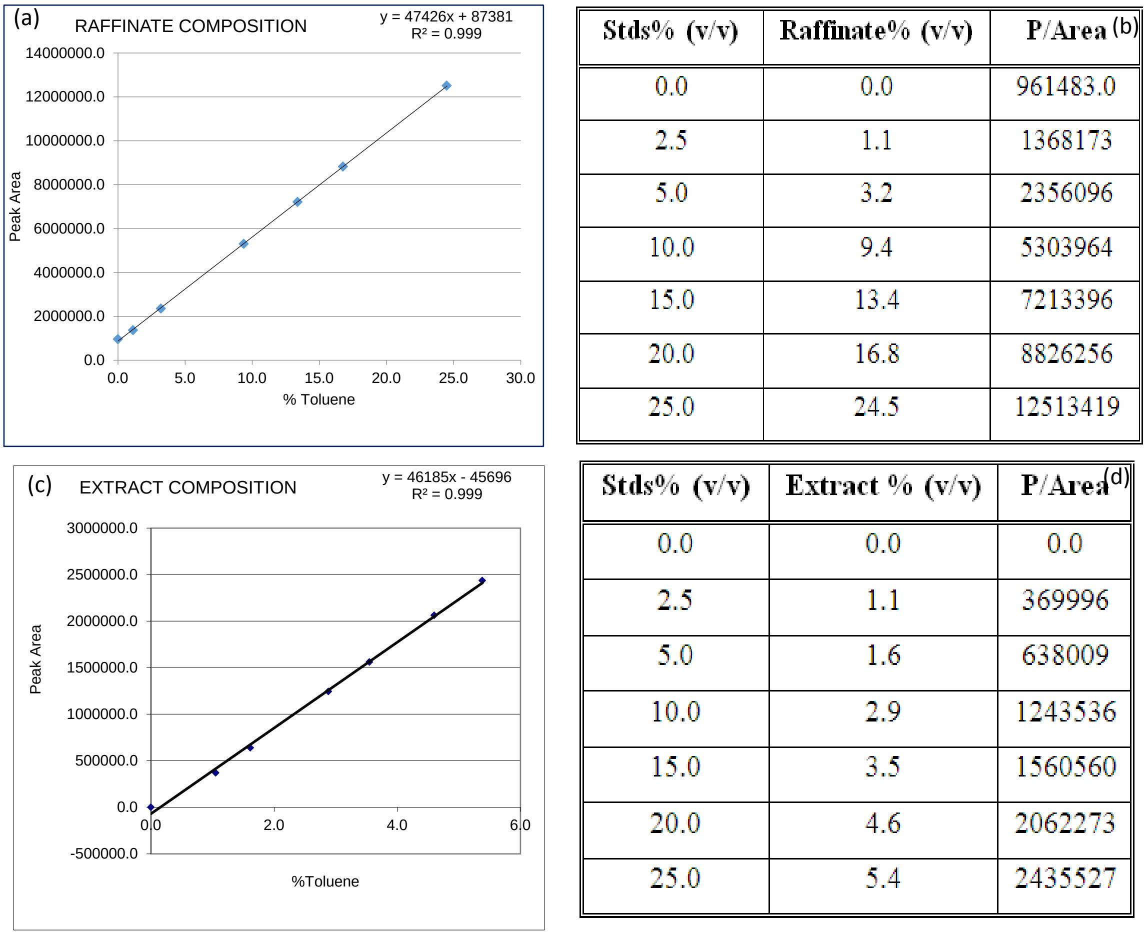
The results obtained from the extraction of model mixtures (2.5 – 25 %) using ionic liquid [EMIM][ESO_4] for both the raffinate and extract phases are shown in Figures 4.10 and 4.11 for benzene and toluene, respectively. It can be seen in these figures that the curves are all linear with coefficient of determination (R^2) of very close to unity in all cases. This displays excellent correlation between dependent variables (peak areas) and independent variables (percentages) and even distribution of extract values across the experimental concentration range.



Std % (v/v)	Raffinate % (v/v)	P/Area
0.0	0	0
2.5	1.7	763630
5.0	3.3	1526320
10.0	6.4	3022506
15.0	9.6	4525361
20.0	12.4	5888185
25.0	18.5	8759661

Std % (v/v)	Extract % (v/v)	P/Area
0.0	0.0	0.0
2.5	1.3	592478
5.0	1.9	860197
10.0	3.6	1696925
15.0	4.7	2227690
20.0	6.0	2831968
25.0	7.7	3639652

Figure 4.10 Benzene composition: Sample curves (a) Raffinate phase (c) Extract phase Sample concentrations in (b) Raffinate phase (d) Extract phase



Stds% (v/v)	Raffinate% (v/v)	P/Area
0.0	0.0	961483.0
2.5	1.1	1368173
5.0	3.2	2356096
10.0	9.4	5303964
15.0	13.4	7213396
20.0	16.8	8826256
25.0	24.5	12513419

Stds% (v/v)	Extract % (v/v)	P/Area
0.0	0.0	0.0
2.5	1.1	369996
5.0	1.6	638009
10.0	2.9	1243536
15.0	3.5	1560560
20.0	4.6	2062273
25.0	5.4	2435527

Figure 4.11 Toluene composition: Sample curves (a) Raffinate phase (c) Extract phase Sample concentrations in (b) Raffinate phase (d) Extract phase

The percentages of benzene in raffinate phases were calculated using equation 4.3:

For 2.5 % (v/v) raffinate phase;

$$x = \frac{y+27826}{475703}$$

$$= \frac{763630+27826}{475703}$$

$$= 1.7\ \%\ (v/v)$$

Similarly, the values for the remaining concentrations were calculated as follows:

For 2.5 % (v/v) extract phase; $x = \frac{y+27826}{475703}$

$$= \frac{592478+27826}{475703}$$

$$= \quad 1.3\ \%\ (v/v)$$

Toluene percentages in the raffinate phase were calculated using equation 4.5:

Thus $x = \frac{y+132146-\text{Blank}}{476890}$ (Blank = Peak area of IL)

For 2.5 % (v/v) raffinate phase; $x = \frac{1368173+132146-961483}{476890}$

$$= \quad 1.1\ \%\ (v/v)$$

Toluene percentages in the extract phase were calculated also using equation 4.5:

Therefore; $x = \frac{y+132146}{476890}$

For 2.5 % (v/v) extract phase; $x = \frac{369996+132146}{476890}$

$$= \quad 1.1\ \%\ (v/v)$$

In addition, the observed linear relationship between the percentages and peak areas in both the raffinate and extract phases indicates the efficiency and consistency of ionic liquid extraction processes. Furthermore, this phenomenon is also demonstrated by evenly distributed values of the extract and raffinate phases for the lowest to the highest concentration. The results of benzene and toluene obtained from these extractions are summarized in Table 4.3 which gives values of extract phases (E), raffinate phases (R), total recovery (R+E), percentages in the extract phase, and recovery values. The percentage in the extract phases and the recovery values (%) are calculated by using general equation 4.6 given below:

$$\% \text{ Recovery} = \frac{\text{Experimenta value}}{\text{Actual value}} \text{ x } 100 \qquad 4.6$$

The extract value of benzene from 2.5 % model mixture in Table 4.3 is given by:

$$\% \text{ Extract} = \frac{\text{Experimenta value}}{\text{Actual value}} \text{ x } 100$$

$$= \frac{1.3}{2.5} \text{ x } 100$$

$$= 52 \ \% \ (\text{v/v})$$

The recovery of benzene from 2.5 % model mixture in Table 4.3 is given by:

$$\% \text{ Recovery} = \frac{\text{Experimenta value}}{\text{Actual value}} \text{ x } 100$$

$$= \frac{3.0}{2.5} \text{ x } 100$$

$$= 120 \ \% \ (\text{v/v})$$

The remaining extract and recovery values in Table 4.3 are calculated in a similar way, including the corresponding values of toluene shown in the same table. The overall extraction results are summarized in Table 4.3 for both the raffinate and extract phases including total recovery values of benzene and toluene from model mixtures over the concentration range of interest.

Table 4.3: Summary of results for the concentration range 2.5 – 25 % (v/v)

Stds/%	**Benzene % (v/v)**						**Toluene % (v/v)**					
	P/Area	R	E	R + E	**Extract**	**Recovery**	P/Area	R	E	R + E	**Extract**	**Recovery**
2.5	763630	1.7	1.3	3.0	**52**	**120**	369996	1.1	1.1	2.2	**44**	**88**
5.0	1526320	3.3	1.9	5.2	**38**	**104**	638009	3.2	1.6	4.8	**32**	**96**
10.0	3022506	6.4	3.6	10.0	**36**	**100**	1243536	9.4	2.9	12.3	**29**	**123**
15.0	4525361	9.6	4.7	14.3	**31**	**95**	1560560	13.4	3.5	16.9	**23**	**113**
20.0	5888185	12.4	7.0	19.4	**35**	**97**	2062273	16.8	4.6	21.4	**23**	**107**
25.0	8759661	18.5	7.7	26.2	**31**	**105**	2435527	24.5	5.4	29.9	**22**	**120**

It can be seen from respective values of these figures that benzene recovery ranges from 95 to 120 % (v/v) and toluene recovery ranges from 88 to 123 % (v/v). The curves in Figures 4.12 indicate that the plots between the actual concentrations and recovered concentrations show linear relationships in the experimented concentration range. This consistency again proves the unchanging composition in the structure of 1-ethyl-3-methylimidazolium ethyl sulphate as an extracting agent.

In general, the overall results indicate that the concentrations of aromatic hydrocarbons are relatively lower in the extract phases compared to the raffinate phases. It is also noticed that all results depicted in the curves show linear relationships and hence the linear distribution across the entire concentration range involved in the extraction processes. This indicates the ability of 1-ethyl-3-methylimidazolium ethyl sulphate to extract aromatic components of even at low concentration.

The data presented here do not include alkanes because this study targets the separation of only aromatic hydrocarbons and their subsequent concentrations in the aliphatic-rich phases and ionic liquid-rich phases. The work of previous researchers established that the raffinate phases are almost free of ionic liquids and extract phases contained significantly small amounts of alkane (0.24 – 0.26 % by mass) [43,86].

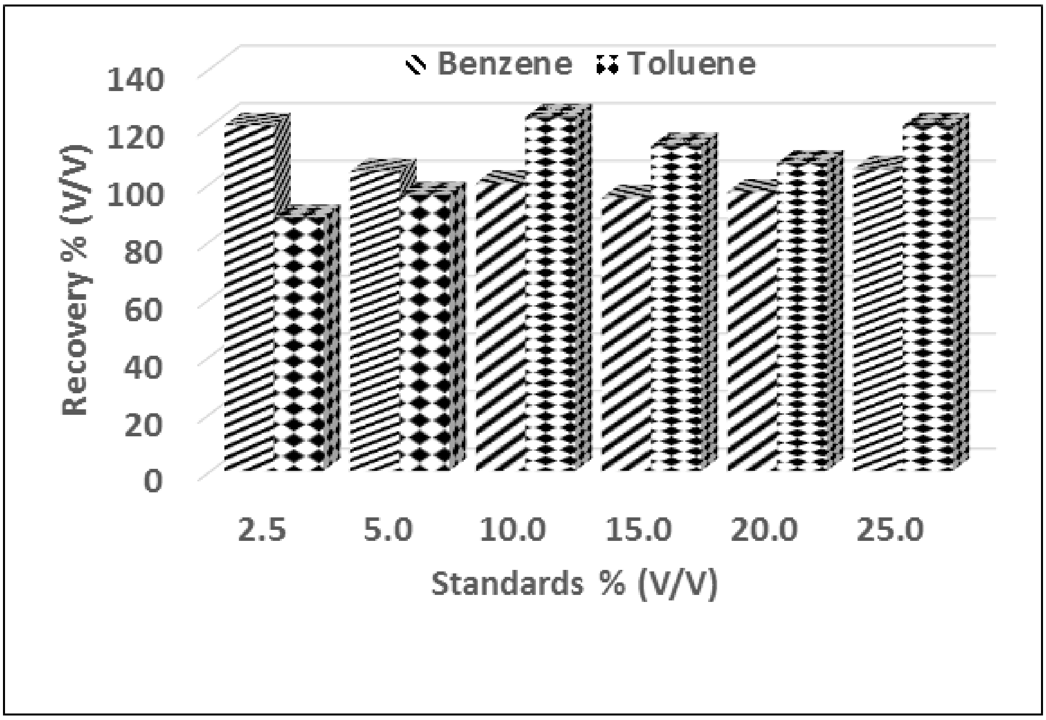


Figure 4.12 Bar graphs comparing the recovery values for benzene and toluene from the model mixtures in the concentration range 2.5 – 25 % (v/v)

The results obtained clearly show that recovery values are slightly higher for benzene than those of toluene. This is in accordance with the findings of previous studies [79] where the study indicated similar trends from different ionic liquids. Therefore this indicates that 1-ethyl-3-methylimidazolium ethyl sulphate has a higher selectivity and a higher solvent capacity for benzene over toluene. The experimental values for the concentration range used are generally in reasonable agreement with those of the original concentrations of the model mixtures. This indicates that the recovery of aromatic hydrocarbons from aromatic/aliphatic hydrocarbon mixtures is possible if the ionic liquids with much higher selectivity and distribution coefficients are available.

Nevertheless, the ionic liquid used in this study does show high efficiency because it was capable of extracting quite significant amount of aromatic hydrocarbons present even at a very low concentration 2.5 %(v/v) in the model mixtures of aliphatic/aromatic hydrocarbons. By comparison, the conventional solvents such as sulpholane are only applicable for the extraction of aromatic hydrocarbons of the concentration range of 20-65 % [62].

It can be seen in Figure 4.13 that there is a steady decrease in recovery percentages as the composition concentration increases for both aromatic components. This phenomenon suggests that the amount of ionic liquid should be increased proportionally in order to ensure optimum and efficient separation. Figure 4.13 also shows that the recovery for benzene and toluene are 95 – 120 % (v/v) and 88 – 123 % (v/v), respectively. These values are within the acceptable range of 80 – 120% (v/v) except for toluene which is slightly higher by 2.5 % margin.

4.2.2 The effects of using recycled ionic liquids in BTEX extractions

4.2.2.1 Quaternary: Benzene +Toluene+ n-Heptane + [EMIM][ESO4]

The results of benzene and toluene from the extractions carried out on 15 and 20 % model mixtures using fresh and recycled ionic liquids are shown in Table 4.4 (a) and Table 4.4 (b), respectively. The comparative recovery values for these two aromatic components are illustrated by bar graphs depicted in Figure 4.13.

Table 4.4 (a) Results of the concentration of benzene in the extract and raffinate phases

[EMIM][ESO$_4$]	Standards % (v/v)	Raffinate [R] % (v/v)		Extract [E] % (v/v)		Overall % (v/v)	
		Extract	**Recovery**	**Extract**	**Recovery**	**Extract**	**Recovery**
Unused	15.0	8.8	58.7	6.4	42.7	15.2	101
Recycled	15.0	9.0	60.0	6.5	43.3	15.5	103
Unused	20.0	12.6	63.0	7.0	35.0	19.6	98
Recycled	20.0	12.4	62.0	7.2	36.0	19.6	98

Table 4.4 (b) Results of the concentration of toluene in the extract and raffinate phases

[EMIM][ESO$_4$]	Standards % (v/v)	Raffinate [R] % (v/v)		Extract [E] % (v/v)		Overall % (v/v)	
		Extract	**Recovery**	**Extract**	**Recovery**	**Extract**	**Recovery**
Unused	15.0	11.0	73.3	4.1	27.3	15.1	101
Recycled	15.0	11.7	78.0	4.0	26.7	15.7	105
Unused	20.0	16.3	81.5	5.2	26.0	21.5	108
Recycled	20.0	16.3	81.5	5.2	26.0	21.5	108

Table 4.4 (c) Summary of results showing the effect of unused and recycled ionic liquid

[EMIM][ESO$_4$]	Standards % (v/v)	Benzene % (v/v)			Toluene % (v/v)		
		Raffinate	**Extract**	**Recovery**	**Raffinate**	**Extract**	**Recovery**
Unused	15.0	58.7	42.7	101	73.3	27.3	101
Recycled	15.0	60.0	43.3	103	78.0	26.7	105
Unused	20.0	63.0	35.0	98	81.5	26.0	108

Recycled	20.0	62.0	36.0	98	81.5	26.0	108

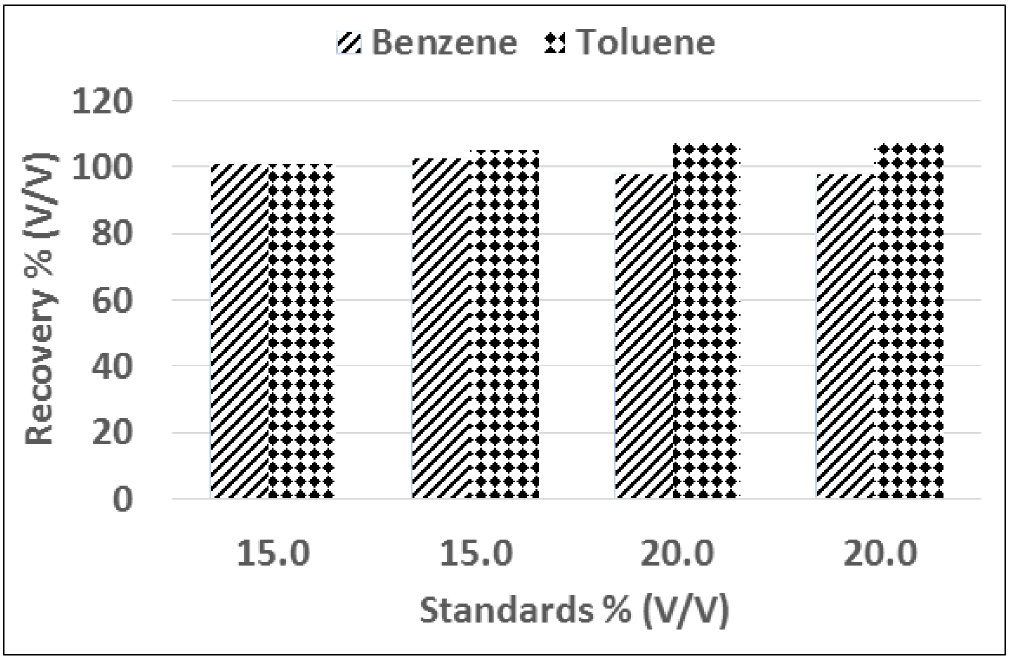


Figure 4.13: Bar graphs comparing actual values and recovery values for benzene and toluene in the concentration range 2.5 – 25 % (v/v)

The model mixtures chosen for this purpose were 15 and 20 % (v/v) of benzene and toluene as aromatic components with n-heptane as an n-alkane. The results obtained from both phases indicated no significant differences between the unused and recycled ionic liquids, thus indicating a potential for high recyclability and cost-effectiveness of the recycled ionic liquid.

It can be seen in Table 4.4 (a) and Table 4.4 (b) as well as in Figure 4.13 that the recovery values in both cases were within the acceptable range of 80 – 120 % (v/v) with benzene range of 98 – 103 % (v/v) and 101 – 108 % (v/v) for toluene. Both fresh and recycled ionic liquids effectively produced almost similar results from all extraction processes performed thus indicating good quality of the recycled ionic liquid.

4.2.2.2 Multi-Components: BTEX + n-Heptane + [EMIM][ESO$_4$]

The chromatograms for the calibration model mixtures of four aromatic components (benzene, toluene, ethylbenzene, and o-xylene) and n-heptane are shown in Figure 4.14. The corresponding calibration curves and peak areas of BTEX are illustrated in Figure 4.15. The chromatograms of the extract and raffinate phases obtained by using ionic liquid 1-ethyl-3-methylimidazolium ethyl sulphate [EMIM][ESO$_4$] for performing BTEX extractions on these model mixtures are also shown in Figure 4.16. (See also Appendix 3 for [EMIM][ESO$_4$], Figs. A7.20 – A721, Appendix 4 for [EMpy][ESO$_4$], Figs. A7.22 – A723). All chromatograms display good resolution of aromatic components, thus permitting precise and accurate measurements of their peak areas. These model mixtures were also used for BTEX separations to investigate the extraction ability of the recycled ionic liquid 1-ethyl-3-methylimidazolium ethyl sulphate. The overall results of obtained from these experiments are shown in Table 4.5 and the bar graphs in Figure 4.17 were used to compare relative recovery values from extracted model mixtures.

It can be seen in Figure 4.17 that the ionic liquid which has been recycled twice shows slightly higher extract values than the ionic liquid that has been recycled once. The reason for this difference could be attributed to the fact that recycled ionic liquids may possibly contain significant amounts of BTEX components before being reused in the extraction processes. The more recycled the ionic liquid the higher the content of the aromatic components it contains; hence the more time it requires for its regeneration. It is therefore essential that the process of regeneration of the ionic liquids should be done over a longer period in order to achieve complete elimination of volatile impurities. It is also important to analyze the regenerated ionic liquids to check if any aromatic hydrocarbons are present or not and to ascertain their content. It must again be remembered that toluene is used as a solvent in the synthesis of ionic liquids. Therefore, freshly prepared ionic liquids are also analyzed as blank samples to check the content of toluene and used for adjustment of results if necessary.

Table 4.5 also reveals a gradual increase in the extract phase results from benzene to o-xylene. (See also Appendix 3 for [EMIM][SO_4], Table A7.1, Appendix 4 for [EMpy][ESO_4], Table A7.2). As mentioned earlier, this trend is associated with the structural features of these aromatic compounds in terms of steric hindrance effects. Therefore, the interaction between ionic liquid and aromatic components is expected to increase from benzene to xylene for the same reason. The overall observation is that the recycled ionic liquids are as effective and efficient as the freshly prepared ones provided they are regenerated properly and completely before using them for further extractions. It can also be seen from Table 4.5 that BTEX recovery values obtained over the concentration range used were all within the acceptable range which is usually between 80 and 120 % (v/v). The raffinate [R] and extract [E] phase results are presented in Table 4.6 which also shows total recovery values for each component.

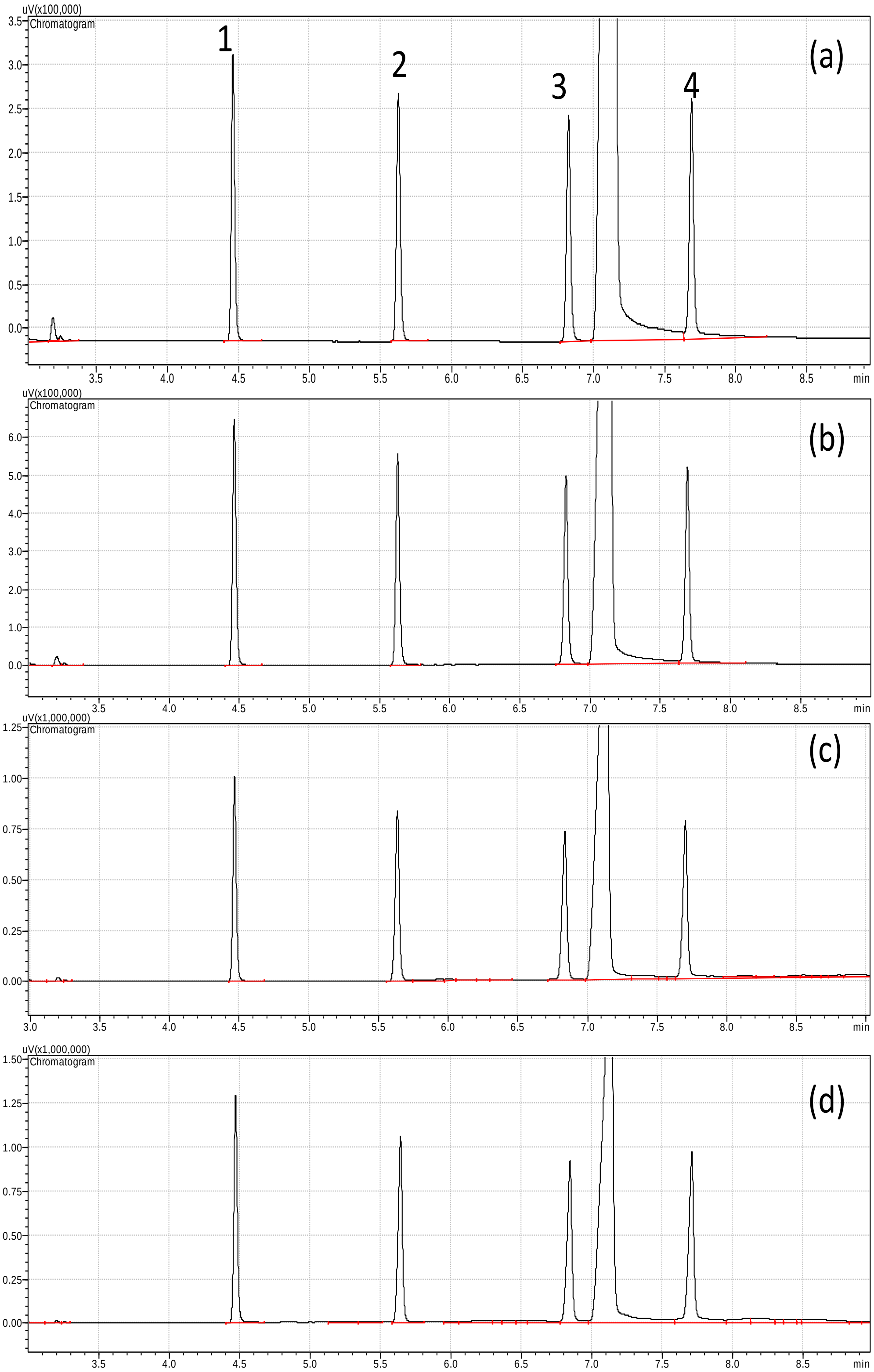
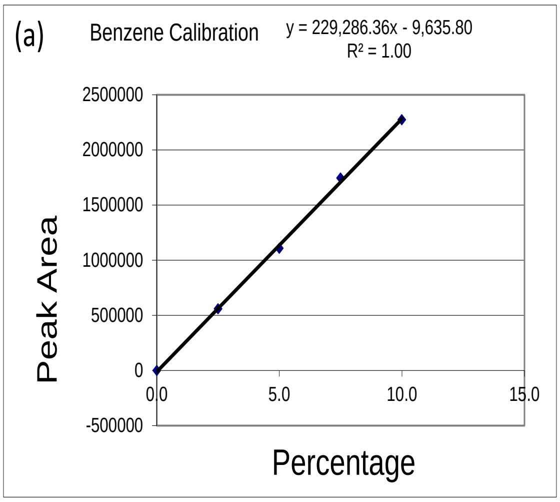
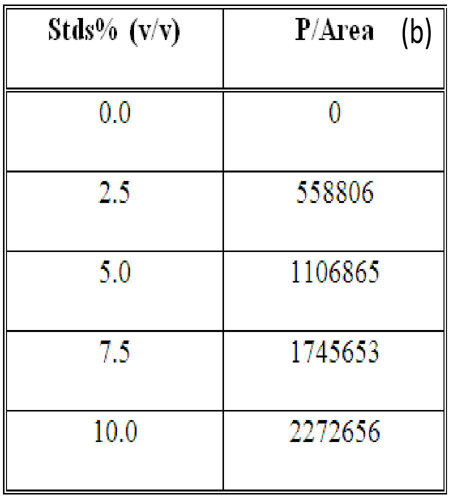
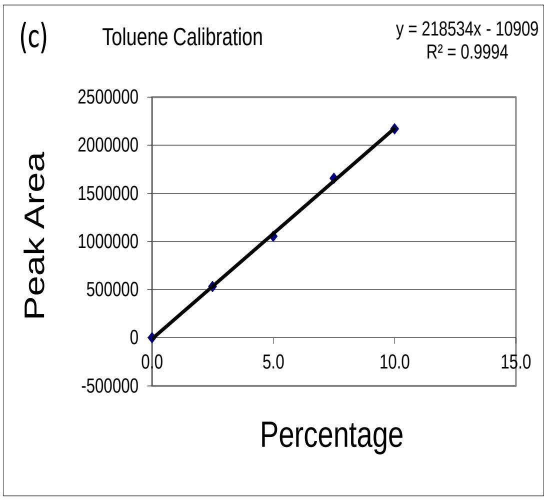


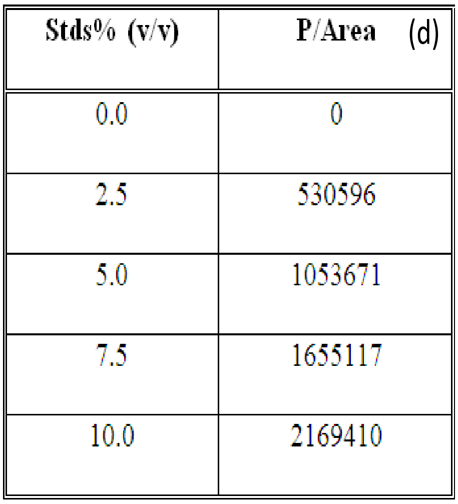
Figure 4.14: Chromatograms for the BTEX calibration standards in n-heptane (a) 2.5 % (v/v) (b) 5.0 % (v/v) (c) 7.5 % (v/v) (d) 10.0 % (v/v)



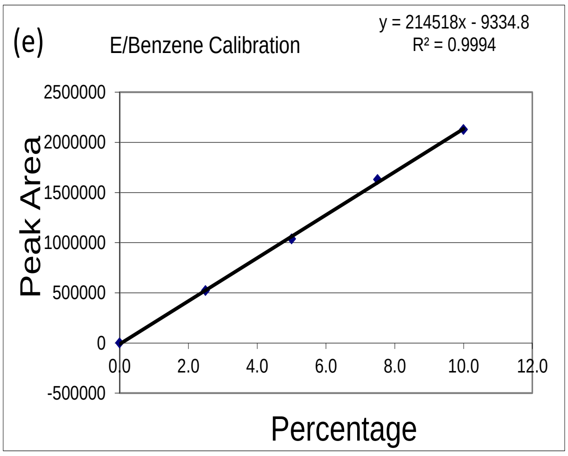


Stds% (v/v)	P/Area (b)
0.0	0
2.5	558806
5.0	1106865
7.5	1745653
10.0	2272656



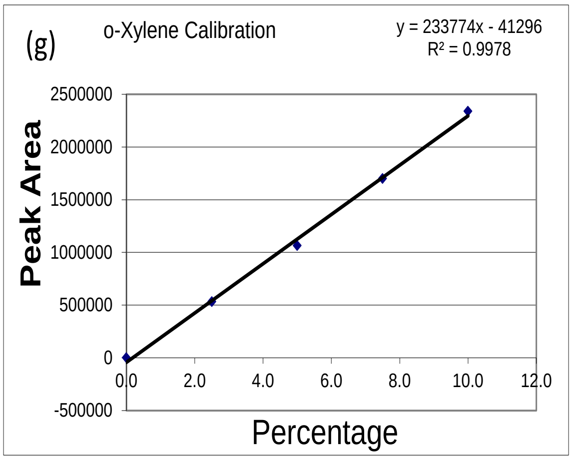


Stds% (v/v)	P/Area (d)
0.0	0
2.5	530596
5.0	1053671
7.5	1655117
10.0	2169410



(f)

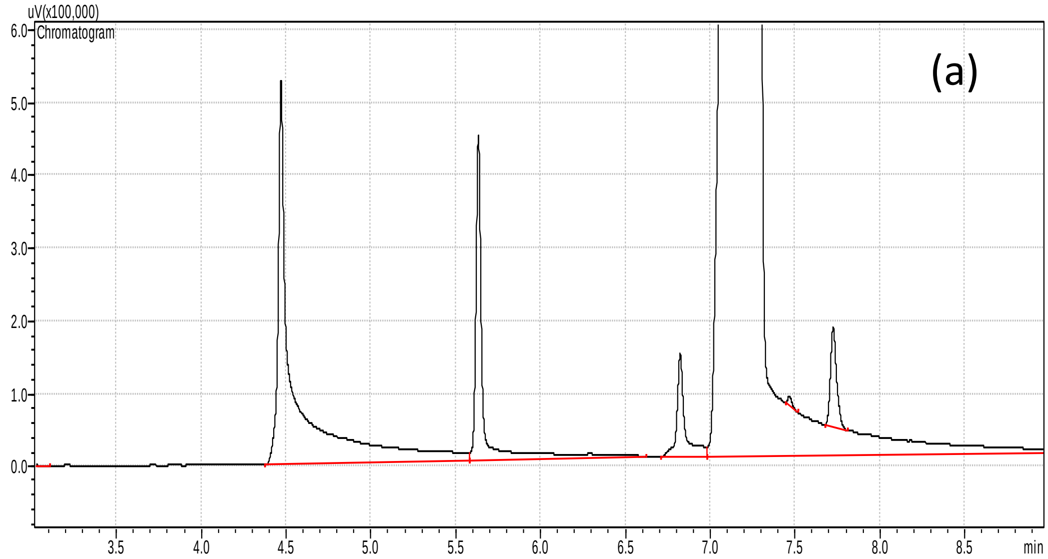
Stds% (v/v)	P/Area
0.0	0
2.5	522505
5.0	1036242
7.5	1629602
10.0	2127926

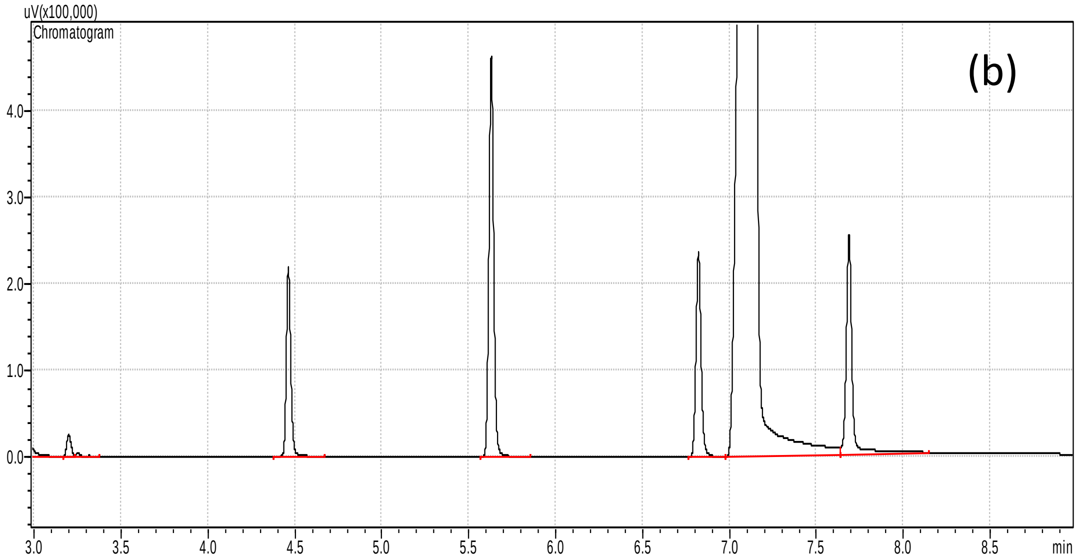


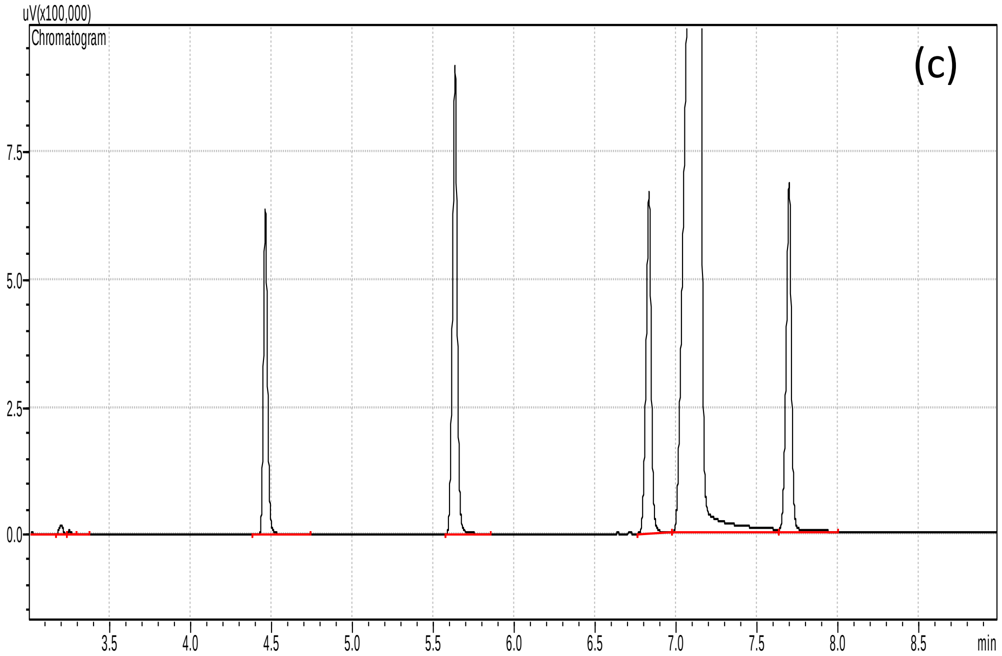
(h)

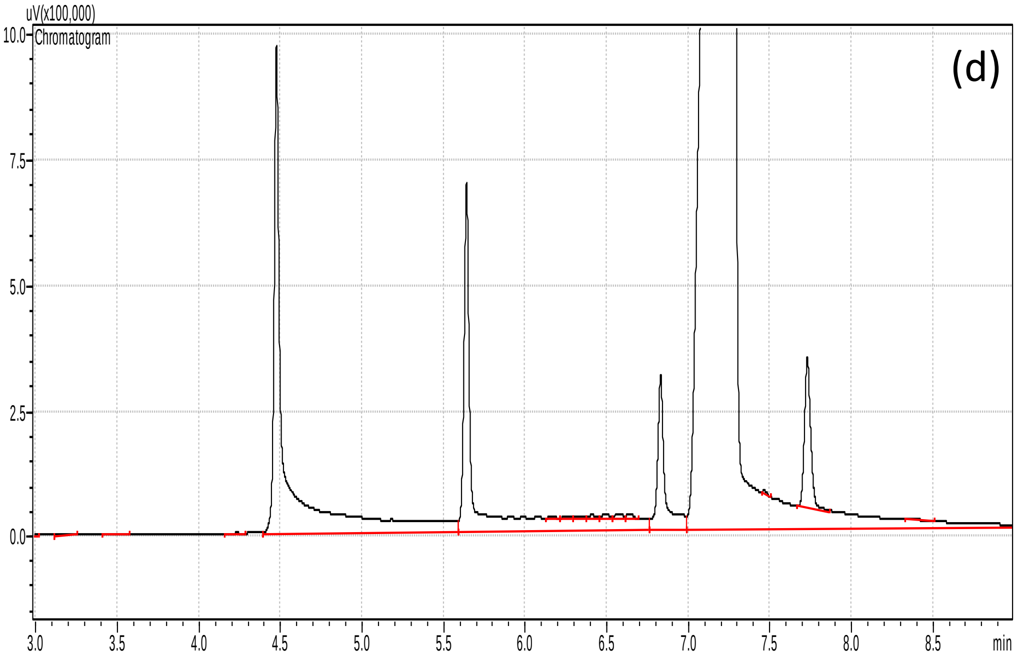
Stds% (v/v)	P/Area
0.0	0
2.5	533310
5.0	1065494
7.5	1700459
10.0	2338596

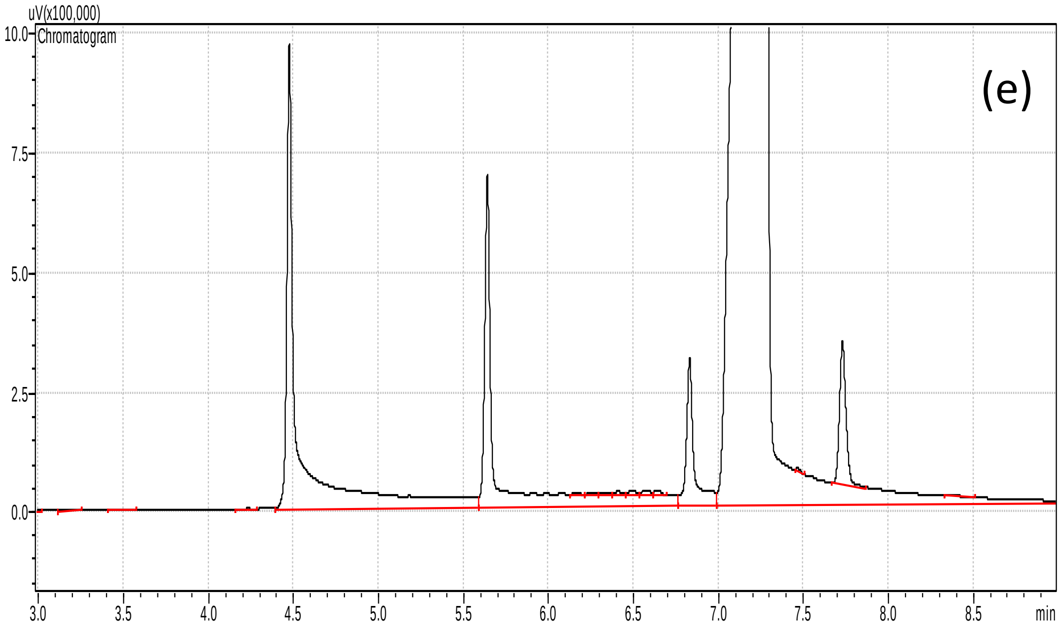
Figure 4.15: Peak areas and calibration curves of BTEX standards for the concentration range 2.5 – 10 % (v/v) using n-heptane as an alkane (a) Benzene peak areas (b) Benzene curve (c) Toluene peak areas (d) Toluene curve Toluene (e) E/Benzene peak areas (f) E/Benzene curve (g) o-Xylene peak areas (h) o-Xylene curve

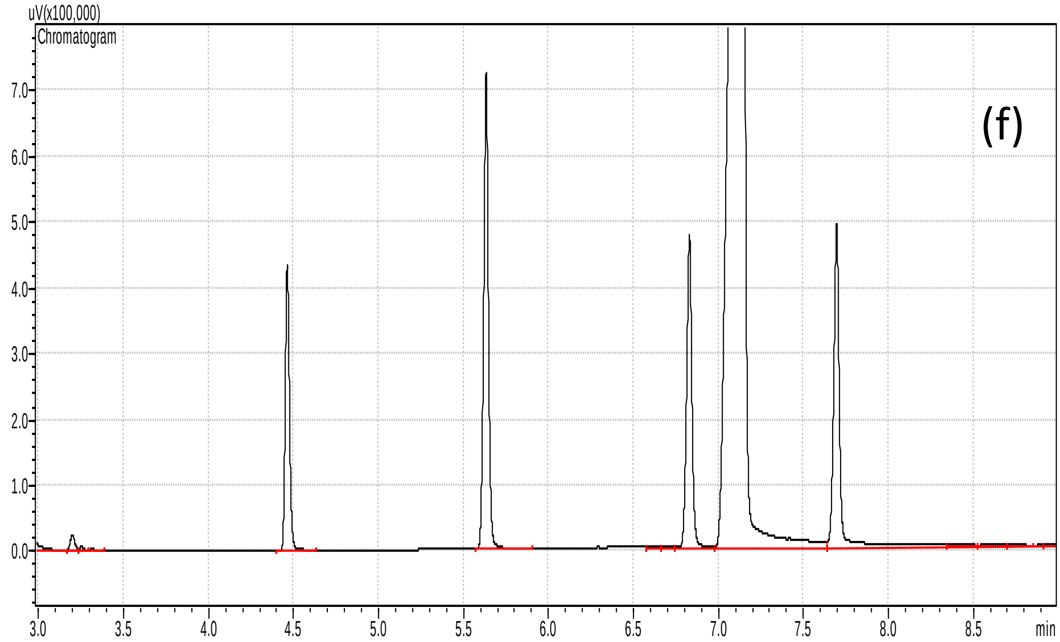

uV(x100,000)
Chromatogram
(a)
6.0
5.0
4.0
3.0
2.0
1.0
0.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
min


uV(x100,000)
Chromatogram
(b)
4.0
3.0
2.0
1.0
0.0
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
min


uV(x100,000)
Chromatogram
(c)
7.5
5.0
2.5
0.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
min


uV(x100,000)
10.0
Chromatogram
(d)
7.5
5.0
2.5
0.0
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
min


uV(x100,000)
Chromatogram
10.0
7.5
5.0
2.5
0.0
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
min
(e)


uV(x100,000)
Chromatogram
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
min
(f)

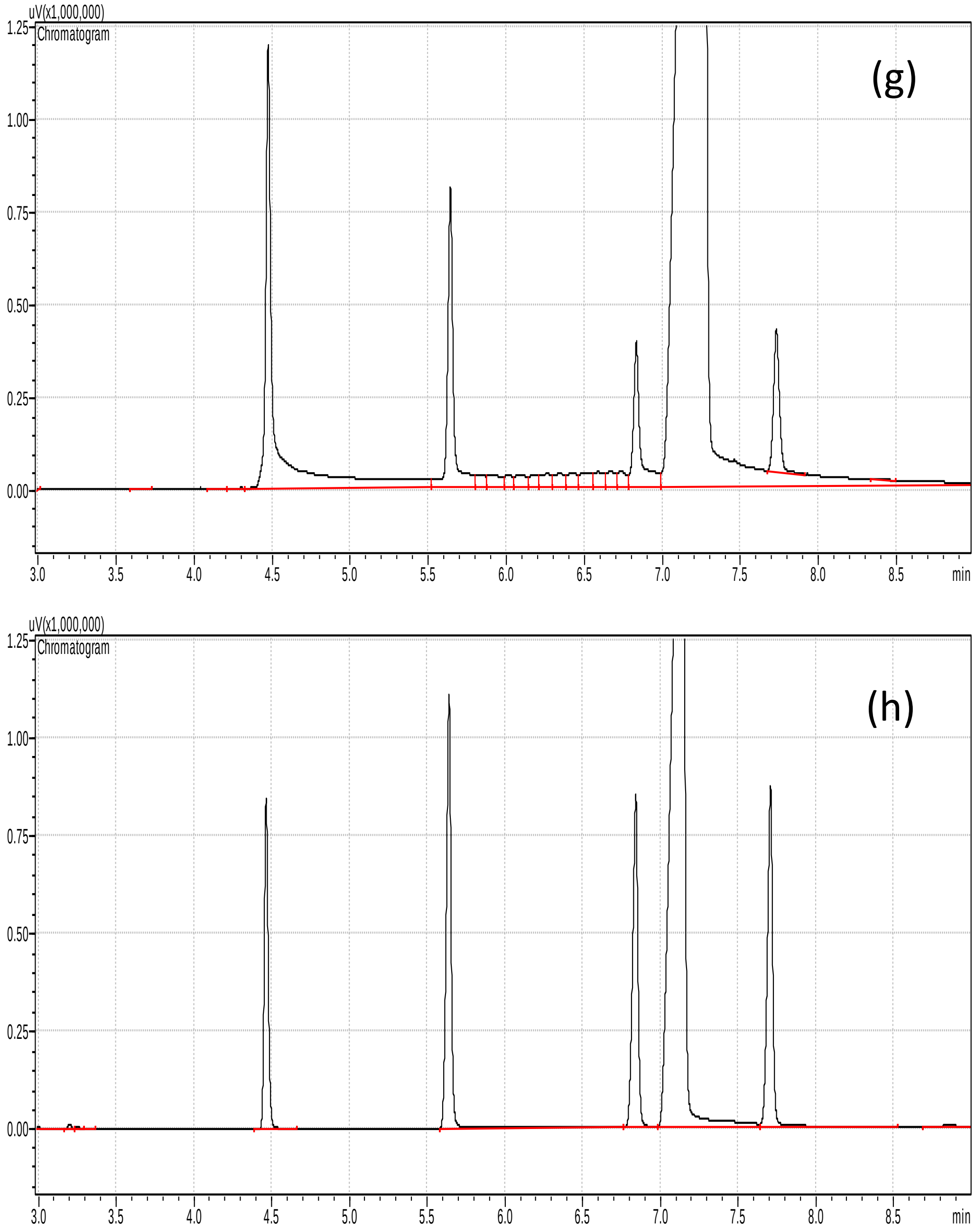


Figure 4.16: Chromatograms for BTEX extractions using [EMIM][ESO$_4$] and heptane: (a) 2.5 % (v/v) Extract phase, (b) 2.5 % (v/v) Raffinate phase, (c) 5 % (v/v) Extract phase, (d) 5 % (v/v) Raffinate phase (e) 7.5 % (v/v) Extract phase, (f) 7.5 % (v/v) Raffinate phase, (g) 10 % (v/v) Extract phase, (h) 10 % (v/v) Raffinate phase

Table 4.5: BTEX recovery for the non-recycled and recycled ionic liquid [EMIM][ESO_4]

BTEX STDS	Benzene			Toluene			Ethylbenzene			o-Xylene		
	Recycled twice IL	**Recycled once IL**	**First-time used IL**	**Recycled twice IL**	**Recycled once IL**	**First-time used IL**	**Recycled twice IL**	**Recycled once IL**	**First-time used IL**	**Recycled twice**	**Recycled once**	**First-time used IL**
2.5	119	98	103	116	108	104	112	96	96	112	88	105
5.0	108	84	98	112	100	102	112	92	97	112	84	100
7.5	111	88	95	103	98	101	106	96	101	91	84	98
10.0	99	88	90	114	118	100	105	97	101	94	82	97

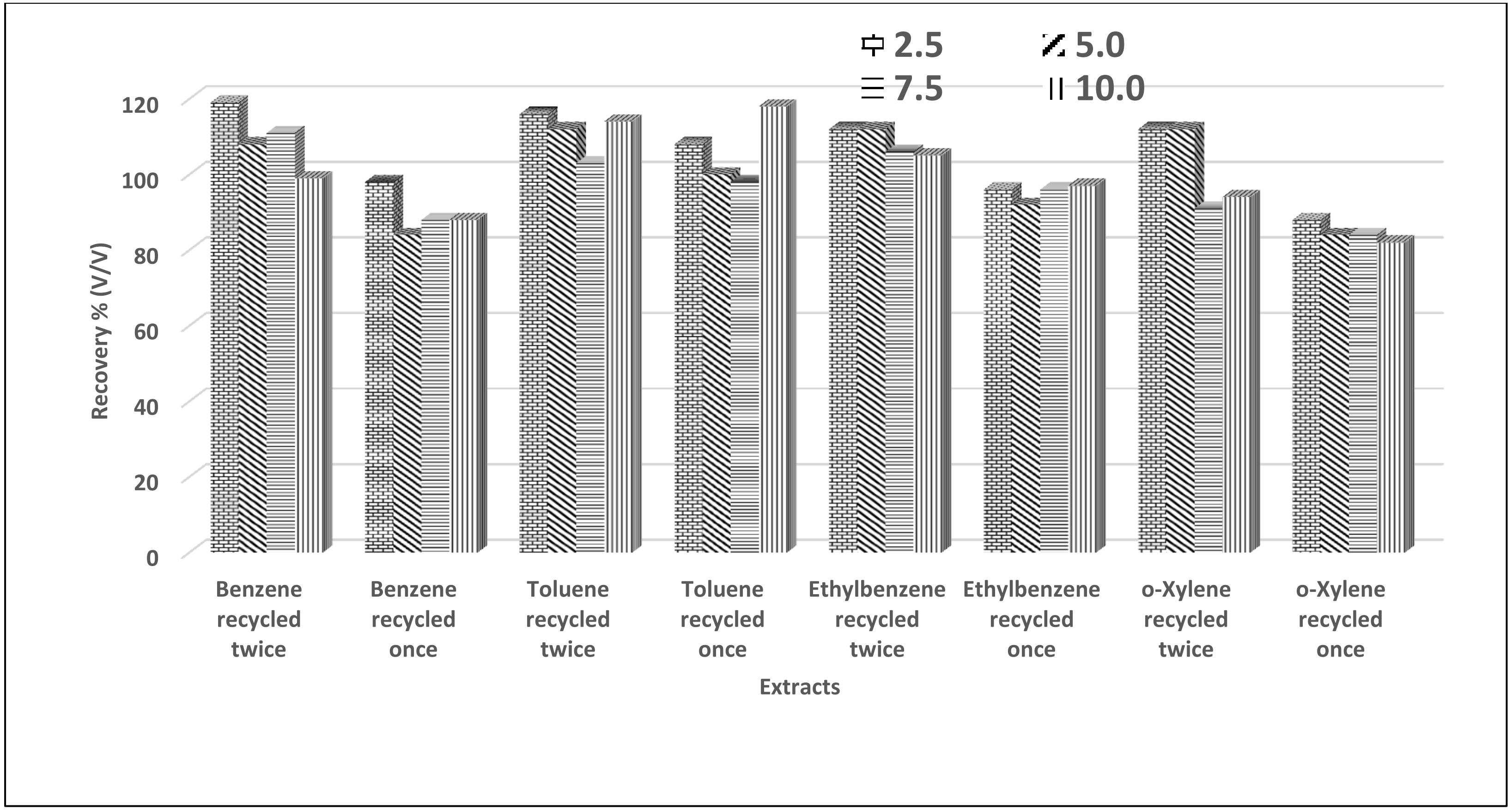


Figure 4.17: Bar graphs comparing the recovery values for the recycled ionic liquid [EMIM][ESO4] used in the extractions involving 2.5 – 10.0 % (v/v) BTEX model mixtures

Table 4.6: Summary for BTEX recovery in the concentration range 2.5 – 10 % (v/v)

[EMIM][ESO4] Ionic Liquid	Actual % (v/v)	Benzene			Toluene			E/benzene			o-Xylene		
		R	E	R + E	R	E	R + E	R	E	R + E	R	E	R + E
Recycled Twice	2.5	83	36	119	88	28	116	92	20	112	96	16	112
Recycled Once	2.5	70	28	98	68	40	108	76	20	96	68	20	88
First Time Use	2.5	65	38	103	77	17	94	83	13	96	89	16	105
Recycled Twice	5.0	70	38	108	92	20	112	94	18	112	102	10	112
Recycled Once	5.0	70	14	84	76	24	100	78	14	92	70	14	84
First Time Use	5.0	64	34	98	88	14	102	87	10	97	88	12	100
Recycled Twice	7.5	69	41	110	87	16	103	91	15	106	80	11	91
Recycled Once	7.5	68	20	88	77	21	98	84	12	96	75	8	83
First Time Use	7.5	63	32	95	86	15	101	91	10	101	86	12	98
Recycled Twice	10.0	67	32	99	89	25	114	91	14	105	84	10	94
Recycled Once	10.0	68	20	88	82	36	118	86	11	97	74	7	81
First Time Use	10.0	63	27	90	86	14	100	92	9	101	86	11	97

4.2.3 The effects of varying the phase settling periods using

4.2.3.1 Multicomponent: BTEX + n-Heptane + [EMIM][ESO$_4$]

This mixture was made up of benzene, toluene, ethylbenzene, o-xylene, n-heptane, and 1-ethyl-3-methylimidazolium ethyl sulphate for 2.5 – 10 % (v/v) concentration range. All mixtures investigated in this multi-component system were treated in the same way as those of the quaternary mixtures with concentration range 2.5 – 25 % (v/v). It was noticed that the resulting mixtures required phase settling periods of between 4 and 12 hours in order to be completely separated into two phases. This facilitated easy separation of the two phases using simple apparatus such as separating funnels for individual analysis. After allowing the raffinate and extract phases to remain separately undisturbed for a longer period, no signs of further phase separations were observed in both individual phases.

The recovery percentages of aromatic components in the extract phases for the model mixtures of the concentration range 2.5 – 10 % (v/v) using 4 and 12 hours phase settling periods are presented in Table 4.7 and 4.8, respectively. It can be seen that the total recovery for each aromatic component falls within an accepted range of 80 – 120 % (v/v) in both cases. The values for the extract phases indicate a general decrease with increasing concentration of the BTEX components. It appears that the 4 hour results are relatively lower than those of 12 hour settling periods. However, in both cases the values tend to decrease from benzene to xylene as was the case in the other experiments. This trend indicates that the solubility of aromatic hydrocarbons in this ionic liquid decreases in the order: benzene > toluene > ethyl benzene > o-xylene. Compared to the other three aromatic hydrocarbons, benzene is the smallest molecule with the least steric hindrance and strongestπ-systems. Xylene, on the other hand, is the most crowded with two methyl groups, hence the relatively weaker π-system. This explains why benzene interaction with the ionic liquid is relatively strong due to the π-π interactions [100, 104-105].

The other observation made is that the results obtained from extraction slightly decrease gradually as the concentration of the model mixtures increase. This observation could indicate a need to increase the amount of ionic liquid added as the concentration of the mixtures to be extracted increases. The slight difference in the extract results observed in these two cases is an indication that the ionic liquid being investigated is capable of achieving a complete phase separation within 4 hours after extraction. However, all extractions carried out in this study were conducted for 12 hour settling period to ensure maximum equilibration time and to avoid any unnecessary repeat of the experiments.

Table 4.7: Summary of results for a 4 Hour settling period

Standards % (v/v)	**Benzene % (v/v)**			**Toluene % (v/v)**			**Ethyl Benzene% (v/v)**			**o-Xylene % (v/v)**		
	R	E	R+E	R	E	R+E	R	E	R+E	R	E	R+E
2.5	71	36	106	70	21	91	73	9	81	74	10	88
5.0	69	34	103	80	16	96	78	8	85	76	9	85
7.5	69	29	98	83	15	98	84	8	92	79	9	88
10.0	66	24	90	82	13	95	85	7	92	80	8	89

Another observation made is that the extraction capacity of [EMIM][ESO$_4$] is slightly higher for the mixtures containing lower number of aromatic components. This phenomenon is indicated by the extraction values obtained for benzene and toluene in Table 4.3 (two aromatic components mixture) with the values obtained for benzene and toluene in Table 4.8 (four aromatic components mixture).

Table 4.8: Summary of results for a12 Hour settling period

Standards % (v/v)	**Benzene % (v/v)**			**Toluene % (v/v)**			**E/Benzene% (v/v)**			**o-Xylene % (v/v)**		
	R	E	R+E	R	E	R+E	R	E	R+E	R	E	R+E
2.5	65	38	103	72	32	104	78	12	90	86	15	101
5.0	64	34	98	82	20	102	81	9	91	87	12	99
7.5	63	31	94	82	20	102	85	9	94	86	12	98
10.0	63	27	90	82	17	100	86	8	95	87	11	98

In addition, it appears that the longer the alkyl chains that are attached to the aromatic rings, the more difficult it is for the molecules to organize themselves in a sandwich structure. This phenomenon supports the observation made by Meindersma et al. [62] that alkyl substitutions on the aromatic ring affect the molecular interaction in the preferred functional groups. Based on BTEX structures, it can be argued that π-π interactions strongly influence the BTEX interactions with the ionic liquids. According to previous researchers [129], the ionic liquid may form a single phase with the mixture in which it has a higher affinity for one component over the other (often hydrogen bonding more strongly with one component than the other). It has been previously reported [90] that ionic liquids and aromatic solutes organize themselves in a sandwich structure in which the ionic liquid cations and the aromatic solutes interact in an alternating structure through π-π interactions with the ionic liquid anions, arranged around this complex.

4.2.3.2 Multicomponent: BTEX + n-Heptane + [EMpy][ESO$_4$]

The resulting mixtures from 4 and 12 hour phase settling periods were completely separated into two phases which were easy to collect using appropriate apparatus, prior to analysis. The separated phase mixtures remain intact with no signs of further phase separation when both were left undisturbed for a long period of time in the laboratory. The extract phase results for BTEX extractions obtained from 4 and 12 hours of phase settling periods using 1-ethyl-3-methylpyridinium ethyl sulphate [EMpy][ESO$_4$] as an ionic liquid are summarized in Table 4.9 and 4.10, respectively. In the case of this ionic liquid, results for a 4 hour settling period appear to be significantly smaller than those obtained from twelve hours of phase settling periods. This finding suggests that 1-ethyl-3-methylpyridinium ethyl sulphate requires more than four hours of settling period to achieve maximum separation of the raffinate and the extract phase. Like in the case of 1-ethyl-3-methylimidazolium ethyl sulphate, the results obtained from using 1-ethyl-3-methylpyridinium ethyl sulphate [EMpy][ESO$_4$]also decrease gradually from benzene to xylene for both 4 and 12 hours of phase settling periods.

In general, overall results appear to be higher than those obtained for 1-ethyl-3-ethylimidazolium ethyl sulphate was used as an extraction solvent, under similar experimental conditions. This effect was observed across the concentration range of all model mixtures and aromatic components extracted. The phenomenon of this kind reveals that the BTEX components interact more strongly with [EMpy][ESO_4] than they do with [EMIM][ESO_4]. It could also be attributed to the fact that the former ionic liquid contains a six-membered ring cation whereas the latter ionic liquid has a five-membered ring cation. Therefore these structural features enhance the solubility of the aromatic compounds in the ionic liquid 1-ethyl-3-methylpyridinium ethyl sulphate. Meindersma et al. [130] noted that the ionic liquids containing the 1-ethyl-3-methylpyridiniumcations have more aromatic character than the imidazolium-based ionic liquids which has relatively less π-character. It can be seen in Table 4.9 that the raffinate phase values obtained by using pyridinium-based ionic liquid follow similar trend as those of imidazolium-based ionic liquid. It is also noticed that the recovery values are within the acceptable range of 80 – 120 % (v/v) [131,132]. This indicates that 1-ethyl-3-methylimidazolium ethyl sulphate and 1-ethyl-3-methylpyridinium ethyl sulphate have the same effects on these two different phase settling periods.

Table 4.9: Summary of results for a 4 Hour phase settling period

Stds % (v/v)	**Benzene % (v/v)**			**Toluene % (v/v)**			**E/Benzene% (v/v)**			**o-Xylene % (v/v)**		
	R	E	R+E	R	E	R+E	R	E	R+E	R	E	R+E
2.5	58	30	88	79	17	96	74	11	85	73	13	86
5.0	58	21	79	78	15	93	81	10	91	81	12	93
7.5	62	20	82	82	14	96	87	9	96	86	10	96
10.0	61	19	80	82	14	96	90	9	99	88	10	98

Table 4.10: Summary of results for a 12 Hour phase settling period

Stds % (v/v)	**Benzene % (v/v)**			**Toluene % (v/v)**			**E/Benzene % (v/v)**			**o-Xylene % (v/v)**		
	R	E	**R+E**	R	E	**R+E**	R	E	**R+E**	R	E	**R+E**
2.5	64	40	104	90	27	117	85	17	102	82	17	99
5.0	54	38	92	82	25	107	87	15	103	85	18	103
7.5	56	37	95	78	22	100	87	14	101	82	17	99
10.0	60	35	95	88	22	110	97	15	112	91	17	108

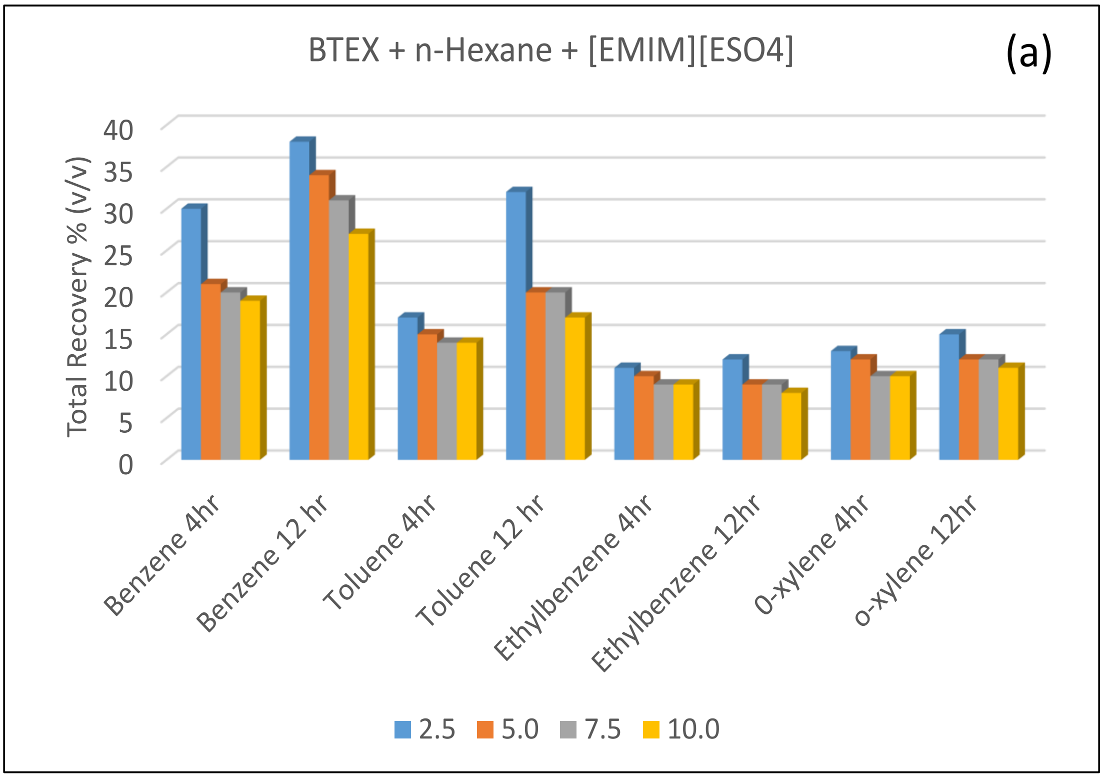
4.2.4 The effect of varying the nature of the alkanes BTEX+[EMIM][ESO4]+n-Hexane; BTEX+[EMpy][ESO4]+n-Hexane

The effect of the nature of the alkane on phase separation was investigated and the results obtained are summarized in Table 4.11 and illustrated as bar graphs in Figure 4.18 for both ionic liquids. These values of n-hexane are comparable with those obtained using n-heptane as an alkane under similar experimental conditions. In general, however, the results obtained from n-heptane are slightly lower than those of n-hexane. This effect is attributed to the chain lengths of alkanes which influence the interaction between BTEX solutes and ionic liquids. It has been reported that an increase in the chain length of the alkanes leads to an increase in the size of the immiscibility region [133]. It was also concluded that the selectivity values were higher for the systems containing alkanes with longer chains in the following order: n-hexane < heptane < octane < nonane.

The chromatograms for the calibration model mixtures containing benzene, toluene, ethylbenzene, and o-xylene (BTEX) in the concentration range 2.5 – 10 % (v/v) are depicted in Figure 4.19, and their respective peak areas and calibration curves shown Figure 4.20. It can be seen that all calibration curves were all linear with determination coefficient (R^2) values very close to unity which indicates a high degree of precision. These calibration curves were therefore used for the calculation of the values shown in Table 4.11.

Table 4.11: Summary of results comparing 4 Hours and 12 Hours settling periods

BTEX Stds % (v/v)	BTEX + n-Hexane + [EMIM][ESO$_4$]							
	Benzene % (v/v)		Toluene % (v/v)		E/Benzene% (v/v)		o-Xylene % (v/v)	
	4 Hrs	12 Hrs	4 Hrs	12 Hrs	4 Hrs	12 Hrs	4 Hrs	12 Hrs
2.5	30	38	17	32	11	12	13	15
5.0	21	34	15	20	10	9	12	12
7.5	20	31	14	20	9	9	10	12
10.0	19	27	14	17	9	8	10	11
BTEX Stds % (v/v)	**BTEX + n-Hexane + [EMpy][ESO$_4$]**							
	4 Hrs	12 Hrs	4 Hrs	12 Hrs	4 Hrs	12 Hrs	4 Hrs	12 Hrs
2.5	41	49	28	52	17	24	13	26
5.0	38	47	25	32	15	15	11	18
7.5	40	45	22	27	14	14	10	17
10.0	35	36	22	26	15	14	10	17



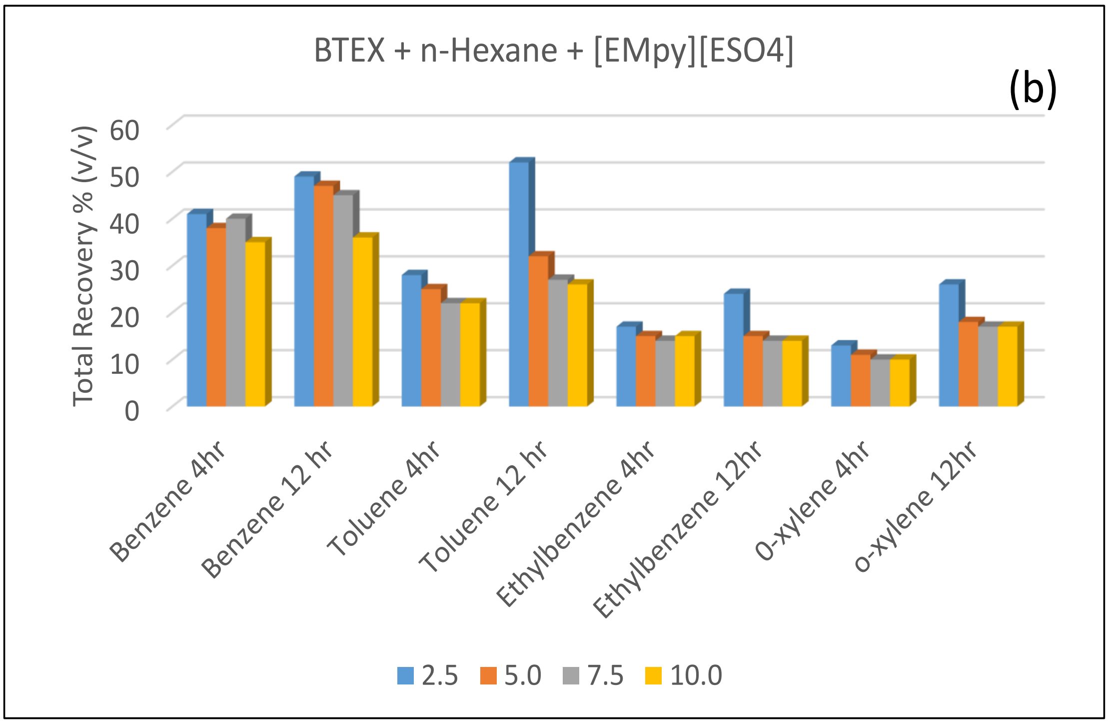
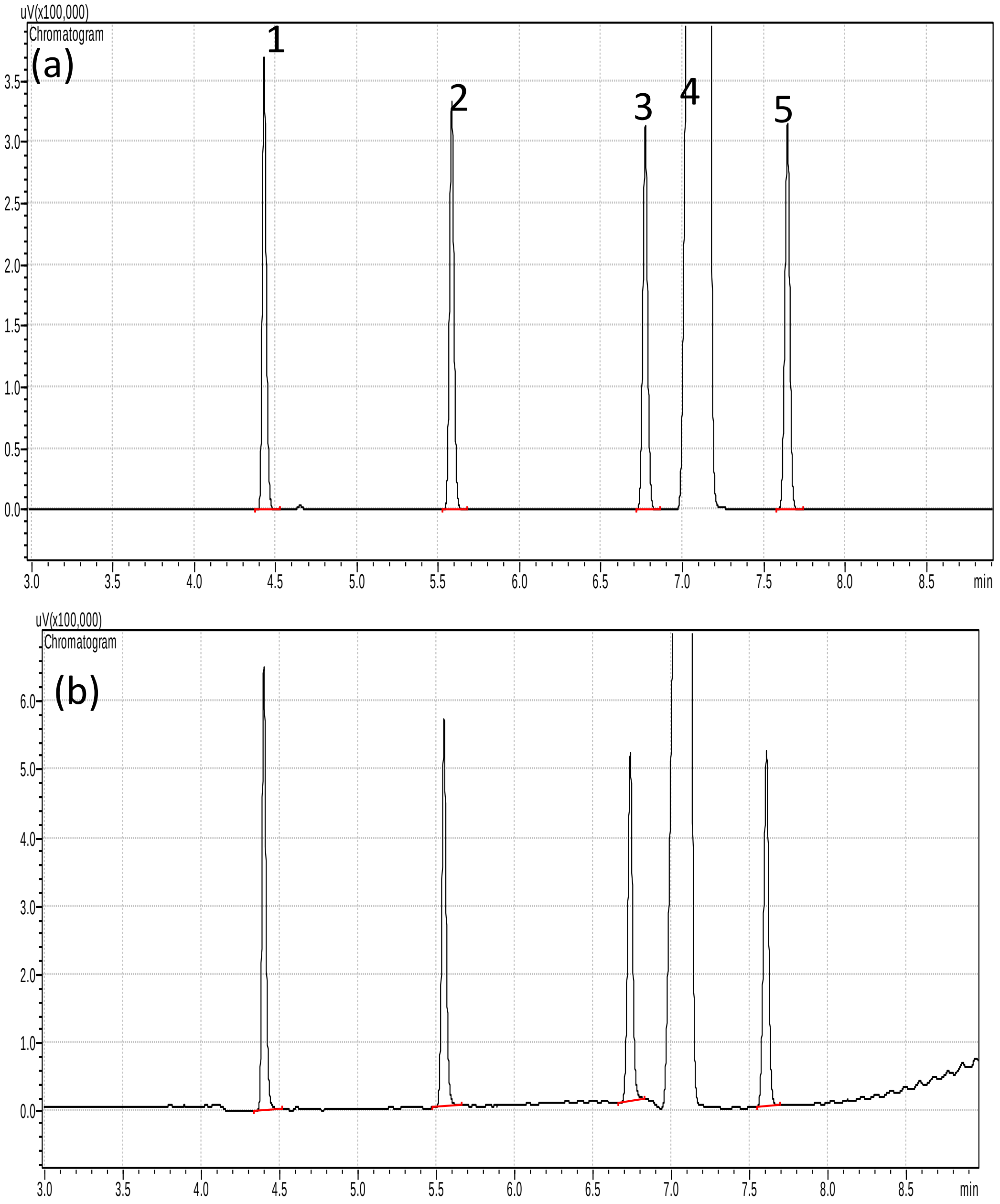


Figure 4.18: Bar graphs comparing BTEX extract phase results of a 4 hr and a 12 hr settling period for (a) [EMIM][ESO_4] (b) [EMpy][ESO_4]


uV(x100,000)
Chromatogram
(a)
1
2
3
4
5
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
min
uV(x100,000)
Chromatogram
(b)
6.0
5.0
4.0
3.0
2.0
1.0
0.0
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
min

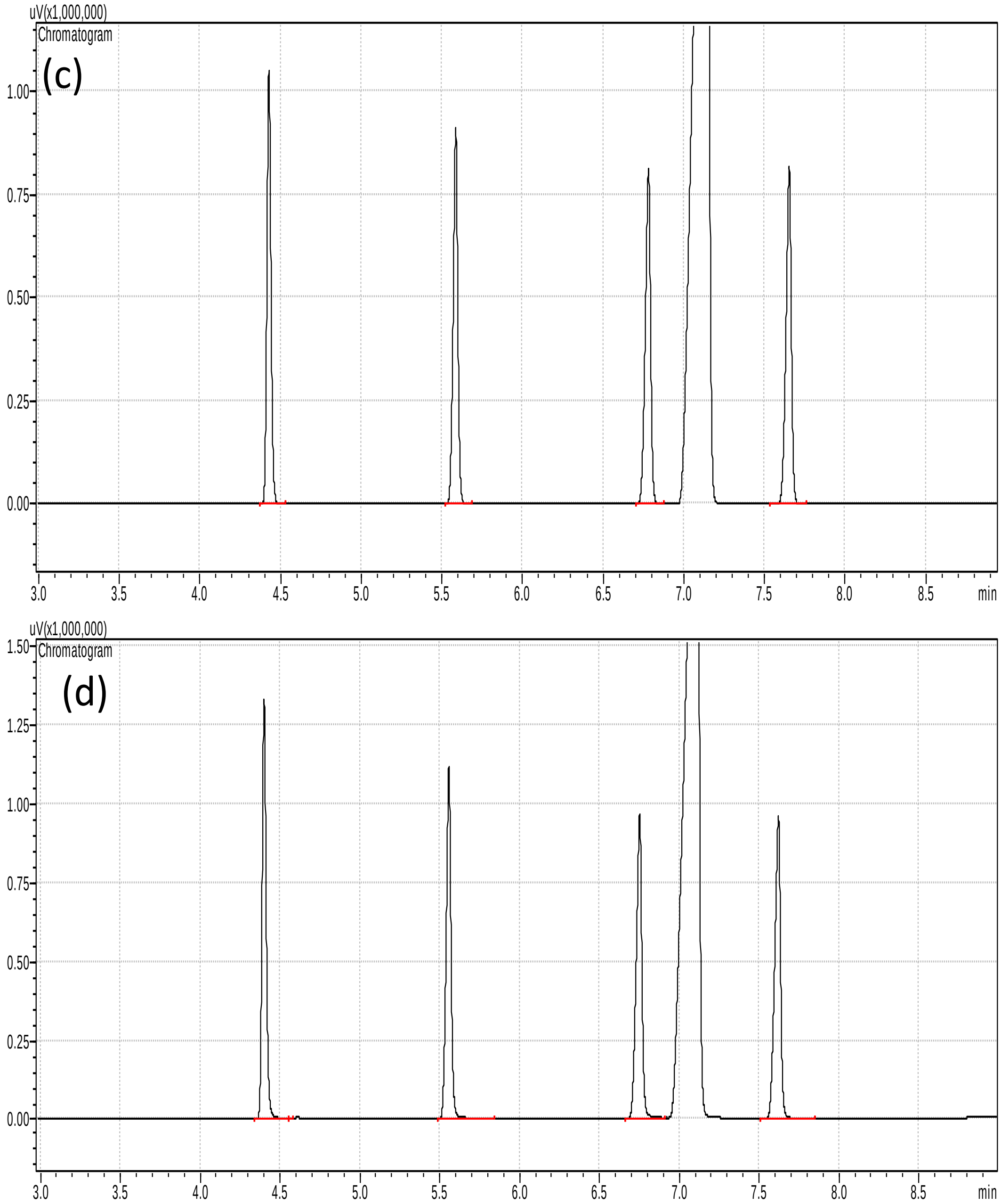
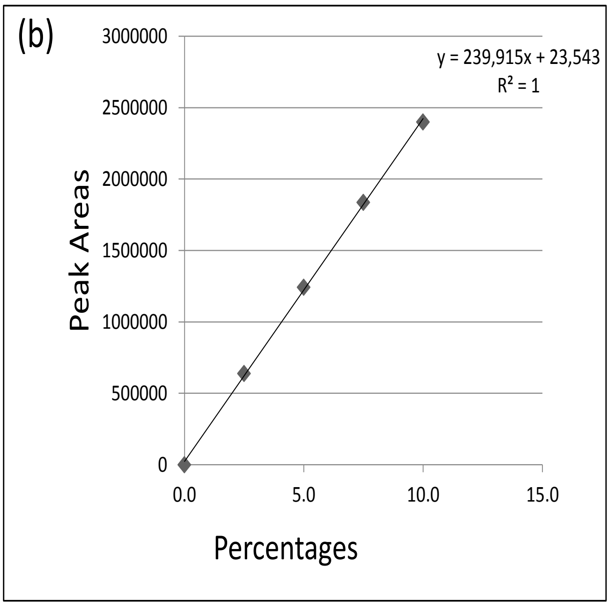


Figure 4.19: Chromatograms for the BTEX calibration standards in n-hexane (a) 2.5 % (v/v) (b) 5.0 % (v/v) (c) 7.5 % (v/v) (d) 10.0 % (v/v)

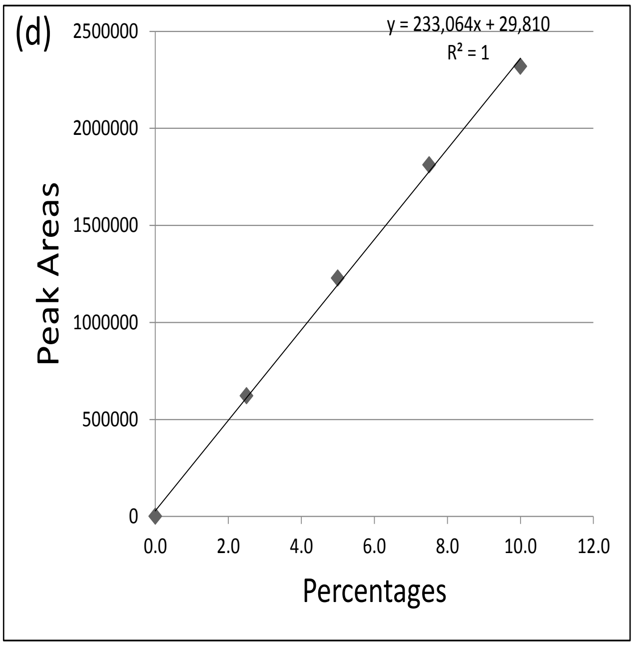
(a)

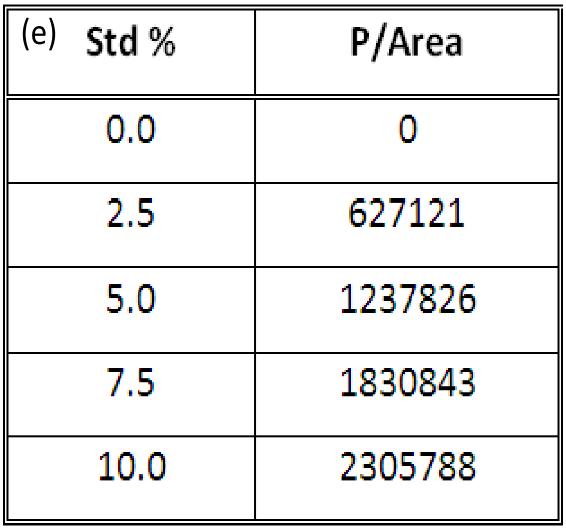
Std %	P/Area
0.0	0
2.5	637269
5.0	1242667
7.5	1836155
10.0	2399492



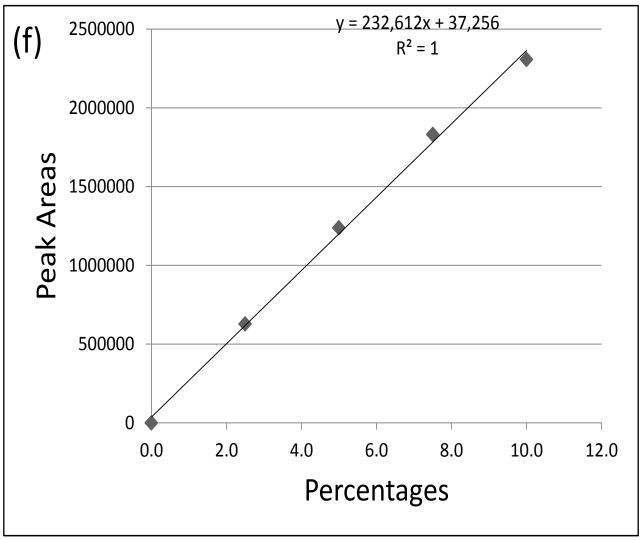
(c)

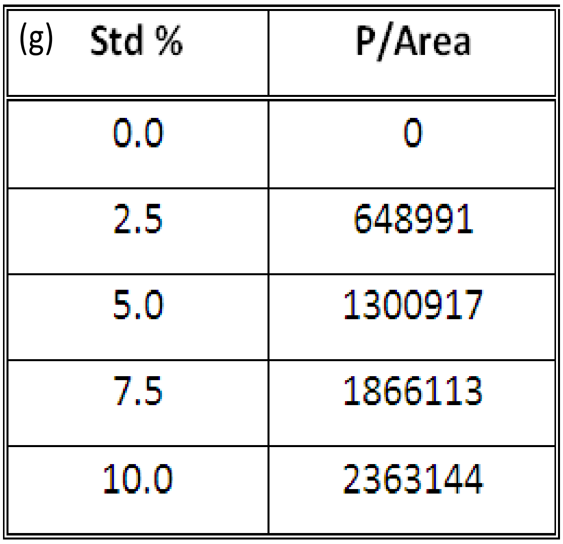
Std %	P/Area
0.0	0
2.5	620092
5.0	1227124
7.5	1810188
10.0	2318258





(e) Std %	P/Area
0.0	0
2.5	627121
5.0	1237826
7.5	1830843
10.0	2305788





(g) Std %	P/Area
0.0	0
2.5	648991
5.0	1300917
7.5	1866113
10.0	2363144

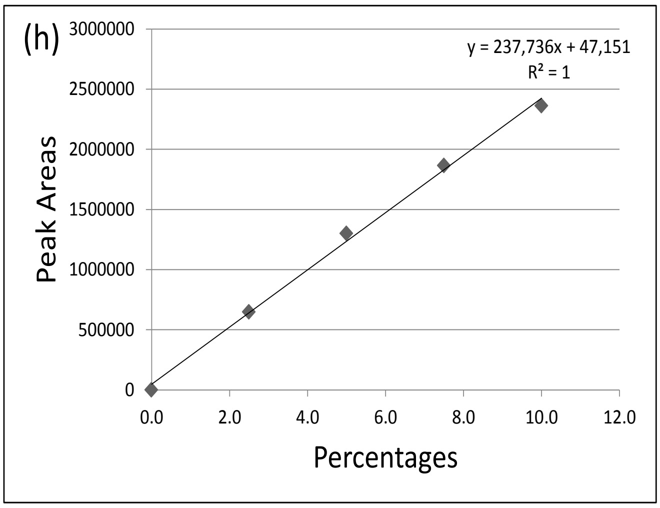
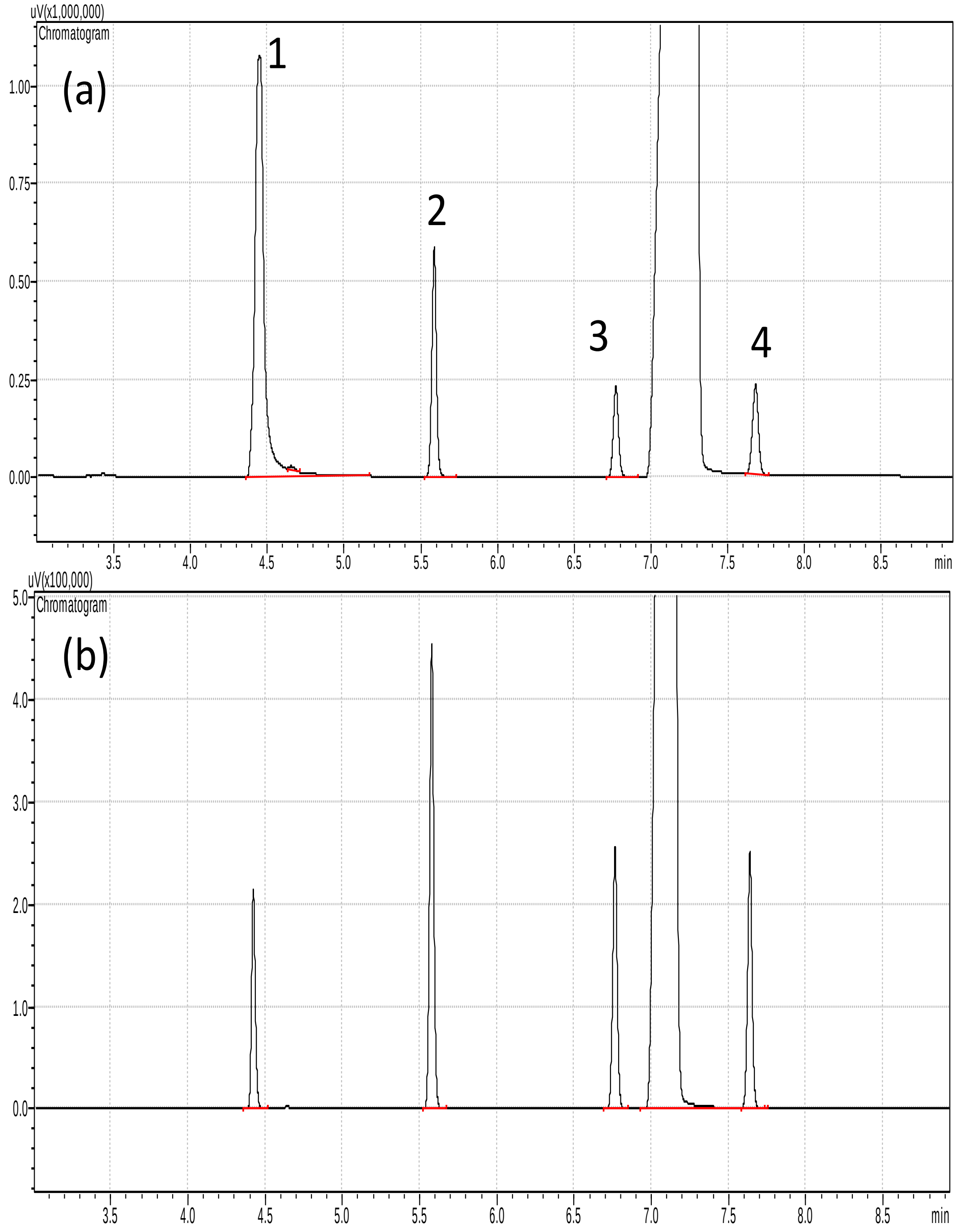
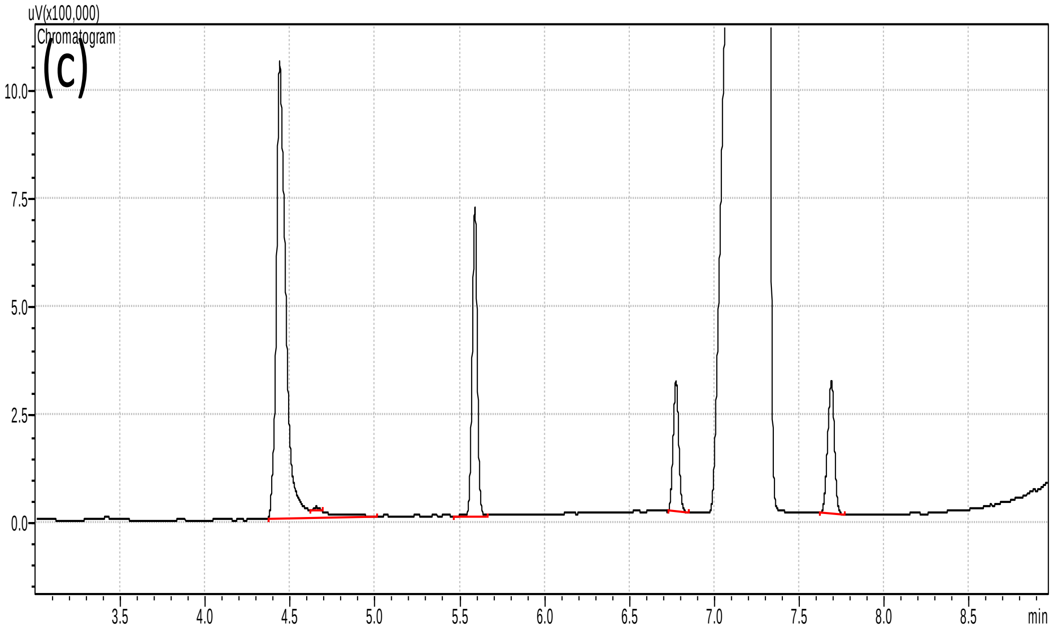
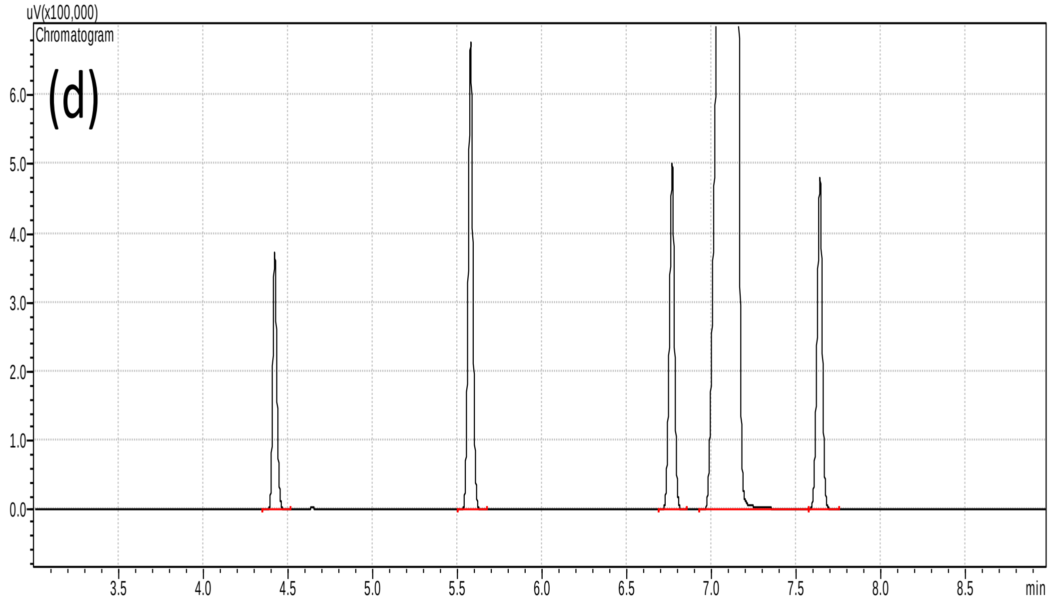
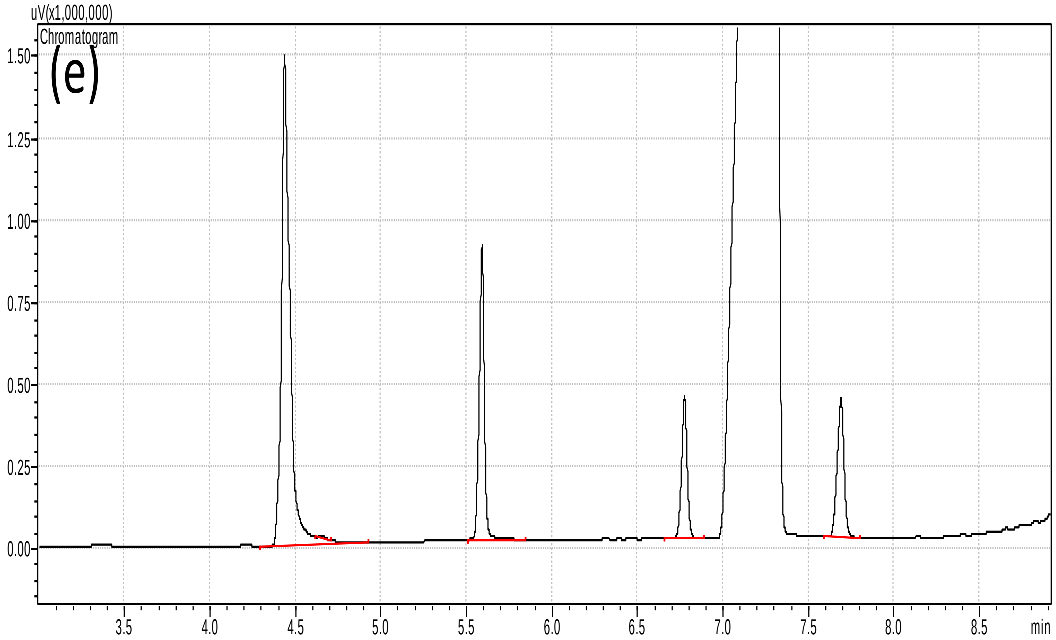


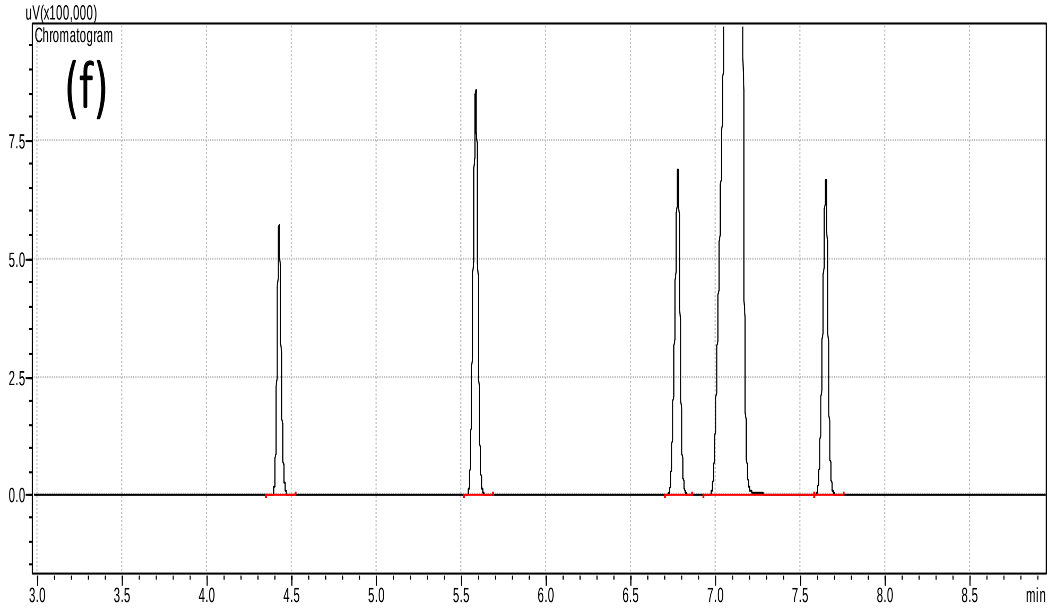
Figure 4.20: Peak areas and calibration curves of BTEX standards for the concentration range 2.5 – 10 % (v/v) using n-hexane as an alkane (a) Benzene peak areas (b) Benzene curve (c) Toluene peak areas (d) Toluene curve Toluene (e) E/Benzene peak areas (f) E/Benzene curve (g) o-Xylene peak areas (h) o-Xylene curve


uV(x1,000,000)
Chromatogram
(a)
1
2
3
4
1.00
0.75
0.50
0.25
0.00
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
min
uV(x100,000)
Chromatogram
(b)
5.0
4.0
3.0
2.0
1.0
0.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
min


uV(x100,000)
Chromatogram
(c)
10.0
7.5
5.0
2.5
0.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
min


uV(x100,000)
Chromatogram
(d)
6.0
5.0
4.0
3.0
2.0
1.0
0.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
min


uV(x1,000,000)
Chromatogram
(e)
1.50
1.25
1.00
0.75
0.50
0.25
0.00
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
min


uV(x100,000)
Chromatogram
(f)
7.5
5.0
2.5
0.0
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
min

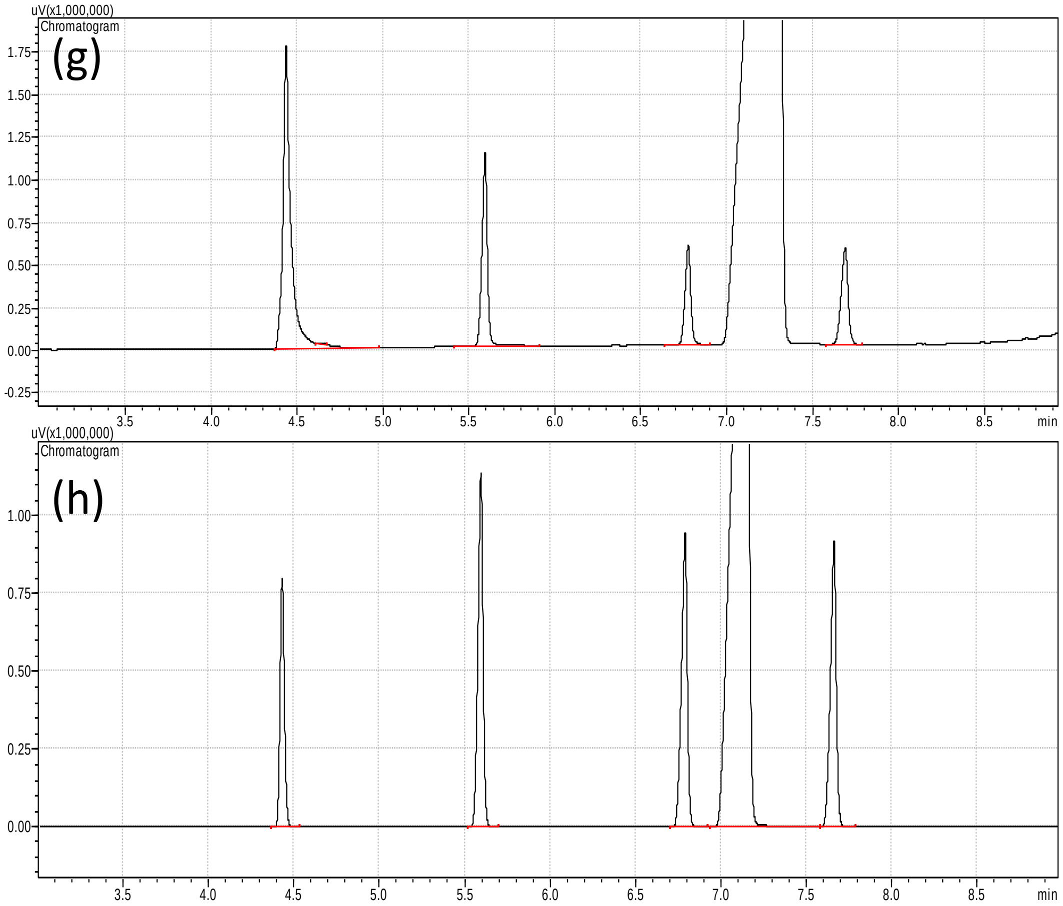


Figure 4.21: Chromatograms for BTEX extractions using [EMIM][ESO_4] and hexane: (a) 2.5 % (v/v) Extract phase, (b) 2.5 % (v/v) Raffinate phase, (c) 5 % (v/v) Extract phase, (d) 5 % (v/v) Raffinate phase (e) 7.5 % (v/v) Extract phase, (f) 7.5 % (v/v) Raffinate phase, (g) 10 % (v/v) Extract phase, (h) 10 % (v/v) Raffinate phase

The results of individual BTEX components for both the extract and raffinate phases obtained for the extraction of model mixtures containing benzene, toluene, ethylbenzene, and o-xylene (BTEX) in the concentration range 2.5 – 10 % (v/v) in n-hexane using 1-ethyl-3-methylpyridinium ethyl sulphate are given in Figure 4.25. These bar graphs show the amounts of individual aromatic components present in the extract and raffinate phases as well as their respective percentage recoveries. It is noticed from these tables that the average percentage of total recovery are: benzene, 116 % (v/v);

toluene, 120 % (v/v); ethylbenzene, 119 % (v/v); and o-xylene, 119 % (v/v). These values give an overall average recovery range of 116 – 120 % (v/v) for all BTEX components in this experiment. This range meets the design specifications which are typically 80 – 120 % mean percent recovery for any sample type.

Table 4.12: BTEX results from a 4 hour settling period using [EMpy][ESO4] and n-hexane

BTEX % (v/v)	Benzene % (v/v)			Toluene % (v/v)			Ethyl Benzene % (v/v)			o-Xylene % (v/v)		
	R	E	R+E	R	E	R+E	R	E	R+E	R	E	R+E
2.5	57	75	132	31	99	130	82	43	125	77	47	124
5.0	51	52	103	52	61	114	85	28	113	82	34	116
7.5	53	61	114	58	54	112	85	28	113	80	32	112
10.0	58	55	113	73	50	123	95	28	123	90	32	122

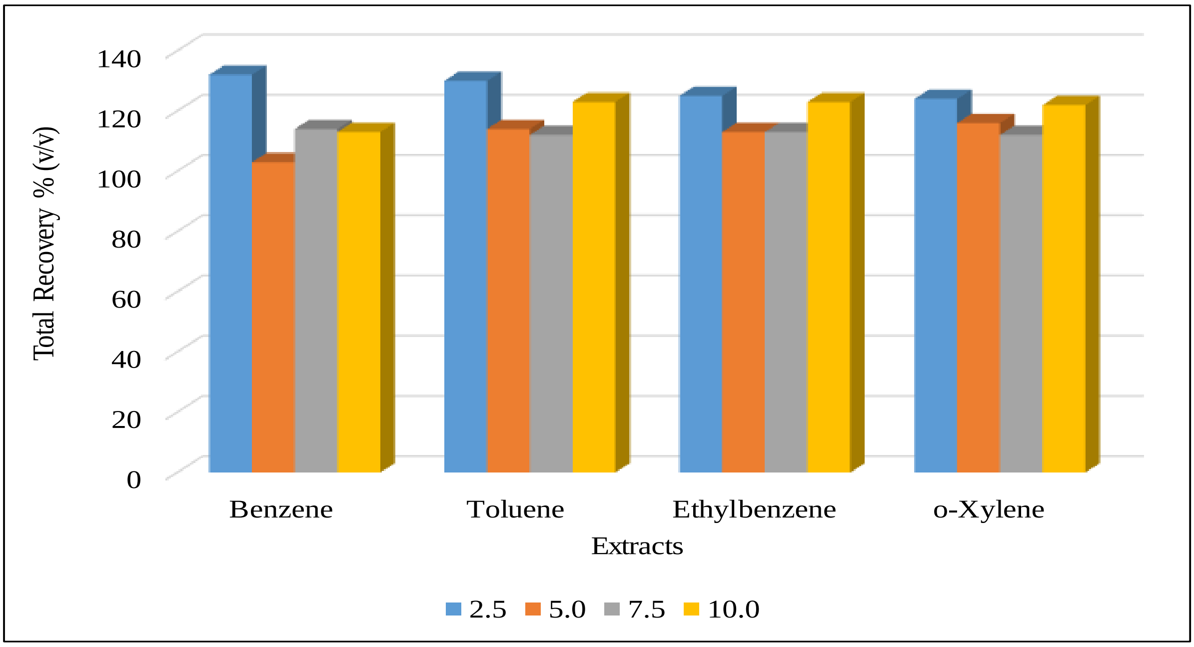


Figure 4.22: Bar graphs representing the extract results from 2.5 – 10.0 % (v/v) model mixtures using ionic liquid [EMpy][ESO4] as an extractive solvent.

The results obtained from a 4 hour phase settling period using 1-ethyl-3-methylpyridinium ethyl sulphate as an ionic liquid and n-hexane as an alkane are summarized in Table 4.10 for easy comparison and interpretation. The values are higher than those obtained for 1-ethyl-3-methylimidazolium ethyl sulphate under similar conditions. The results suggest that the BTEX solutes interact more strongly with [EMpy][ESO_4] than they do with the ionic liquid [EMIM][ESO_4]. This could be attributed to the fact that the former contains a six-membered ring cation whereas the latter has a five-membered ring cation. This phenomenon enhances the solubility of the BTEX components in 1-ethyl-3-methylpyridinium ethyl sulphate. The previous studies have shown that the ionic liquids containing the 1-ethyl-3- methylpyridinium cations have more aromatic character than the imidazolium-based ionic liquids which has relatively less π-character [130].

4.2.5 The effects of BTEX extraction stages using [EMIM][ESO_4] and [EMpy][ESO_4]

4.2.5.1 Overview

The establishment of the number of extraction cycles required for a complete recovery of aromatic components from alkane/aromatic mixtures was regarded as crucial for cost purposes. Such investigation was also envisaged as necessary in order to have a proper design for the BTEX extraction recovery plants. It is however not possible to perform many extraction stages on a laboratory scale due to small quantities of the sample mixtures used in the extraction processes. This limitation on a laboratory scale extraction processes necessitates the investigation of this using a pilot extraction plant involving larger quantities of samples. In the laboratory scale, the sample mixture is re-extracted several times using regenerated ionic liquids for each repeated extraction. On the other hand, the pilot plant would be expected to perform such extractions on the basis of successive stages. In this way, the plant is expected to be capable of carrying out a larger number of extraction stages than the laboratory infrastructure can achieve.

It was established that in order to achieve a toluene recovery of at least 98%, the number of extraction stages must be higher than six. The number of equilibrium stages (Ns) was determined as a function of the rotating speed of the disc contactor in his pilot-plant extraction experiments [62,86]. Some of their ionic liquids were better in terms of distribution coefficients but having lower selectivity. For example, 4-methyl-N-butylpyridinium tetrafluoroborate with 10 % (v/v) toluene/heptane mixture (D = 0.51, S = 45.5) whereas [EMIM][ESO$_4$] (D = 0.22, S = 50.5) and [EMpy][ESO$_4$] (D = 0.31 , S = 54.2) [30].

4.2.5.2 BTEX+[EMIM][ESO$_4$]/EMpy][ESO$_4$]+ n-Hexane

The effects of the number of extraction stages were tested on model mixtures containing 5 and 10 % (v/v) aromatic components in n-hexane as an alkane. The results obtained for three stages of extractions are shown in Table 4.13 using both the imidazolium-based and pyridinium-based ionic liquids.

Table 4.13: Summary of extract phase results showing the effects of the number of extraction stages for BTEX separation

Extract Stages 5 %	**[EMIM][ESO$_4$] for BTEX % (v/v)**				**[EMpy][ESO$_4$] for BTEX % (v/v)**			
	Benzene	Toluene	E/Benzene	o-Xylene	Benzene	Toluene	E/Benzene	o-Xylene
First	21	25	10	12	52	61	28	34
Second	12	21	7	8	25	27	11	12
Third	12	21	8	8	25	27	11	12
Total	45	67	25	28	102	115	50	58
Extract Stages 10 %	**[EMIM][ESO$_4$] for BTEX % (v/v)**				**[EMpy][ESO$_4$] for BTEX % (v/v)**			
	Benzene	Toluene	E/Benzene	o-Xylene	Benzene	Toluene	E/Benzene	o-Xylene
First	19	24	9	10	55	54	29	33
Second	18	13	8	9	20	26	10	11
Third	15	12	9	10	20	25	10	11
Total	52	49	26	29	95	115	49	55

The results in Table 4.13 indicate that the recovery of the BTEX components can be improved by increasing the number of extraction stages. For both ionic liquids, the first stage recovery values are higher than those obtained in the second and third stages. It can be seen that the second and third stages achieve almost similar results. In both 5 and 10 % (v/v) model mixtures, toluene showed higher percentage recovery than other components and its three stage total recovery reaches 67 and 49 %, respectively.

4.3 Extraction of BTEX using new ionic liquids

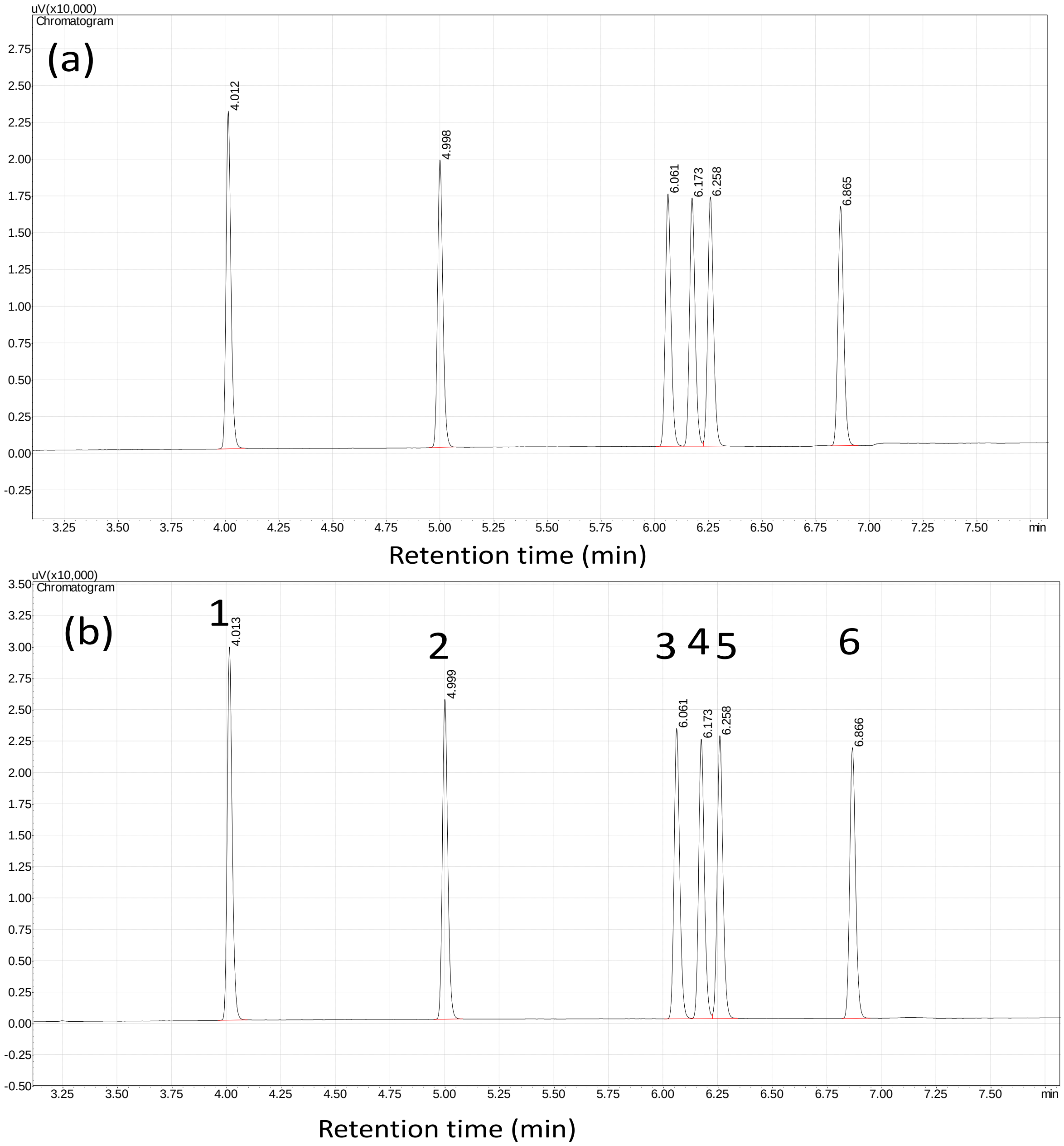
4.3.1 Introduction

The new ionic liquids 1-butyl-1-methyl-2-pyrrolidonium bromide [BNMP][Br] and 1, 1- dimethyl-2-pyrrolidonium iodide[MNMP][I] were used to extract the components of BTEX from aromatic/aliphatic mixtures. These ionic liquids were investigated in the extraction of six BTEX components (benzene, toluene, ethylbenzene, p-xylene, m-xylene, and o-xylene) from (1) model mixtures (0.5 and 10 % (v/v), (2) reformate samples, and (3) spent solvent samples [73]. According to Table 4.23 the extraction results obtained from the new ILs used in this project were generally comparable to those of imidazolium- and pyridinium-based ILs. However, [EMpy][ESO_4] showed highest values for benzene and toluene whilst [BNMP][Br] offered highest values for ethylbenzene and xylene isomers, followed by [MNMP][I].

4.3.2 Calibration of GC-FID by Model Mixtures

The instrument was calibrated using BTEX model mixtures in the concentration range 2.5 – 10 % (v/v) from which the respective calibration curves were constructed. These mixtures were subsequently employed to model the extraction of aromatic components by ionic liquids. The relationship between the concentrations and peak areas of aromatic components were deduced from GC chromatograms in Figure 4.23. (See also Appendix 4, Figs. 7.29 – 7.32). The corresponding peak areas and calibration curves are shown in Figure 4.24.

It can be notice from the chromatograms in Figure 4.23 that the retention times for the components in the mixtures have become shorter than those for the chromatograms in Figure 4.19. This phenomenon was due to the cutting-off the contaminated ends of the analytical column which resulted in the shorter retention times of the components in the Figure 4.23 than in the Figure 4.19. However, the separation of aromatic components was not affected by the shortening of the analytical column length.



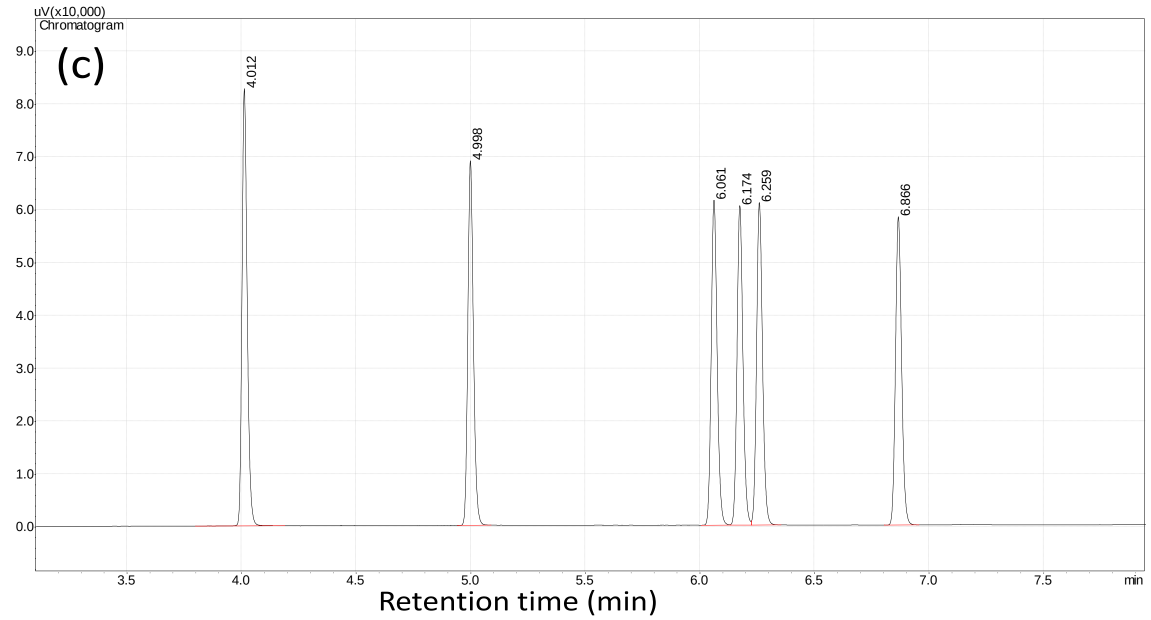
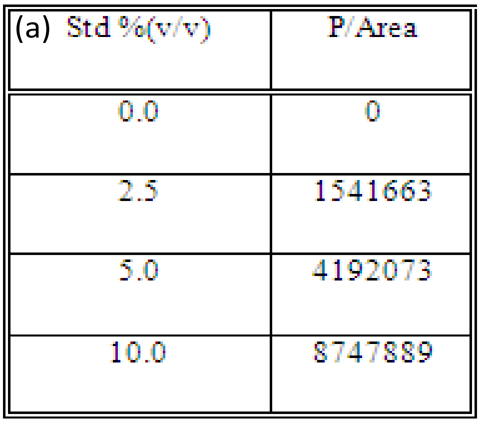
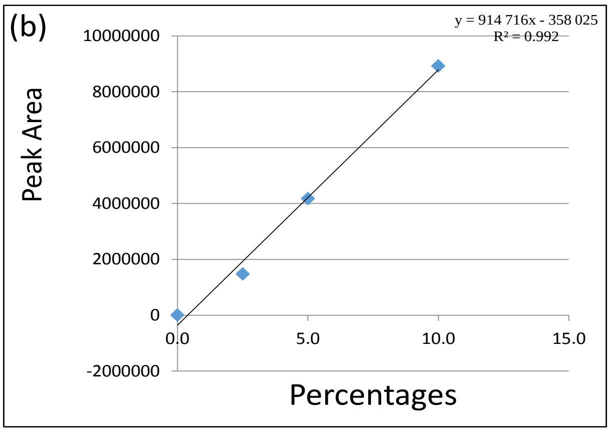
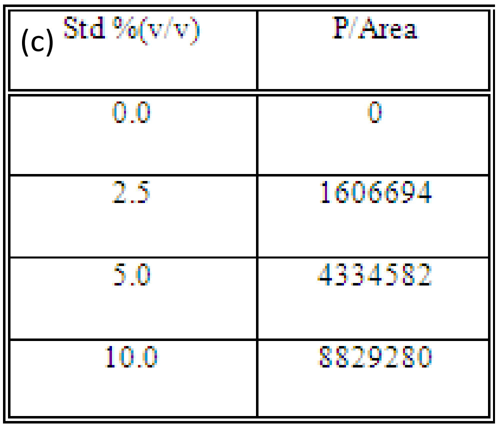


Figure 4.23: Chromatograms for BTEX model mixtures (a) 2.5 % (v/v) (b) 5 % (v/v) (c) 10 % (v/v) where 1 = benzene, 2 = toluene, 3 = ethylbenzene, 4 = p-xylene, 5 = m-xylene, and 6 = o-xylene.

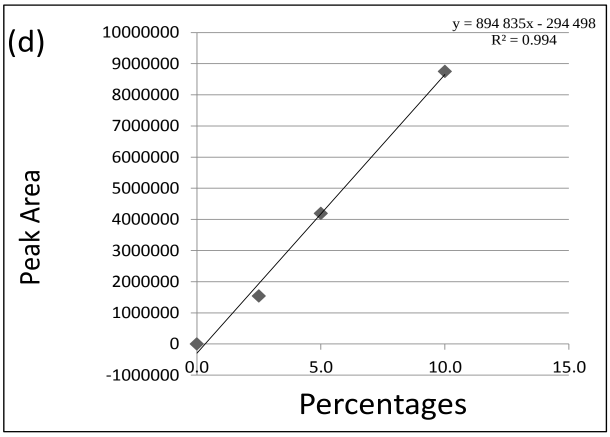


(a) Std %(v/v)	P/Area
0.0	0
2.5	1541663
5.0	4192073
10.0	8747889

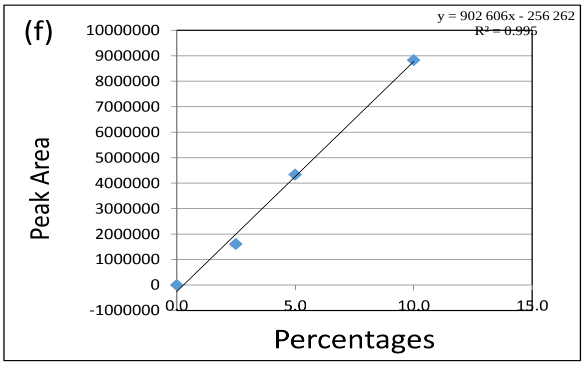




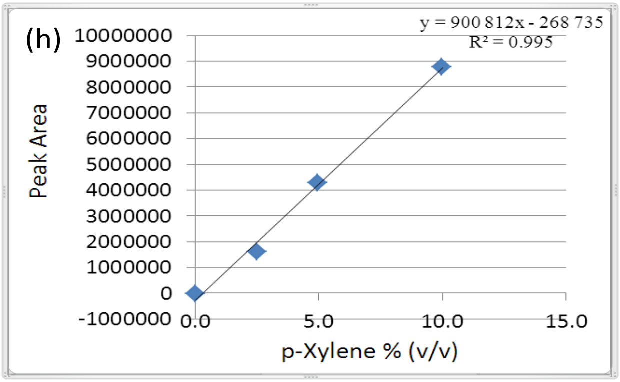
(c) Std %(v/v)	P/Area
0.0	0
2.5	1606694
5.0	4334582
10.0	8829280



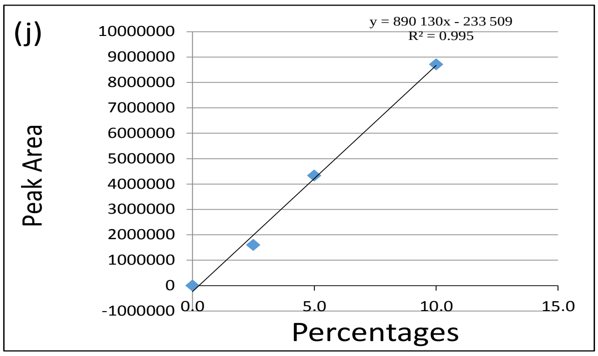
(e) Std %(v/v)	P/Area
0.0	0
2.5	1588118
5.0	4290621
10.0	8810532



(g) Std %(v/v)	P/Area
0.0	0
2.5	1588118
5.0	4290621
10.0	8810532



(i) Std %(v/v)	P/Area
0.0	0
2.5	1603054
5.0	4333265
10.0	8706919



(k) Std %(v/v)	P/Area
0.0	0
2.5	1629486
5.0	4405452
10.0	8930049

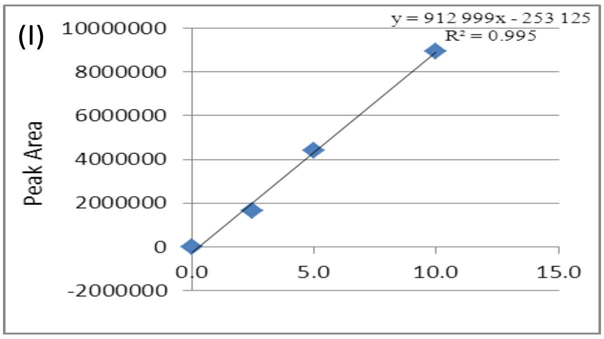
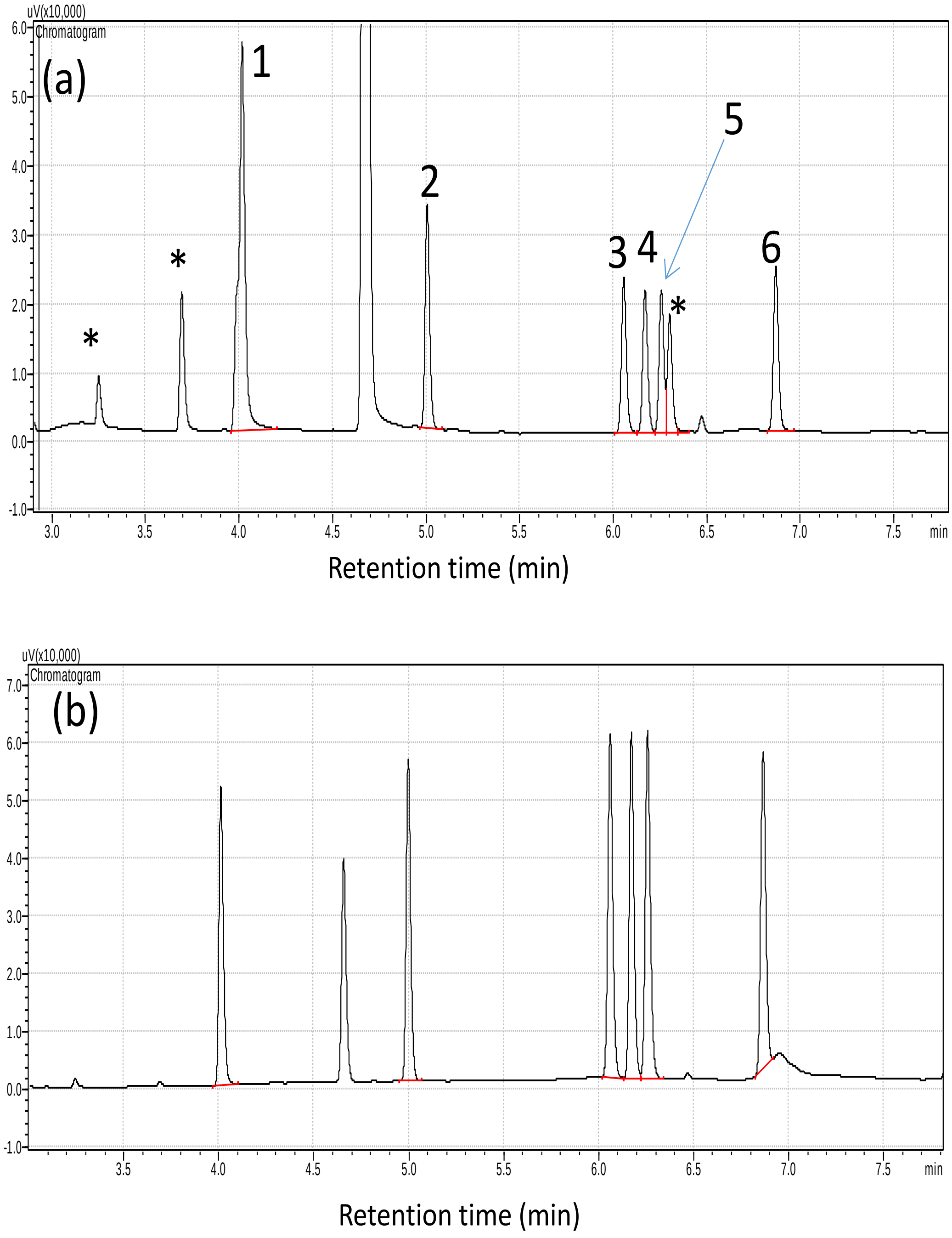


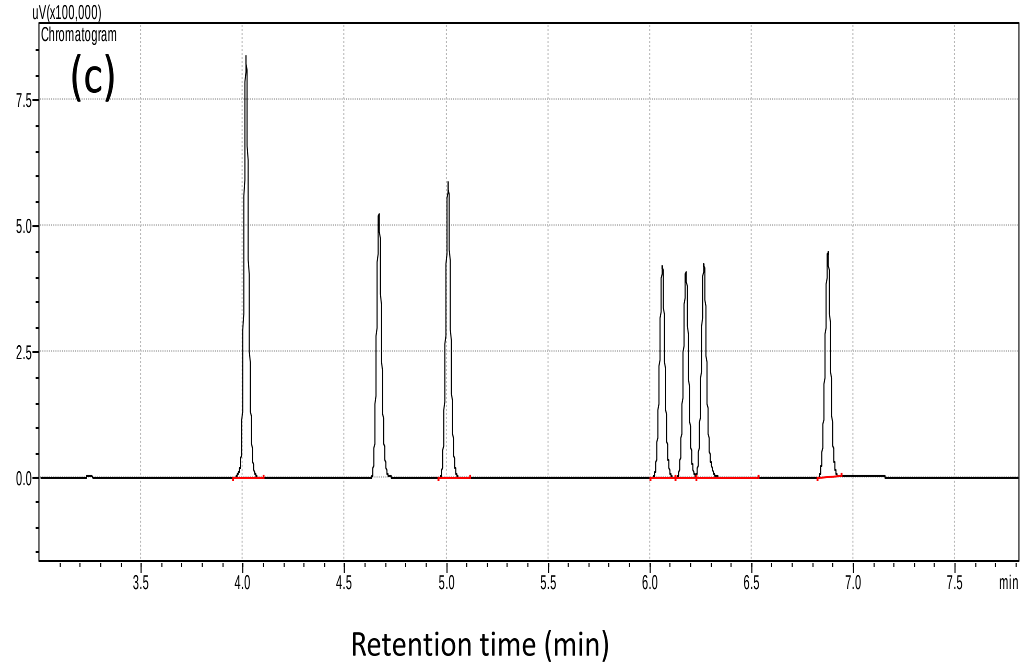
Figure 4.24: Peak areas and calibration curves of 2.5 – 10 % (v/v) BTEX standards (a) and (b) benzene (c) and (d) toluene (e) and (f) ethylbenzene (g) and (h) p-xylene (i) and (j) m-xylene (k) and (l) o-xylene

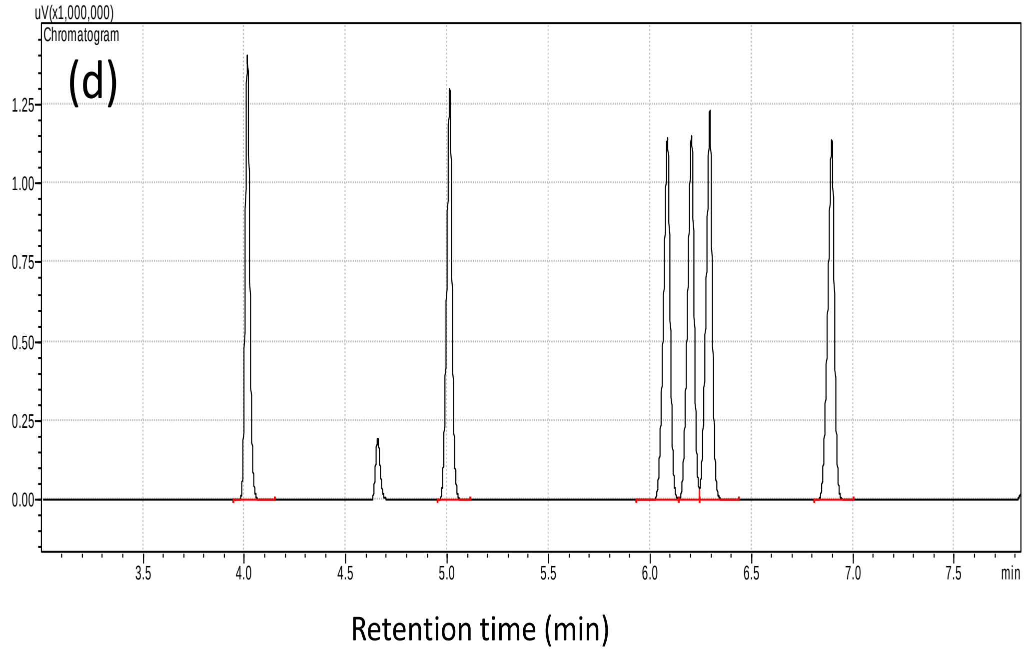
4.3.3 Extractions of Model Mixtures by [BNMP][Br] and [MNMP][I]

The chromatograms of the extract and raffinate phases for 0.5 and 10 % (v/v) BTEX components in the model mixtures using 1-butyl-1-methyl-2-pyrrolidonium bromide [BNMP][Br] for a 3-hour optimal extraction period at 40°C are shown in Figure 4.25. (See also Appendix 4, Figures A7.28 – 7.29 and A7.33 – 7.34). The chromatogram in Figure 4.25 (a) shows four visible impurities (indicated by *) with retention times (mins) 3.25, 3.70, 4.68, and 6.35, respectively. It can be noticed that there is only one visible impurity appearing at 4.68 mins in Figures 4.25 (b), 4.25 (c), and 4.25 (d) for which its size decreases gradually with concentration of BTEX model mixtures. It also appears that the raffinate phase of each mixture contains significantly smaller impurity than the extract phase. This suggests that these impurities came from the ionic liquid since the raffinate phase contains very little ionic liquid. It can also be seen in these chromatograms that all BTEX components were well resolved with reasonable baseline.

The ability of the new ionic liquids 1-butyl-1-methyl-2-pyrrolidonium bromide [BNMP][Br] and 1, 1- dimethyl-2-pyrrolidonium iodide[MNMP][I] were first tested in the model mixtures containing 0.5 and 10 % (v/v) of individual components of BTEX. The extraction results of percentages recovery for each ionic liquid are summarized and presented in Table 4.14. In all cases, the extract phases indicate almost similar trends of results whereas the raffinate phases of a 0.5 % (v/v) model mixture show relatively lower values of BTEX components. Consequently, the total recovery values of a 0.5 % (v/v) are relatively lower (av. 85 %) than those of 10 % (v/v) mixtures (av. 100 %). Overall results for both ionic liquids show no significant difference between their extraction values. (Also see Appendix 3, Tables A7.3).




uV(x100,000)
Chromatogram
(c)
7.5
5.0
2.5
0.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
min
Retention time (min)


uV(x1,000,000)
Chromatogram
(d)
1.25
1.00
0.75
0.50
0.25
0.00
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
min
Retention time (min)

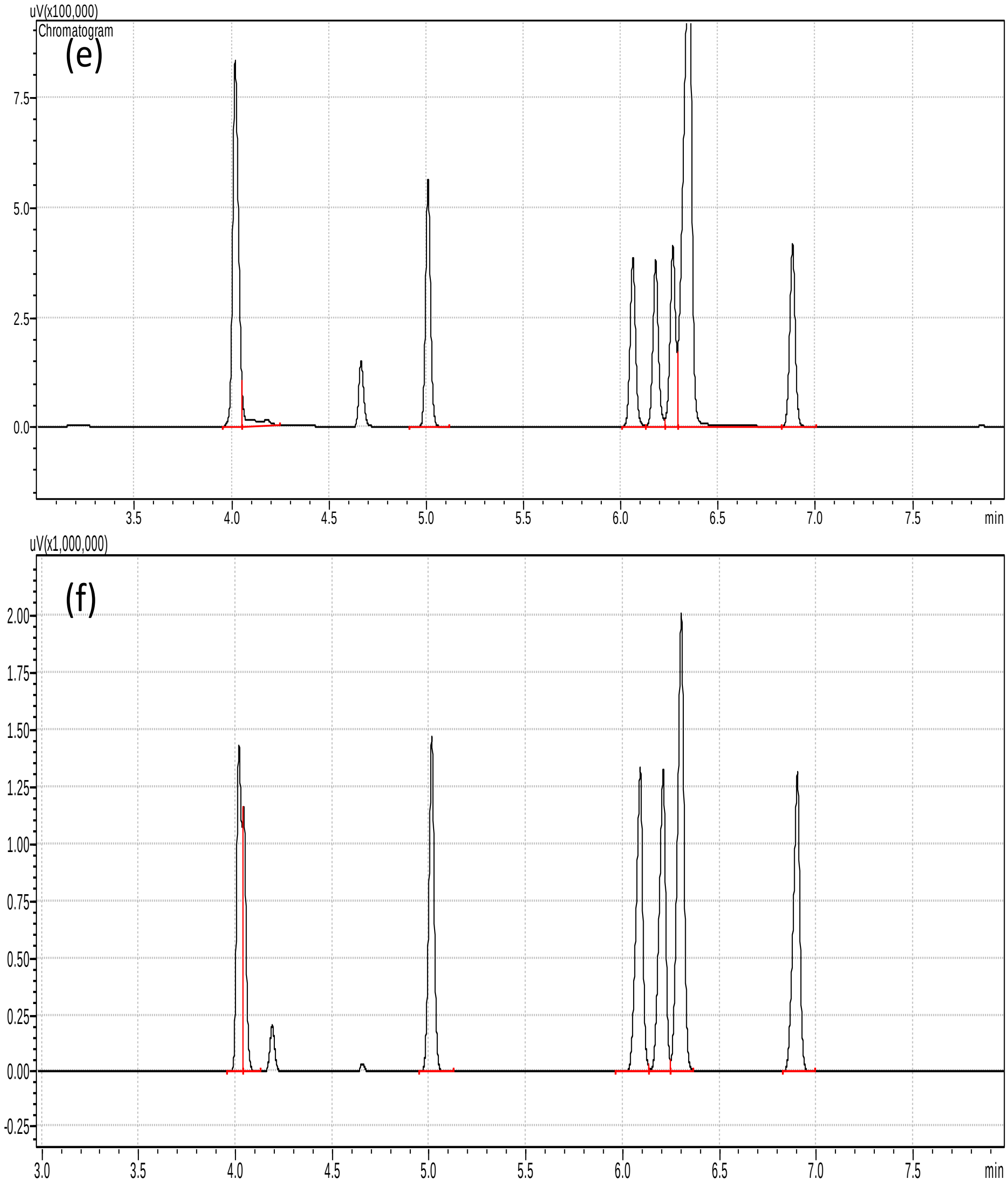


Figure 4.25: Chromatograms for the components of six BTEX extracted by [MNMP][I] (a) 0.5 % (v/v) Extract phase (b) 0.5 % (v/v) Raffinate phase; [BNMP][Br] (c) 10 % (v/v) Extract phase (d) 10 % (v/v) Raffinate phase; [MNMP][I] (e) 10 % (v/v) Extract phase (f) 10 % (v/v) Raffinate phase where 1 = Benzene, 2 = Toluene, 3 = Ethylbenzene, 4 = p-Xylene, 5 = m-Xylene, 6 = o-Xylene, * = impurities in ionic liquids

Table 4.14: Summary of results for BTEX recovery from model mixtures

Standards % (v/v)	**Recovery of BTEX from the model mixtures %volume using [BNMP][Br]**						
	Phases	**Benzene**	**Toluene**	**E/ Benzene**	**p-Xylene**	**m-Xylene**	**o-Xylene**
0.5	E	40	31	23	21	21	24
	R	47	53	59	60	63	56
	R + E	**87**	**84**	**82**	**81**	**84**	**80**
10.0	E	38	29	22	22	23	24
	R	62	69	73	73	74	71
	R + E	**100**	**98**	**95**	**95**	**97**	**95**
	Recovery of BTEX from the model mixtures /%volume using [MNMP][I]						
10.0	E	48	28	21	21	22	22
	R	57	79	88	88	86	84
	R + E	**105**	**107**	**109**	**109**	**108**	**106**

The reasonable extract values obtained from both ionic liquids could be explained in terms of the nature of interactions between ionic liquids and BTEX molecules. Cations of ionic liquids interact strongly with pi electrons of aromatic rings through cation-π interactions. There are also π-π interactions strong interactions occurring between pi electrons of ionic liquids and aromatic π electrons through aromatic characters. Pyrrolidonium-based ionic liquids contain highly polarizable anions (Br^- and I^-), hence they can interact strongly with aromatic molecules. The presence of the carbonyl groups (-C=O) in both ionic liquids provides additional π-π interactions with aromatic hydrocarbons. On the basis that the π-systems of the substituted benzenes interact well with the π-systems of both ionic liquids, confirms the presence of the carbonyl group in both ionic liquids; hence these ionic liquids are expected to give very similar results for extraction processes.

The values shown in Table 4.14 are based on the concentrations of respective BTEX model mixtures against the values obtained from the extract phases. (See Appendix 4, Table A7.3). As the tables indicate, these results reveal a general increase in percentages extracted in the following order: p-xylene< m-xylene <ethylbenzene< o-xylene < toluene < benzene. This observation is rationalized as follows: Benzene is the smallest molecule with the least steric hindrance and strongest π-systems. The BTEX molecules, which have methyl groups, are sterically hindered in their interactions with the ionic liquids. Further it appears that the electron withdrawing property of methyl groups lead to relatively weaker π-systems.

4.3.4 Extraction of BTEX from reformates

4.3.4.1 4.3.4.1 Analysis of BTEX in reformates

Samples of reformates sourced from Engen Oil Refinery, South Africa, were analyzed for BTEX using a Gas Chromatograph (GC) fitted with Flame Ionization Detector (FID). The results obtained were compared with results from literature [102] as well as those from independent source [5]. This analysis was performed as a means of validating the reliability of the analytical method. The experimental and reported values for the concentration of individual aromatic components (BTEX) in reformates are shown in Table 4.15. The chromatograms depicted in Figure 4.26 (a) which shows both aliphatic and aromatic component peaks and Figure 4.26 (b) showing only aromatic component peaks. (See also Appendix 4, Figs A7.24 – 7.26).

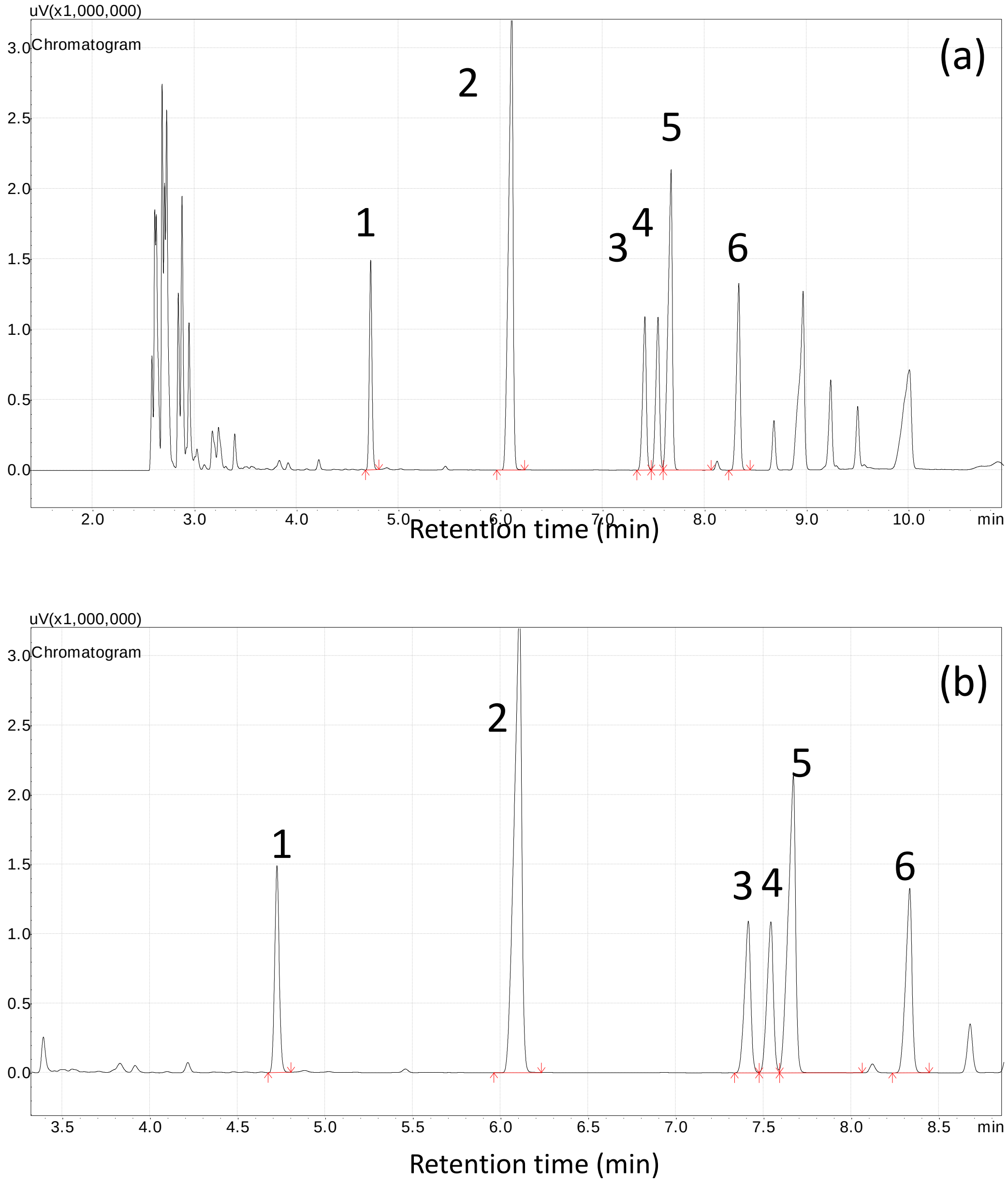


Figure 4.26: Chromatograms for the results in the reformate samples showing: (a) Both aliphatic and aromatic components (b) Only aromatic components where 1= Benzene 2 = Toluene 3 = Ethylbenzene 4 = p-Xylene 5 = m-Xylene 6 = o-Xylene

Table 4.15: Results showing the concentration of BTEX in the reformate samples

BTEX % (v/v)	Concentration of BTEX in the reformate samples % (v/v)						
	Benzene	Toluene	E/ Benzene	p-Xylene	m-Xylene	o-Xylene	Total
2.5	3.6	13.7	3.5	3.6	8.2	4.3	37
10.0	3.9	14.3	3.6	3.7	8.5	4.5	39
Averages	3.7	14.0	3.6	3.7	8.3	4.4	38
	3.7	14.0	20.0				38
Engen [5]	3.8	13.3	21.1				38
Lit. [103]	3.4	14.9	20.0				38
Averages	3.6	14.1	20.5				37

4.3.4.2 Analysis of the reformate replicates

Replicate analysis of reformate samples were carried out so that the variability associated with the measurements could be estimated. In this study, each replicate comprises eight samples which were all analyzed on one day. The chromatograms of nine replicate samples are shown in Appendix 5, Figs. A7.35 – 7.44). The replicate batches were analyzed over a period of one month. The random samples were obtained from the same industry to ensure true representation of the underlying phenomenon being investigated. The results of the four reformate replicates are presented in Table 4.16 which shows eight samples analyzed per replicate batch. For a given sample of eight measurements, the sample average, sample standard deviation (s), standard error of the mean, and relative standard deviation (RSD) are determined for each component of BTEX.

Table 4.16: Statistical results obtained from replicates of reformate samples

Statistical data of replicate 1 (n = 8)						
Sample	**Benzene/%**	**Toluene/%**	**E/Benzene/%**	**p-Xylene/%**	**m-Xylene/%**	**o-Xylene/%**
1	3.87	14.67	3.86	3.89	8.79	3.98
2	3.42	12.94	3.31	3.39	7.74	4.22
3	3.64	13.71	3.52	3.59	8.19	4.38
4	3.86	14.26	3.65	3.73	8.49	5.11
5	4.69	17.49	4.50	4.59	10.62	4.60
6	4.05	15.03	3.83	3.91	8.93	5.14
7	4.45	16.73	4.37	4.40	10.02	5.14
8	3.91	14.58	3.85	3.78	8.61	4.39
Mean 1	3.98	14.93	3.86	3.91	8.93	4.62
SD	0.41	1.51	0.40	0.40	0.95	0.46
Mean Error	0.14	0.53	0.14	0.14	0.34	0.16
RSD	10.3	10.1	10.4	10.3	10.6	9.9
Statistical data of replicate 2 (n = 8)						
Sample	**Benzene/%**	**Toluene/%**	**E/Benzene/%**	**p-Xylene/%**	**m-Xylene/%**	**o-Xylene/%**
1	3.40	12.95	3.24	3.25	7.71	3.92
2	3.00	11.4	2.74	2.80	6.77	3.39
3	3.20	12.09	2.93	2.98	7.17	3.61
4	3.39	12.59	3.05	3.11	7.45	3.75
5	4.12	15.49	3.81	3.88	9.36	4.42
6	3.56	13.28	3.21	3.27	7.83	3.95
7	3.92	14.81	3.70	3.70	8.81	4.44
8	3.44	12.87	3.23	3.15	7.55	3.76
Mean	3.50	13.18	3.24	3.27	7.83	3.91
SD	0.36	1.35	0.36	0.36	0.85	0.37
Mean Error	0.13	0.48	0.13	0.13	0.30	0.13
RSD	10.4	10.3	11.2	11	10.9	9.4

Statistical data of replicate 3 (n = 8)						
Sample	**Benzene/%**	**Toluene/%**	**E/Benzene/%**	**p-Xylene/%**	**m-Xylene/%**	**o-Xylene/%**
1	3.56	12.72	3.35	3.35	7.54	4.00
2	3.16	11.23	2.88	2.92	6.65	3.49
3	3.36	11.89	3.05	3.09	7.03	3.71
4	3.55	12.37	3.17	3.21	7.29	3.84
5	4.29	15.17	3.90	3.95	9.10	4.48
6	3.72	13.04	3.32	3.36	7.66	4.03
7	4.08	14.51	3.79	3.78	8.58	4.50
8	3.60	12.64	3.34	3.25	7.39	3.85
Mean	3.66	12.95	3.35	3.37	7.65	3.99
SD	0.37	1.31	0.35	0.34	0.81	0.35
Mean Error	0.13	0.46	0.12	0.12	0.29	0.12
RSD	10.0	10.1	10.4	10.2	10.5	8.8
Statistical data of replicate 4 (n = 8)						
Sample	**Benzene/%**	**Toluene/%**	**E/Benzene/%**	**p-Xylene/%**	**m-Xylene/%**	**o-Xylene/%**
1	3.05	11.52	3.16	3.16	7.10	3.85
2	2.73	10.17	2.71	2.76	6.26	3.36
3	2.89	10.77	2.88	2.92	6.62	3.56
4	3.05	11.20	2.99	3.03	6.86	3.69
5	3.64	13.74	3.67	3.73	8.56	4.30
6	3.18	11.81	3.13	3.17	7.21	3.87
7	3.47	13.14	3.57	3.57	8.07	4.32
8	3.08	11.45	3.15	3.07	6.95	3.70
Mean	3.14	11.73	3.16	3.18	7.20	3.83
SD	0.29	1.18	0.33	0.32	0.76	0.34
Mean Error	0.10	0.42	0.12	0.11	0.27	0.12
RSD	9.4	10.1	10.3	10.1	10.5	8.8

The results in Table 16 show that the average relative standard deviation (about 10%) of BTEX components in all replicate samples were found to be within an acceptable value of <20%. The values indicate that RSD obtained from replicates is within the acceptable range and that the replicates are repeatable with good precision.

4.3.4.3 Determination of LOD and LOQ from calibration curves

The values of Limit of detection (LOD) and limit of limit of quantification (LOQ) shown in Table 4.17 were determined from the calibration curves according to the formulae:

$$\text{LOD} = 3(S_y/m) \quad \text{and} \quad \text{LOQ} = 10(S_y/m)$$

S_y and m values in Table 4.17were obtained from LINEST function using MS Excel.

Table 4.17: LOD and LOQ values of BTEX calculated by LINEST function

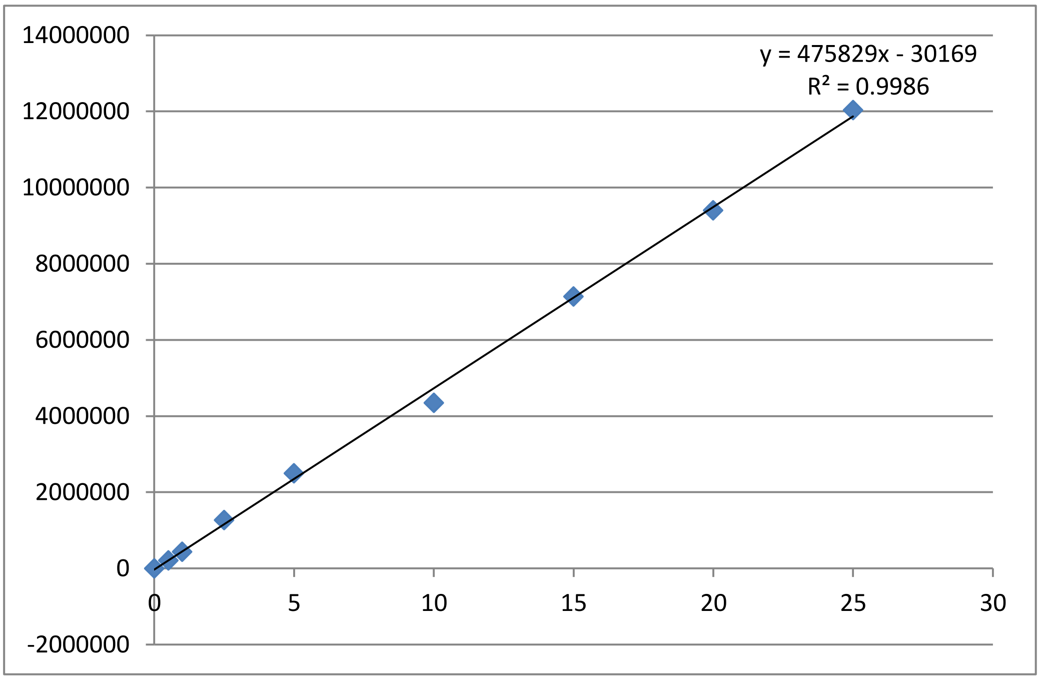
Benzene/%	P/Area	LINEST function				LOD	LOQ
0.0	0	Slope, m	229286	-9635.8	y-intercept, b		
2.5	558806	SD of m, Sm	3572.90276	21879	SD of b, Sy	**0.29**	**0.95**
5.0	1106865	R^2	0.99927207	28246	SD of regression, Sr		
7.5	1745653	F-statisctic	4118.2627	3	Degree of freedom, F		
10.0	2272656	SSregr	3.2858E+12	2.39E+09	SSresid		

Toluene/%	P/Area	LINEST FUNCTION				LOD	LOQ
0.0	0	Slope, m	220278	-14194.8	y-intercept, b		
2.5	530596	SD of m, Sm	3387.10768	20742	SD of b, Sy	**0.28**	**0.94**
5.0	1053671	R^2	0.99929119	26777	SD of regression, Sr		
7.5	1665878	F-statisctic	4229.46261	3	Degree of freedom, F		
10.0	2185837	SSregr	3.0327E+12	2.15E+09	SSresid		

E/Benzene/%	P/Area	LINEST FUNCTION				LOD	LOQ
0.0	0	Slope, m	221881	-25455	y-intercept, b		
2.5	522505	SD of m, Sm	4132.88843	25309	SD of b, Sy	**0.34**	**1.14**
5.0	1037949	R^2	0.99896023	32673	SD of regression, Sr		
7.5	1649056	F-statisctic	2882.25185	3	Degree of freedom, F		
10.0	2210234	SSregr	3.0769E+12	3.2E+09	SSresid		

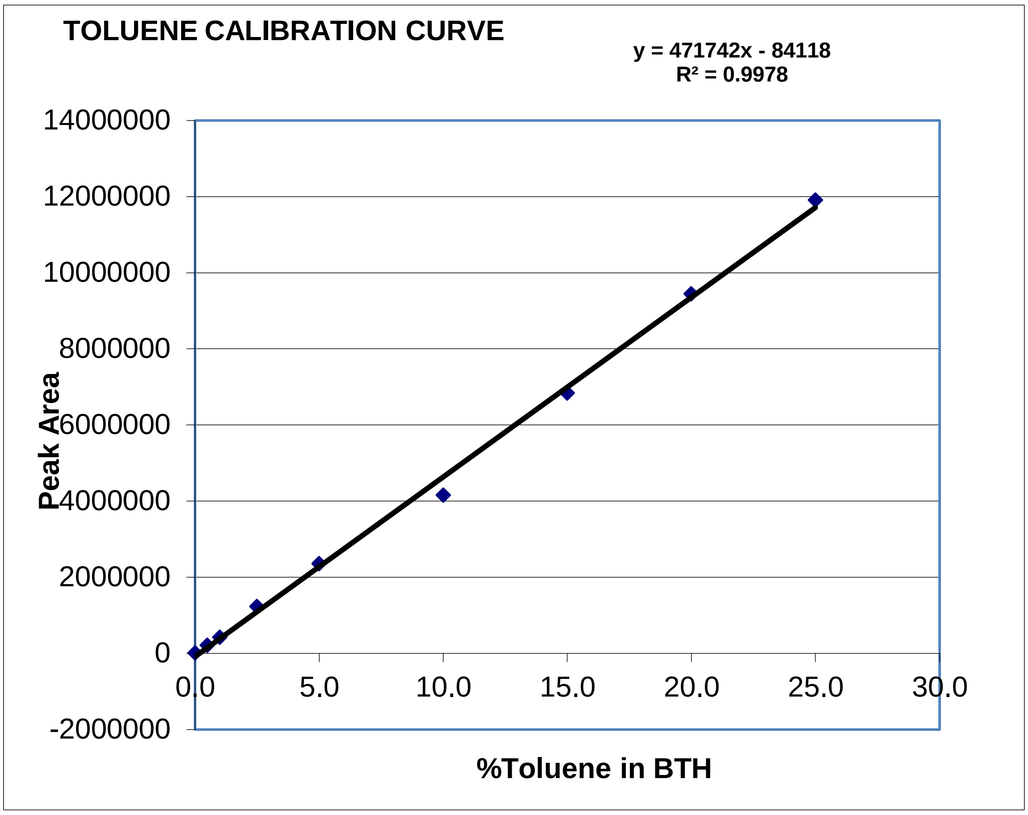
o-Xylene/%	P/Area	LINEST FUNCTION				LOD	LOQ
0.0	0	Slope, m	263155	-43523	y-intercept, b		
2.5	645012	SD of m, Sm	11116.9148	68077	SD of b, Sy	**0.78**	**2.59**
5.0	1147525	R^2	0.99467467	87887	SD of regression, Sr		
7.5	1913568	F-statisctic	560.345493	3	Degree of freedom, F		
10.0	2655164	SSregr	4.3282E+12	2.32E+10	SSresid		

Table 4.18 : LOD and LOQ of Benzene for the concentration range 0.5 – 25 % (v/v)

%Std	**P/Area**	**LINEST FUNCTION**				**LOD**	**LOQ**
0.0	0	Slope, m	475829	-30169	y-intercept, b		
0.5	210365	SD of m, Sm	6750	83664	SD of b, Sy	**0.53**	**1.76**
1.0	436378	R^2	0.9986	177196	SD of Regression, Sr		
2.5	1266939	F-Statisctic	4968.7445	7	Degrees of freedom, F		
5.0	2495691	SSregr	1.5601E+14	2.1979E+11	SSresid		
10.0	4341559						
15.0	7135476						
20.0	9399778						
25.0	12032787						

Tables 4.18 – 4.19 show LOD and LOQ values obtained from the calibration curves of benzene and toluene for the concentration range 0.5 – 25 % (v/v), respectively. The calibration curves are also included.

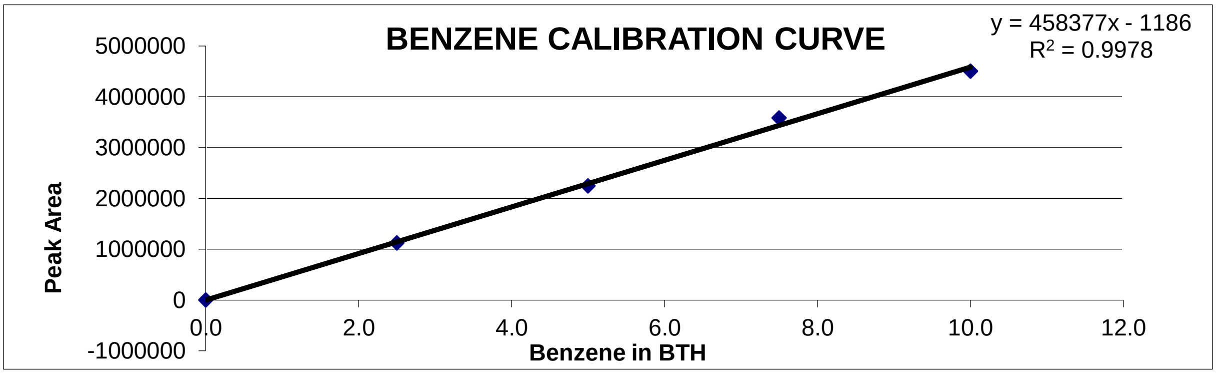
Table 4.19: LOD and LOQ of Toluene for the concentration range 0.5 – 25 % (v/v)

Toluene/%	**P/Area**	**LINEST FUNCTION**				**LOD**	**LOQ**
0.0	0	Slope, m	471742	-84118.25478	y-intercept, b		
0.5	206841	SD of m, Sm	8426.458924	104437	SD of b, Sy	**0.66**	**2.21**
1.0	414490	R^2	0.997771512	221193	SD of Regression, Sr		
2.5	1221878	F-statisctic	3134.143005	7	Degrees of freedom, F		
5.0	2352397	SSregr	1.53343E+14	3.42486E+11	SSresid		
10.0	4144468						
15.0	6829938						
20.0	9440778						
25.0	11899761						

The respective values of LOD and LOQ for benzene and toluene for the concentration range 2.5 – 10 % (v/v) are presented in Table 4.20 – 4.21. The calibration curves for both benzene and toluene are included in each table alongside with values to show the parameters of interest.

Table 4.20: LOD and LOQ for Benzene and Toluene calibration curves: 2.5 – 10 %

%Std	P/Area	BENZENE LINEST FUNCTION				LOD	LOQ
0.0	0	Slope, m	458377	-1186	y-intercept, b		
2.5	1124856	SD of m, Sm	12538	76777	SD of b, Sy	**0.50**	**1.67**
5.0	2246378	R^2	1	99118	SD of regression, Sr		
7.5	3580243	F-statisctic	1337	3	Degrees of freedom		
10.0	4502022	SSregr	13131855884376	29473414177	SSresid		



%Std	P/Area	TOLUENE LINEST FUNCTION				LOD	LOQ
0.0	0	Slope, m	447564	-2415.8	y-intercept, b		
2.5	1098633	SD of m, Sm	11598.58	71026	SD of b, Sy	**0.48**	**1.59**
5.0	2190999	R^2	0.997989	91695	SD of regression, Sr		
7.5	3487038	F-statisctic	1489.019	3	Degree of freedom, F		
10.0	4400344	SSregr	1.25E+13	25223810966	SSresid		

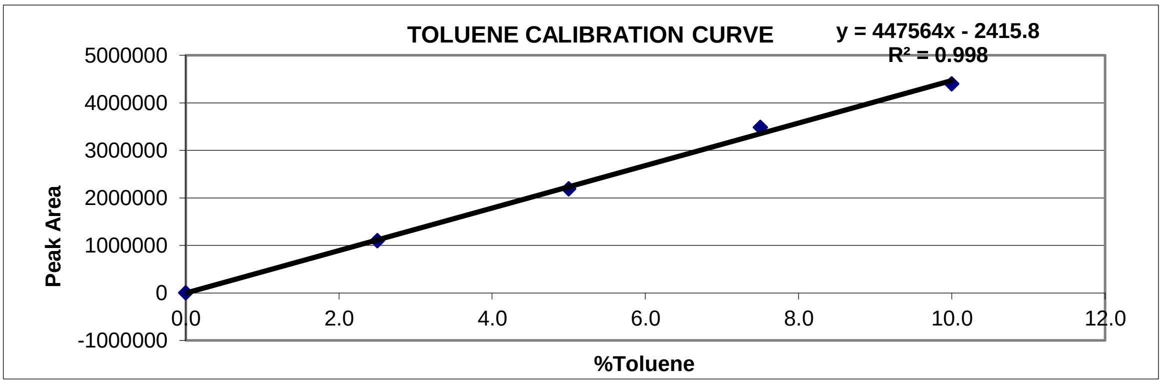
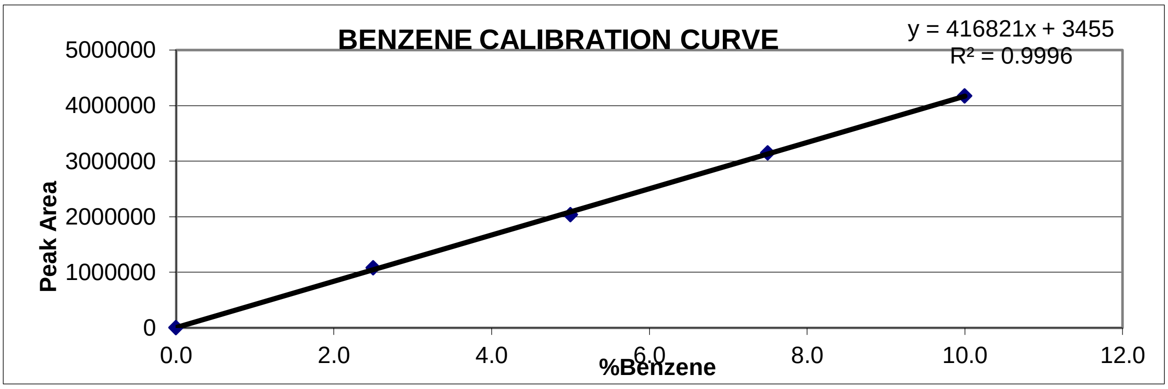
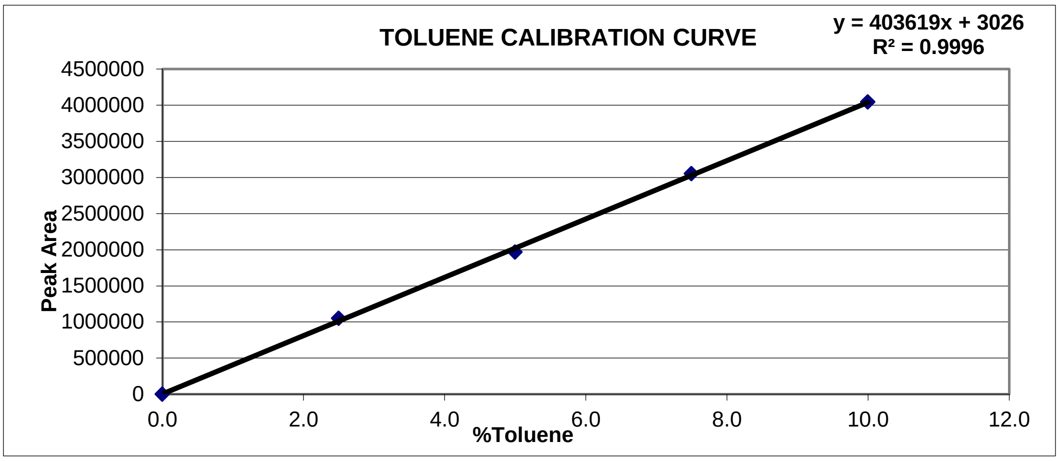


Table 4.21: LOD and LOQ for Benzene and Toluene calibration curves: 2.5 – 10 %

% Std	P/Area	LINEST FUNCTION				LOD	LOQ
0.0	0	Slope, m	416821	3455	y-intercept, b		
2.5	1079500	SD of m, Sm	4786.087	29309	SD of b, Sy	**0.21**	**0.70**
5.0	2034685	R^2	0.999605	37837	SD of regression, Sr		
7.5	3147199	F-statisctic	7584.685	3	Degree of freedom, F		
10.0	4176410	SSregr	1.09E+13	4294992703	SSresid		



%Std	P/Area	LINEST FUNCTION				LOD	LOQ
0.0	0	Slope, m	403619	3026	y-intercept, b		
2.5	1046079	SD of m, Sm	4915.946	30104	SD of b, Sy	**0.22**	**0.75**
5.0	1966556	R^2	0.999555	38864	SD of regression, Sr		
7.5	3049385	F-statisctic	6741.071	3	Degree of freedom, F		
10.0	4043584	SSregr	1.02E+13	4531223227	SSresid		



The overall results showing the values of LOD and LOQ for different concentration range of aromatic components were summarized and presented in Table 4.22.

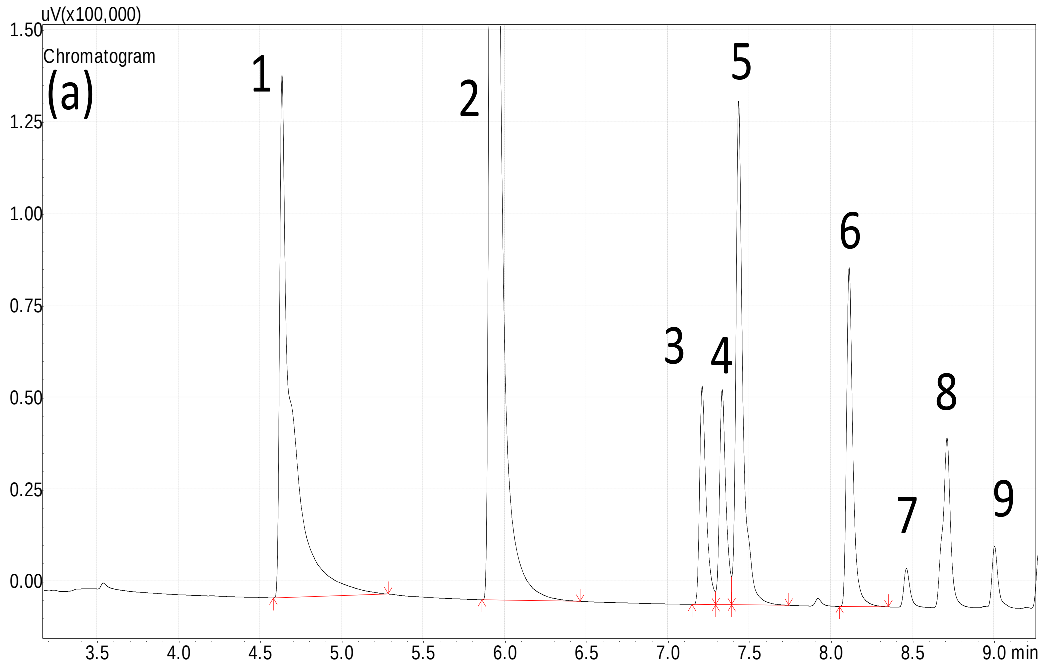
Table 4.22: LOD and LOQ for Benzene and Toluene calibration curves: 2.5 – 10 %

Aromatic Components	**LOD and LOQ values for varied concentration range**					
	0.5 – 25 % (v/v)		**2.5 – 10 % (v/v)**		**2.5 – 10 % (v/v)**	
	LOD	**LOQ**	**LOD**	**LOQ**	**LOD**	**LOQ**
Benzene	0.53	1.76	0.50	1.67	0.21	0.70
Toluene	0.66	2.21	0.48	1.59	0.22	0.75

BTEX Components for the concentration range 2.5 – 10 %				
Components	**Benzene**	**Toluene**	**E/Benzene**	**o-Xylene**
LOD	0.29	0.28	0.34	0.78
LOQ	0.95	0.94	1.14	2.59

4.3.4.2 4.4 Extraction of the reformate mixtures using the ionic liquids: [EMIM][ESO_4], [EMpy][ESO_4], [BNMP][Br], and [MNMP][I]

The chromatograms obtained from reformate extractions using four afore-mentioned ionic liquids are depicted in Figure 4.27 for both the extract and raffinate phases. It can be seen in these figures that the scales were chosen to make toluene peak height to be off-scale for the purpose of making other peaks to be on scale. However, its peak areas (instead of peak heights) were used in all calculations regarding the concentration of all BTEX components.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Chromatogram
(a)
1.50
1.25
1.00
0.75
0.50
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0.00
1
2
3
4
5
6
7
8
9
3.5
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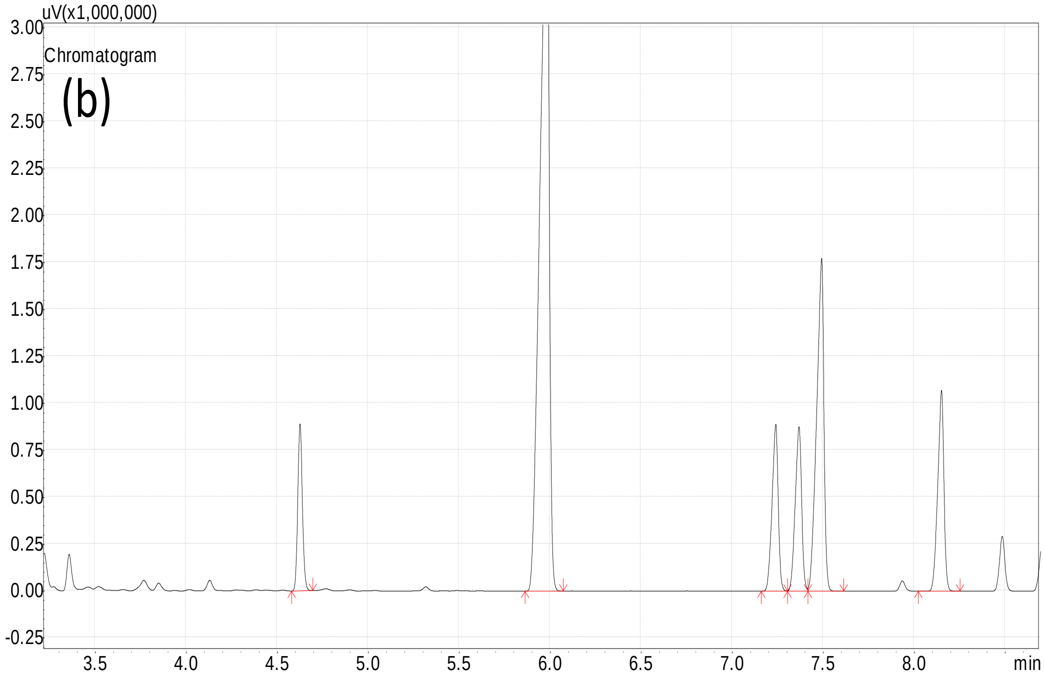
9.0 min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Chromatogram
(b)
3.00
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2.50
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1.00
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7.0
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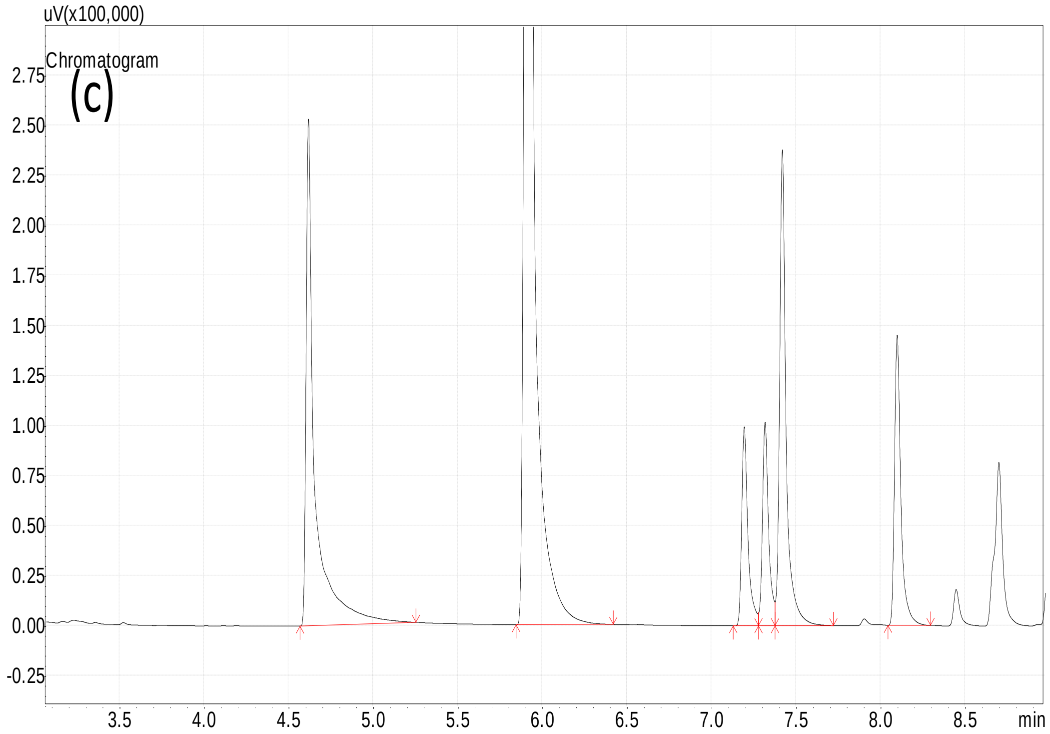
min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Chromatogram
(c)
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2.00
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1.25
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0.50
0.25
0.00
-0.25
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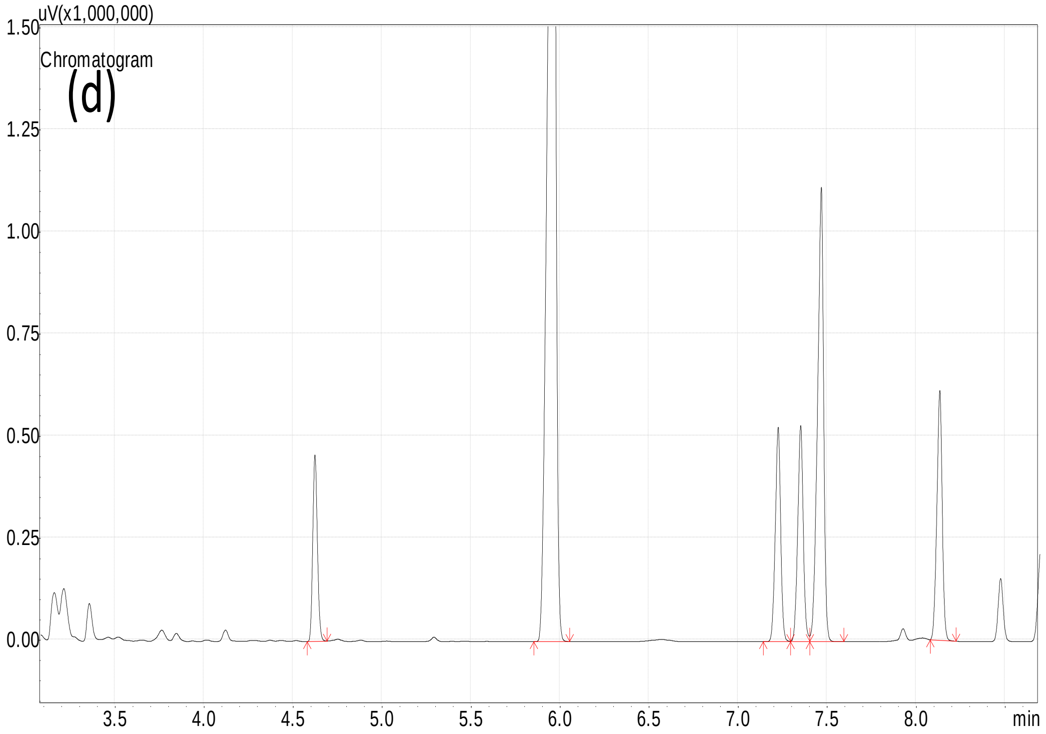
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Chromatogram
(d)
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1.00
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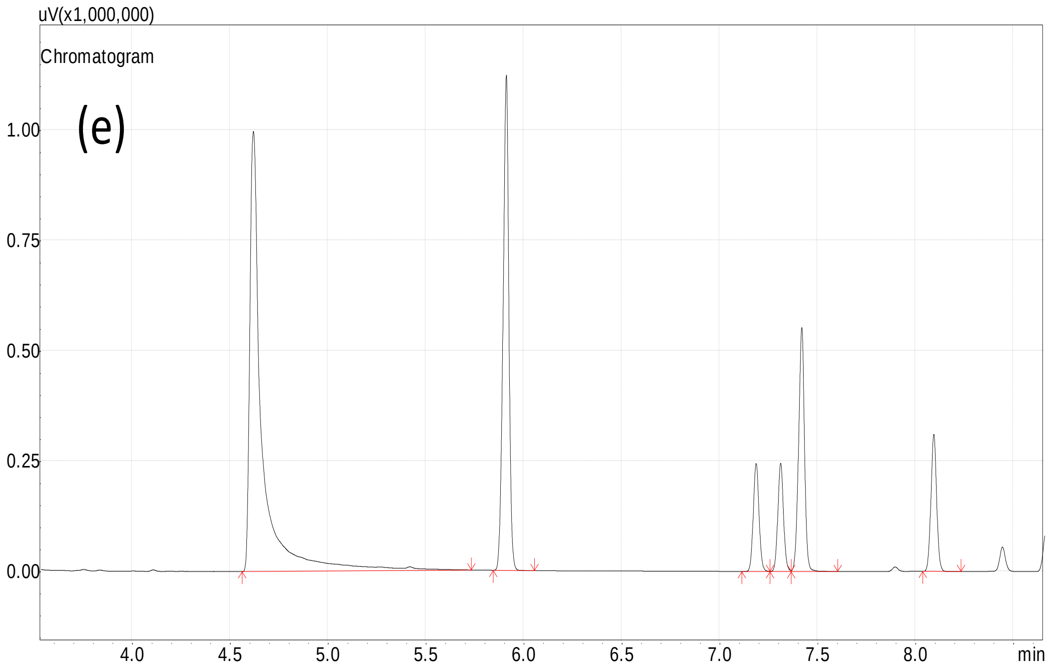
min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Chromatogram
(e)
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0.50
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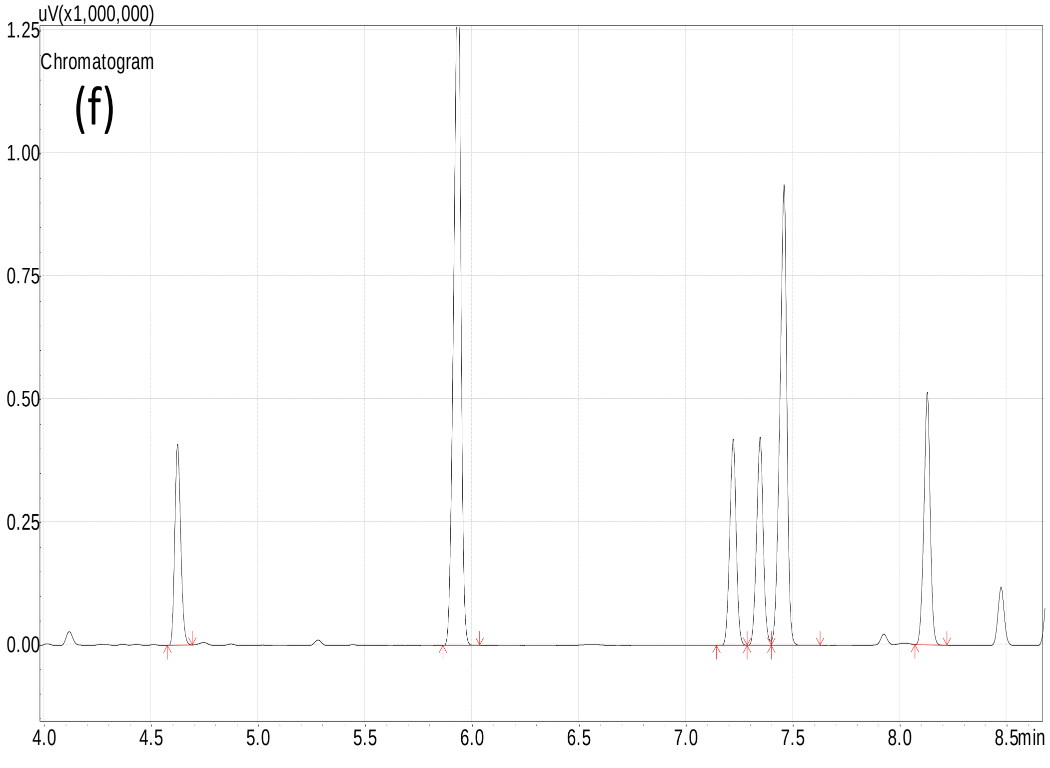
5.0
5.5
6.0
6.5
7.0
7.5
8.0
min


uV(x1,000,000)
1.25
Chromatogram
(f)
1.00
0.75
0.50
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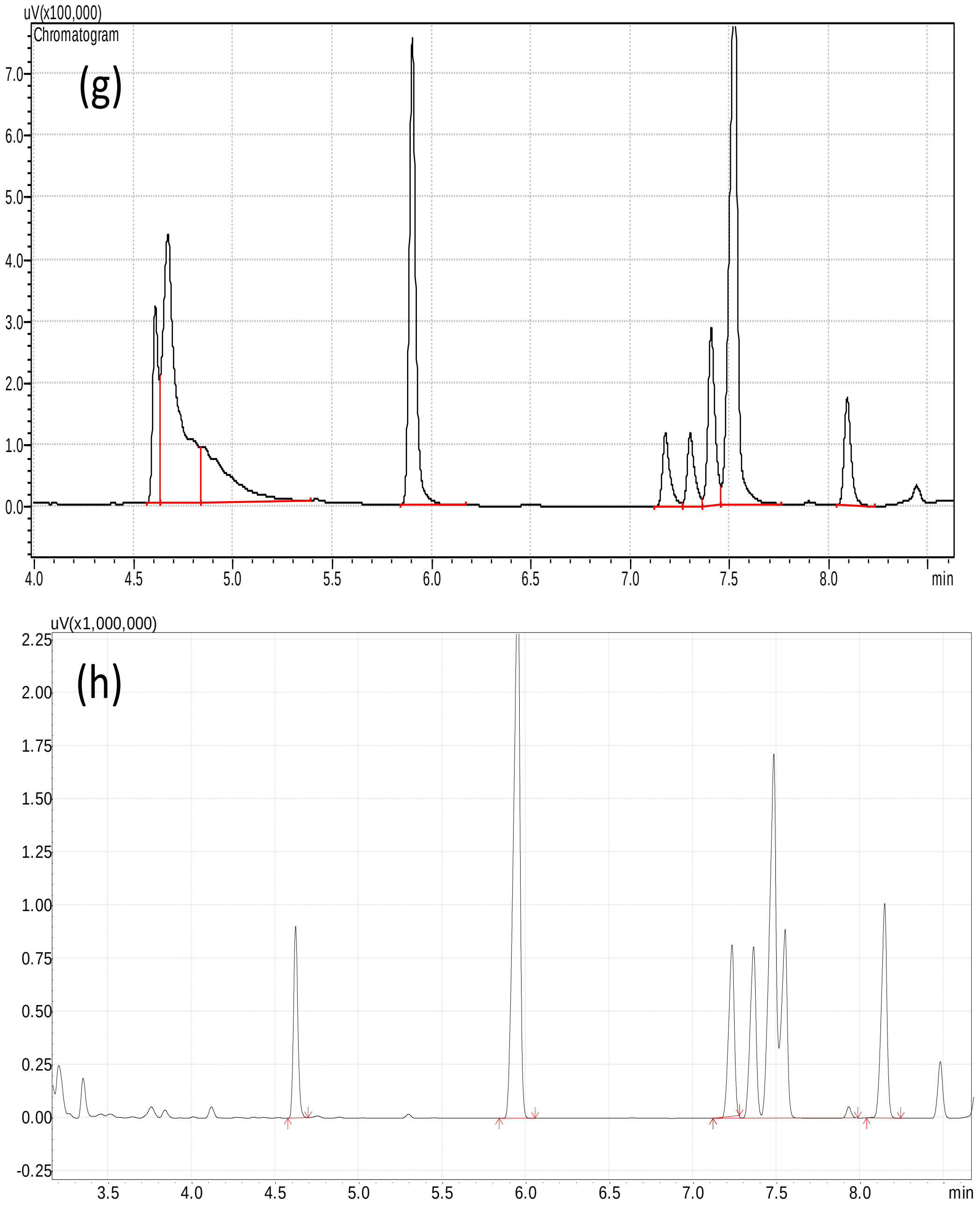


Figure 4.27: Chromatograms showing BTEX components in reformate extraction phases using four ionic liquids (a) Extract phase for [EMIM][ESO_4] (b) Raffinate phase for [EMIM][ESO_4] (c) Extract phase for [EMpy][ESO_4] (d) Raffinate phase for [EMpy][ESO_4], (e) Extract phase for [BNMP][Br] (f) Raffinate phase for [BNMP][Br] (g) Extract phase for [MNMP][I] (h) Raffinate phase for [MNMP][I], 1 = Benzene, 2 = Toluene, 3 = Ethylbenzene, 4 = p-Xylene, 5 = m-Xylene, 6 = o-Xylene.

The comparative results for the extraction of BTEX from reformates using ionic liquids [MNMP][I] and [EMIM][ESO_4] are shown in Figure 4.28 as bar graphs. (See Appendix 3, Tables A7.17 and A7.18). It can be seen in these graphs that the recovery values for both ionic liquids were within the specification range 80 – 120 % (v/v) as it was for the model mixtures. The results of extract and raffinate phases obtained from these two ionic liquids do not differ significantly as shown in Table 4.23. This suggests that these ionic liquids are competitive in their extraction ability for BTEX components from the reformate samples.

Table 4.23: Summary of results obtained from reformate extractions using ionic liquids: [EMIM][ESO_4], [EMpy][ESO_4], [MNMP][I]

Reformate	**[EMIM][ESO_4]**			**[EMpy][ESO_4]**			**[BNMP][Br]**			**[MNMP][I]**		
	E	R	R+E	E	R	R+E	E	R	R+E	E	R	R+E
Benzene	36	76	112	45	68	113	42	67	110	34	79	113
Toluene	27	80	107	47	55	102	29	77	106	22	86	108
E/benzene	13	91	104	17	91	108	28	78	107	19	85	104
p-Xylene	12	90	102	17	93	110	27	81	109	19	87	106
m-Xylene	11	92	103	15	94	109	25	87	112	16	89	105
o-Xylene	13	87	100	18	90	108	27	96	112	19	83	102

The comparative results obtained from the extraction of reformates are presented in Table 4.24 and also depicted in Figure 4.28 for all four ionic liquids ([BNMP][Br], [MNMP][I], [EMIM][ESO_4], and [EMpy][ESO_4]) as extraction solvents for BTEX. (Refer to Appendix 3, Table A7.18.)

Table 4.24: Summary of extract results from reformate mixtures comparing four ILs

Ionic Liquids	Recovery of BTEX from Reformate Mixtures/%volume					
	Benzene	**Toluene**	**E/Benzene**	**p-Xylene**	**m-Xylene**	**o-Xylene**
[EMIM][ESO$_4$]	36	29	13	12	11	13
[EMpy][ESO$_4$]	45	47	17	17	15	18
[BNMP][Br]	42	29	28	27	25	27
[MNMP][I]	34	22	19	19	16	19

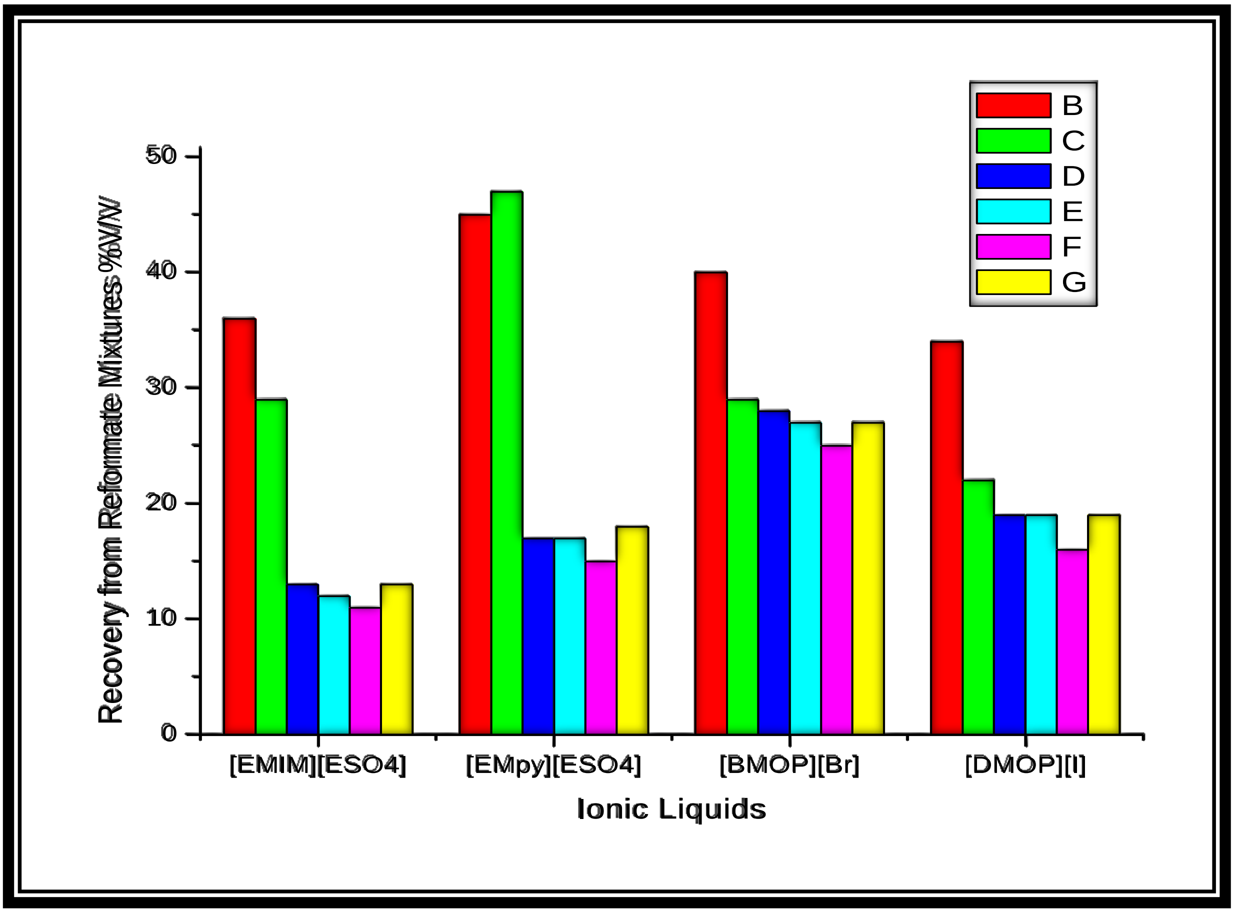


Figure 4.28: Bar graphs comparing the extraction ability of four ionic liquids; where B = Benzene, C=Toluene, D = Ethylbenzene, E= p-Xylene, F= m-Xylene and G=o-Xylene.

The results in Table 4.24 and Figure 4.28 reveal a general increase in percentages extracted in the following order: ethyl benzene ≤ xylenes < toluene < benzene. It can also be seen that the extraction capacity of ionic liquids follow the order: [EMpy][ESO_4] > [BNMP][Br] > [MNMP][I] > [EMIM][ESO_4]. This observation can be explained in terms of nature of molecular interactions occurring between ionic liquids and BTEX components. Cations of ionic liquids interact strongly with π electrons of aromatic rings through cation-π interactions. There are also π-π interactions strong interactions occurring between π electrons of ionic liquids and aromatic π electrons through aromatic characters. Pyrrolidonium-based ionic liquids contain highly polarizable anions (Br^- and I^-) therefore they can interact strongly with aromatics. The presence of carbonyl groups (-C=O) in the ILs provides additional π-π interactions with aromatics.

The trend observed with BTEX order can be explained in terms of steric hindrance and effects of attached groups on the π systems of the substituted benzenes as described above. In addition, it appears that the longer the alkyl chains attached to the aromatic rings, the more difficult it is for the molecules to organize themselves in a sandwich structure. This is in accordance with the observation made by Meindersma et al. [130] that alkyl substitution on the aromatic ring affects the molecular interaction in the preferred functional groups. Further support for the perceived enhanced BTEX interactions with the ionic liquids may be deduced from the views of Poole et al. [129] and Hansmeier et al. [90].The former suggests that hydrogen bonding between BTEX and the ionic liquid may give rise to stronger interactions whereas the latter proposes that ionic liquids and aromatic solutes organize themselves in a sandwich structure in which the ionic liquid cations and the aromatic solutes interact in an alternating structure through π-π interactions with the ionic liquid anions, arranged around this complex.

4.4 Extraction of aromatic hydrocarbons from paint solvent wastes

4.4.1 Overview

Solvent-based paint manufacturing plants produce significant quantities of hazardous solvent wastes. The cost of treating such wastes is high and therefore, reducing the quantity of waste is becoming the crucial issue in these industries. Waste minimization options would be beneficial for the plant owners as well as for the environment. Reusing spent solvents or used solvents will also reduce the amount of solvents disposed of as wastes.

The spent paint solvents or paint solvent wastes containing aromatic components (BTEX) which were used as solvents in paint manufacturing were also investigated in this study. The ability of ionic liquids 1-ethyl-3-methylimidazolium ethyl sulphate and 1-ethyl-3-methylpyridinium ethyl sulphate were experimented on various samples of spent paint solvents for the extraction of aromatic hydrocarbons. The recovery values obtained from the experiments agreed with those obtained from model mixtures investigated under similar conditions.

4.4.2 Analysis of BTEX in spent paint solvents

The spent solvent samples were obtained from paint manufacturing industries stored in large containers for disposal. Before sampling, the storage tanks were agitated for a while to homogeneous the content. Two different samples were then collected in suitable containers or vessels for experimentation in this study: (1) non-recycled spent solvents, and (2) recycled spent solvents. These spent solvents were analyzed directly to determine the concentration (%) of aromatic component using GC-FID. The guard column was used as a pre-column to prevent the nonvolatile materials from entering the analytical column thus causing disruption in the analysis. Standards of appropriate concentration range of BTEX components were used to calibrate the instrument. All standards gave linear curves of concentrations versus peak areas which gave the assurance that the instrument was in a good condition.

It was ascertained from GC analysis that the aromatic components present in both spent solvents were only toluene, ethyl benzene and three xylene isomers. The level of their concentrations in the non-recycled and recycled spent solvents is illustrated in Table 4.25. (See also Table A7.19 in Appendices.) The chromatograms for both the non-recycled and recycled spent solvents are depicted in Figure 4.29. As mentioned earlier, both chromatograms confirm the absence of benzene and the presence of five aromatic components in the spent solvents. It can be seen in Table 4.25 that the non-recycled spent solvents contained higher concentration of aromatic components than recycled spent solvents.

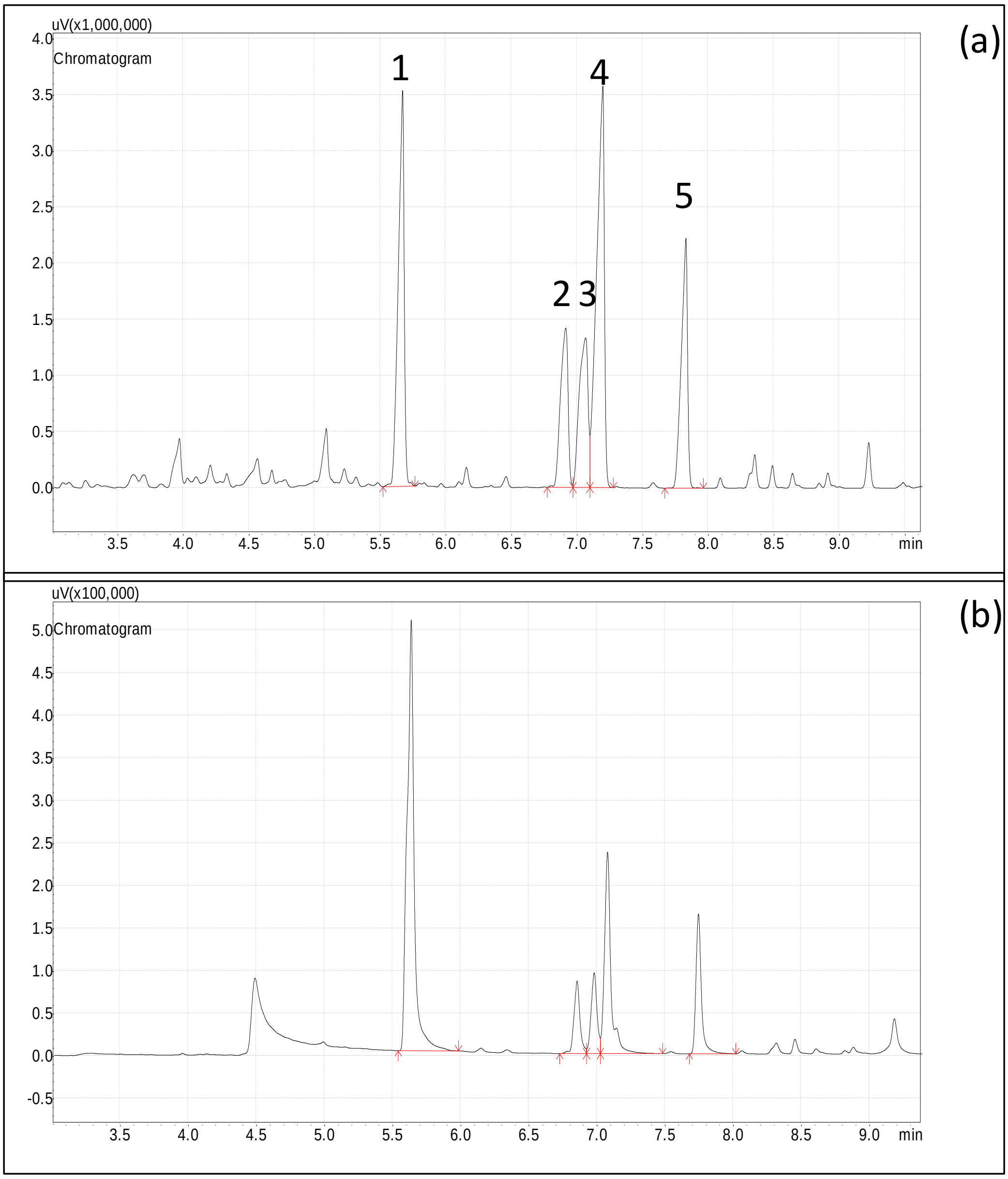


Figure 4.29: Chromatogram for the content of BTEX in (a) non-recycled and (b) recycled spent paint solvents where 1 = Toluene 2 = Ethylbenzene 3 = p-Xylene 4 = m-Xylene 5 = o-Xylene

Table 4.25: Content of aromatic components in non-recycled and recycled spent paint waste solvents

Aromatic Components	Non-recycled Spent Solvent		Recycled Spent Solvent	
	Peak Area	% (v/v)	Peak Area	% (v/v)
Benzene	Nil	Nil	Nil	Nil
Toluene	18493790	21.0	10997818	12.6
E/Benzene	6168467	7.1	5638492	6.5
p-Xylene	6652490	7.7	6279380	7.3
m-Xylene	15830365	18.0	14501377	17.6
o-Xylene	7260821	8.2	6860663	7.8

4.4.3 Extraction of BTEX from spent paint waste solvents using non-recycled and recycled ionic Liquids

This section investigates the effect of two non-recycled and recycled ionic liquids for the extraction of aromatic components in spent paint solvents. The results obtained are presented in Table 4.26 for both ionic liquids [EMIM][ESO_4] and [EMpy][ESO_4]. (Also refer to Table A7.20 in Appendices.) The overall results obtained indicate that both ionic liquids are effective as extraction solvents for the recovery of aromatic components from spent paint solvents. However, the ionic liquid 1-ethyl-3-methylpyridinium ethyl sulphate shows higher extracting capacity for aromatic components than 1-ethyl-3-methylimidazolium ethyl sulphate. This could be attributed to the former being more aromatic character than the latter. The stronger the π-systems, the more pronounced the interactions between the ionic liquid and aromatic components.

Table 4.26: Results showing the recyclability of ionic liquids [EMIM][ESO_4] and [EMpy][ESO_4] for the extraction of spent paint waste solvents using

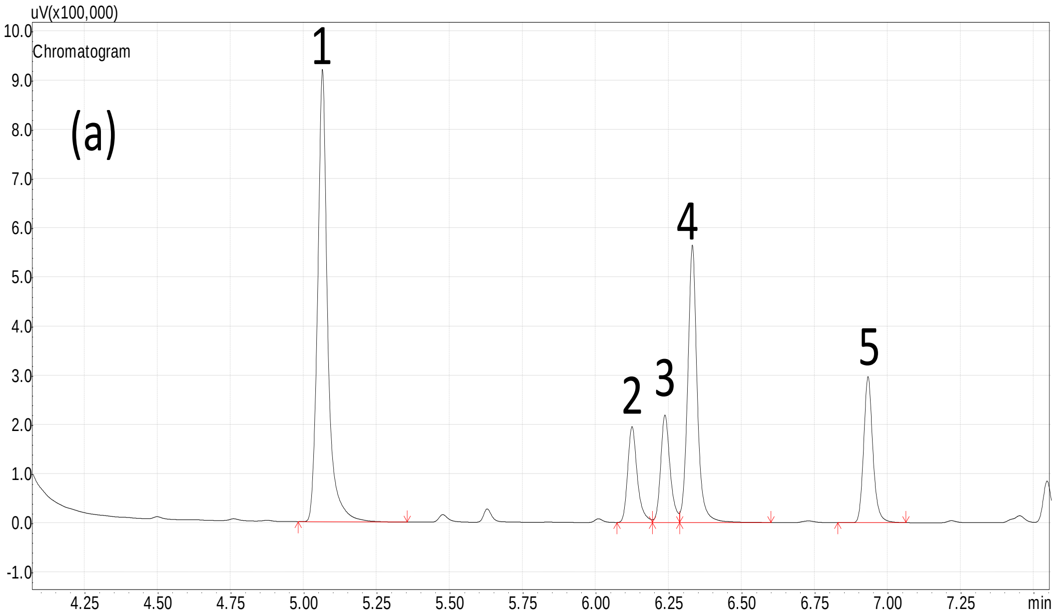
Aromatic Components	**Recovery % (v/v) of each aromatic component**			
	EMIM][ESO_4] Non-recycled	**EMIM][ESO_4] Recycled**	**[EMpy][ESO_4] Non-recycled**	**[EMpy][ESO_4] Recycled**
Toluene	30	29	40	37
Ethyl Benzene	23	18	29	25
p-Xylene	23	19	30	26
m-Xylene	18	17	27	26
o-Xylene	27	23	33	29

It can also be seen in Table 4.26 that the recycled and non-recycled ionic liquids show almost the same extraction effects with the former having slightly lower values. The order of extractability of aromatic components follows the same as with other mixtures: m-xylene < p-xylene < ethyl benzene <o-xylene < toluene. The attributes to this order has been explained in sections 4.2.3.1 and 4.2.3.2 and this is in accordance to the previous studies done elsewhere [62,118].

4.4.4 Extraction of aromatics from spent paint solvents in three stages Mixture: Spent solvent + [EMIM][ESO4]/[EMpy][ESO4] + n-Hexane

The chromatograms obtained from the three stages of aromatics extraction by recycled 1-ethyl-3-methylpyridinium ethyl sulphate are shown in Figure 4.30. Extract results from recycled and non-recycled [EMIM][ESO$_4$] are reported in Tables 4.27 and 4.28, respectively. Tables 4.29 and 4.30 present the extract results obtained from non-recycled and recycled [EMpy][ESO$_4$], respectively. Overall results are summarized in Table 4.31 for both recycled and non-recycled ionic liquids. (See also Tables A7.21 – A7.24 in Appendices for a detailed data.)

These results indicate that, in all experiments performed, the toluene content is higher than those of the other aromatic components. Also noticeable in these results is that pyridinium-based ionic liquid has generally much higher extraction capacity than the imidazolium-based ionic liquid. The results also reveal that there is not much difference between non-recycled and recycled ionic liquids in terms of extraction efficiency. The overall outcome of this investigation confirms that ionic liquids are recyclable for many extractions of TEX from non-aqueous mixtures of mainly containing aliphatic and aromatic hydrocarbons.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Chromatogram
(a)
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2
3
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10.0
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8.0
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3.0
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0.0
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4.25
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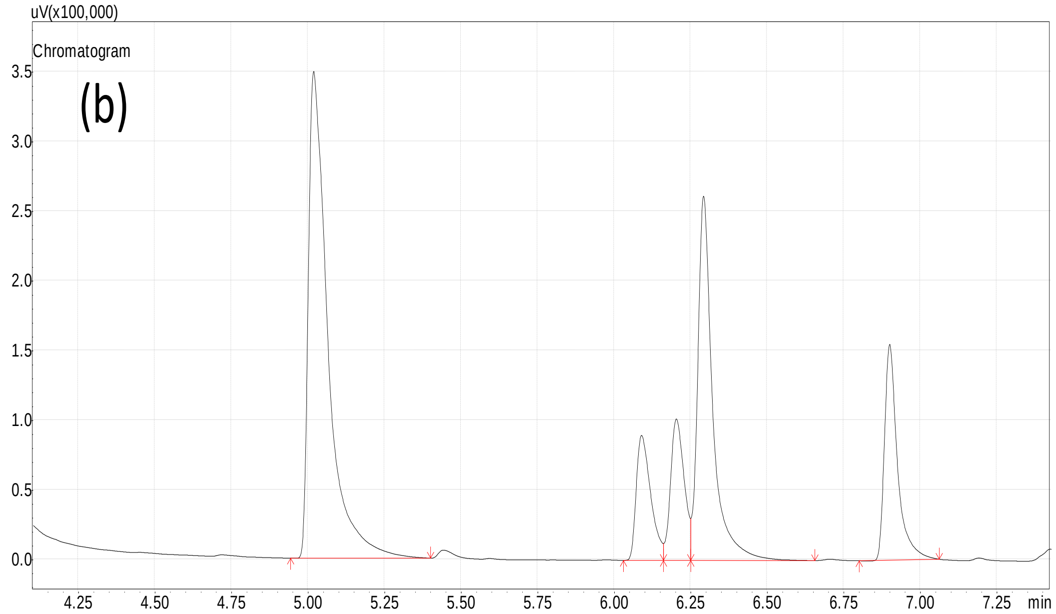
uV(x100,000)
Chromatogram
(b)
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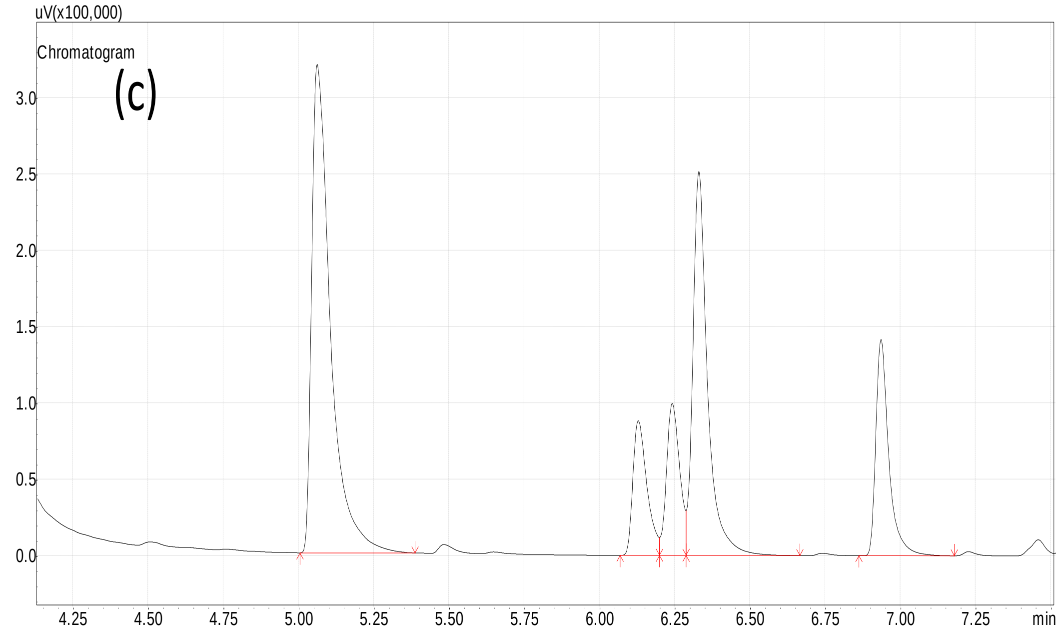
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Chromatogram
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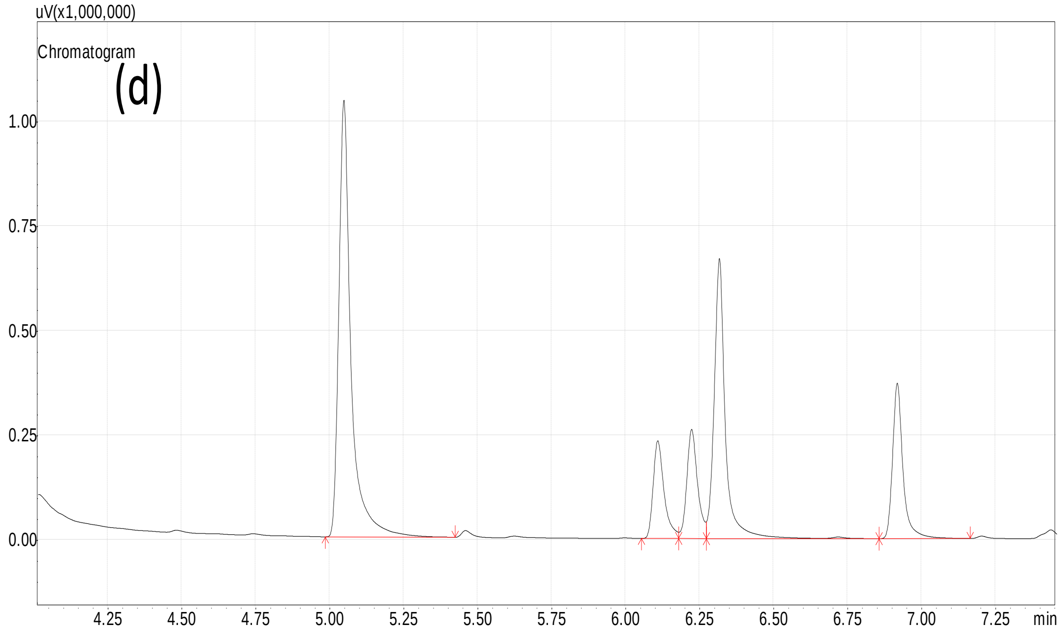
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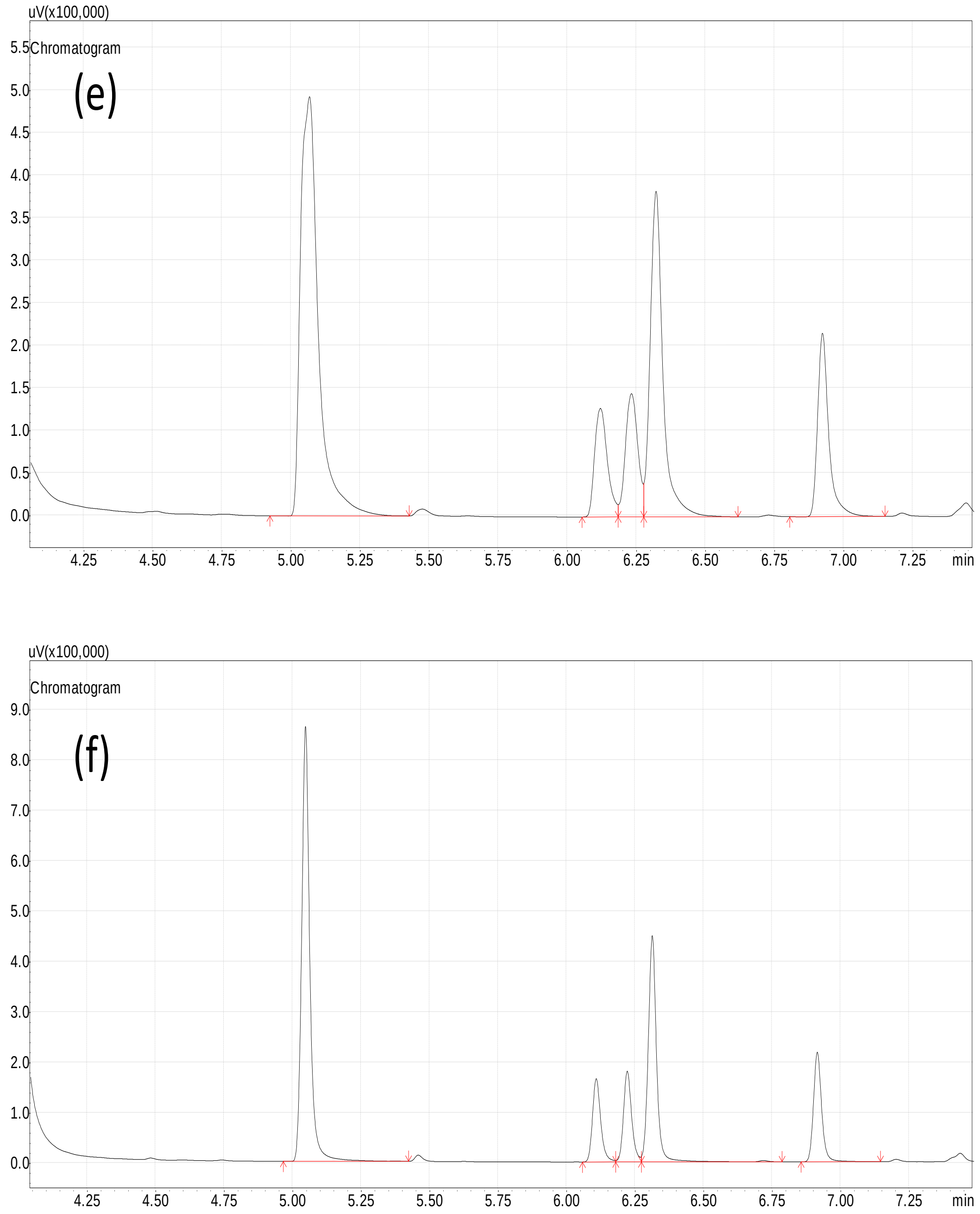

Figure 4.30: Extract phase chromatograms showing aromatics components extracted by recycled ILs: [EMpy][ESO_4] (a) First stage extraction (b) Second stage extraction (c) Third stage extraction and [EMIM][ESO_4] (d) First stage extraction (e) Second stage extraction (f) Third stage extraction; where 1= Toluene 2 = Ethylbenzene 3 = p-Xylene 4 = m-Xylene 5 = o-Xylene

Table 4.27: Results showing three stages of spent paint waste solvent extractions using recycled [EMIM][ESO$_4$]

Aromatic Components	**1stStage % (v/v)**		**2ndStage % (v/v)**		**3rdStage % (v/v)**		**Total % (v/v)**
	Extract	**Recovery**	**Extract**	**Recovery**	**Extract**	**Recovery**	
Toluene	2.37	12.0	1.66	8.4	1.61	8.2	29
E/Benzene	0.51	7.6	0.37	5.5	0.35	5.2	18
p-Xylene	0.57	7.9	0.42	5.8	0.39	5.4	19
m-Xylene	0.95	5.6	0.97	5.7	0.93	5.5	17
o-Xylene	0.66	9.0	0.52	7.1	0.50	6.8	23

Table 4.28: Results showing three stages of spent paint waste solvent extractions using non-recycled [EMIM][ESO$_4$

Aromatic Components	**1stStage % (v/v)**		**2ndStage % (v/v)**		**3rdStage % (v/v)**		**Total % (v/v)**
	Extract	**Recovery**	**Extract**	**Recovery**	**Extract**	**Recovery**	
Toluene	2.16	10.9	1.94	9.8	1.78	9.0	30
E/Benzene	0.51	7.6	0.50	7.5	0.49	7.3	23
p-Xylene	0.60	8.3	0.54	7.5	0.52	7.2	23
m-Xylene	0.94	5.5	1.08	6.4	1.04	6.1	18
o-Xylene	0.70	9.6	0.64	8.8	0.59	8.1	27

Table 4.29: Results showing three stages of spent paint waste solvent extractions using non-recycled [EMpy][ESO$_4$

Aromatic Components	**1st Stage % (v/v)**		**2nd Stage % (v/v)**		**3rd Stage % (v/v)**		**Total % (v/v)**
	Extract	**Recovery**	**Extract**	**Recovery**	**Extract**	**Recovery**	
Toluene	3.08	15.6	2.65	13.4	2.18	11.0	40
E/Benzene	0.74	11.0	0.62	9.3	0.55	8.2	29
p-Xylene	0.84	11.7	0.69	9.6	0.60	8.3	30
m-Xylene	2.00	11.8	1.44	8.5	1.13	6.7	27
o-Xylene	1.03	14.1	0.78	10.7	0.62	8.5	33

Table 4.30: Results showing three stages of spent paint waste solvent extractions using recycled [EMpy][ESO$_4$

Aromatic Components	**1st Stage % (v/v)**		**2nd Stage % (v/v)**		**3rd Stage % (v/v)**		**Total % (v/v)**
	Extract	**Recovery**	**Extract**	**Recovery**	**Extract**	**Recovery**	
Toluene	2.90	13.8	2.50	11.9	2.30	11.0	37
E/Benzene	0.70	9.9	0.56	7.9	0.54	7.6	25
p-Xylene	0.79	10.3	0.63	8.2	0.59	7.7	26
m-Xylene	1.80	10.0	1.60	8.9	1.30	7.2	26
o-Xylene	0.98	12.0	0.77	9.4	0.65	7.9	29

Table 4.31: Summary of results showing total recovery of BTEX in three stages of extractions from paint solvent wastes

Aromatic Components	**[EMIM][ESO$_4$]**		**[EMpy][ESO$_4$]**	
	Non-Recycled	**Recycled**	**Non-Recycled**	**Recycled**
Toluene [% (v/v)]	30	29	40	37
E/Benzene [% (v/v)]	23	18	29	25
p-Xylene [% (v/v)]	23	19	30	26
m-Xylene [% (v/v)]	18	17	27	26
o-Xylene [% (v/v)]	27	23	33	29

5 CHAPTER FIVE: SUMMATIVE CONCLUSIONS AND RECOMMENDATIONS

5.1 Overview

This chapter involves conclusions which are mainly focusing on the following new information regarding the application of ionic liquids in solvent extraction processes:

- Extraction of aromatic components from the multicomponent model mixtures.
- Extractions of aromatic components from the petroleum reformate mixtures.
- Extraction of aromatic components from the paint solvent waste mixtures.
- Validation of the analytical method(s) which were used in this project to determine the concentration of aromatic components in the extract and raffinate phases resulting from extraction processes.

5.2 Findings

5.2.1 Based on main objectives

- Ionic liquids investigated in this study were found to be more efficient than conventional solvents for the separation of aromatic hydrocarbons from reformate and paint solvent waste mixtures
- The methods used for the recovery of ionic liquids from the extract phases were found to be complete and cost effective
- Analytical methods used for determining the concentrations of BTEX components showed adequate degree of precision and accuracy.

5.2.2 Based on extraction efficiency of aromatic components

With regard to the effects of varying the concentrations of BTEX components, the phase settling periods, the nature of alkanes on extraction values, the nature of the cations in the ionic liquids on extractability, and the number of extraction stages, the conclusions noted hereunder are:

- The recovery values decrease with increasing concentrations of BTEX
- The extraction values increase with increasing phase settling periods.
- There was no significant difference between the extraction values obtained from n-hexane and n-heptane although the latter showed slightly higher values.
- The ionic liquid 1-ethyl-3-methylpyridinium ethyl sulphate showed higher recovery values than 1-ethyl-3-methylimidazolium ethyl sulphate.
- The recovery values increased with increasing number of extraction stages.

Overall, the most significant conclusion is: ionic liquids can be used to separate aromatic hydrocarbons, namely, benzene, toluene, ethylbenzene, and xylene isomers (BTEX components) from multi-component mixtures of aromatic/aliphatic solvents. Specifically the separation can be effected by using ionic liquids, 1-ethyl-3-methylimidazolium ethyl sulphate [EMIM][ESO_4], 1-ethyl-3-methylpyridinium ethyl sulphate [EMpy][ESO_4], as well as the new ionic liquids 1-butyl-1-methyl-2-pyrrolidonium bromide[BNMP][Br] and 1, 1- dimethyl-2-pyrrolidonium iodide[MNMP][I]under controlled experimental conditions. As most investigations in this study involved the use of [EMIM][ESO_4] and [EMpy][ESO_4], it was found that the latter ionic liquid was more effective than the former ionic liquid based on the results obtained as can be seen in Table 4.82 of Chapter 4. For the new ionic liquids, it was established that [BNMP][Br] was more effective than its counterpart [MNMP][I] in terms of the results obtained from the extractions involving reformates (petroleum mixtures).

The developed method has significant commercial importance as it can be adapted for industrial plant large scale usage and can also be modified for automation. The latter can be exploited to increase the number of extraction stages to ensure optimum extraction. The overall impression based on comparing the results of the four experimental variations, lead to the following conclusions:

- The selected ionic liquids are capable of recovering aromatic hydrocarbons (BTEX) even at very low concentrations (≤ 0.5 % by volume).
- The trends of BTEX distribution in the extract and raffinate phases, is of a linear relationship as indicated in all the calibration curves of peak areas versus the concentrations of components investigated in this study.
- The ionic liquids used have much higher affinity for aromatic hydrocarbons than aliphatic hydrocarbons as shown in all tables and figures in Chapter 4.

- The solubility of BTEX in the ionic liquids dealt with in this study generally increases in the order: xylene isomers < ethylbenzene < toluene < benzene.

The extraction results indicate that the structural features of the new ionic liquids are well suited for the purpose of interactions with the aromatic solvents. Coupled with other properties such as low toxicity and recyclability, these ionic liquids have the potential to replace conventional organic solvents used in recovery of aromatic solvents from mixtures of organic solvent mixtures, containing aromatic and aliphatic components.

As ionic liquids are considered to be ‘green solvents’ their use in reclaiming valuable organic solvents is good for the protection of the environment from pollution. An added advantage is that these ionic liquids can be synthesized on a large scale as necessary required for industrial and commercial applications.

5.3 Recommendations

The following is highly recommended for any further work to be undertaken in future on this project:

- Use of mass-based methods for the preparation of standards and measurements done on the extract and raffinate phases.
- Further study to determine accurately the content (%wt.) of alkane as well as ionic liquid in each phase (extract and raffinate).
- Future work to include cost analysis and benchmarking to other solvents.
- Use of internal standards in addition to external calibration for verification.
- Use of phase diagrams for multicomponent systems.
- Investigating the extractions of alkene and alkynes as valuable compounds.
- Conduct further investigation on pyrrolidonium- based ionic liquids using a variety of alkyl groups and anions.

- Conduct further investigation on pyrrolidonium- based ionic liquids using a variety of alkyl groups and anions.

- Design and use of a pilot project to do experiments on a small industrial scale.

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7 APPENDICES

Appendix 1: FTIR-ATR Spectra for Ionic Liquids [EMIM][ESO_4] and [EMpy][ESO_4]

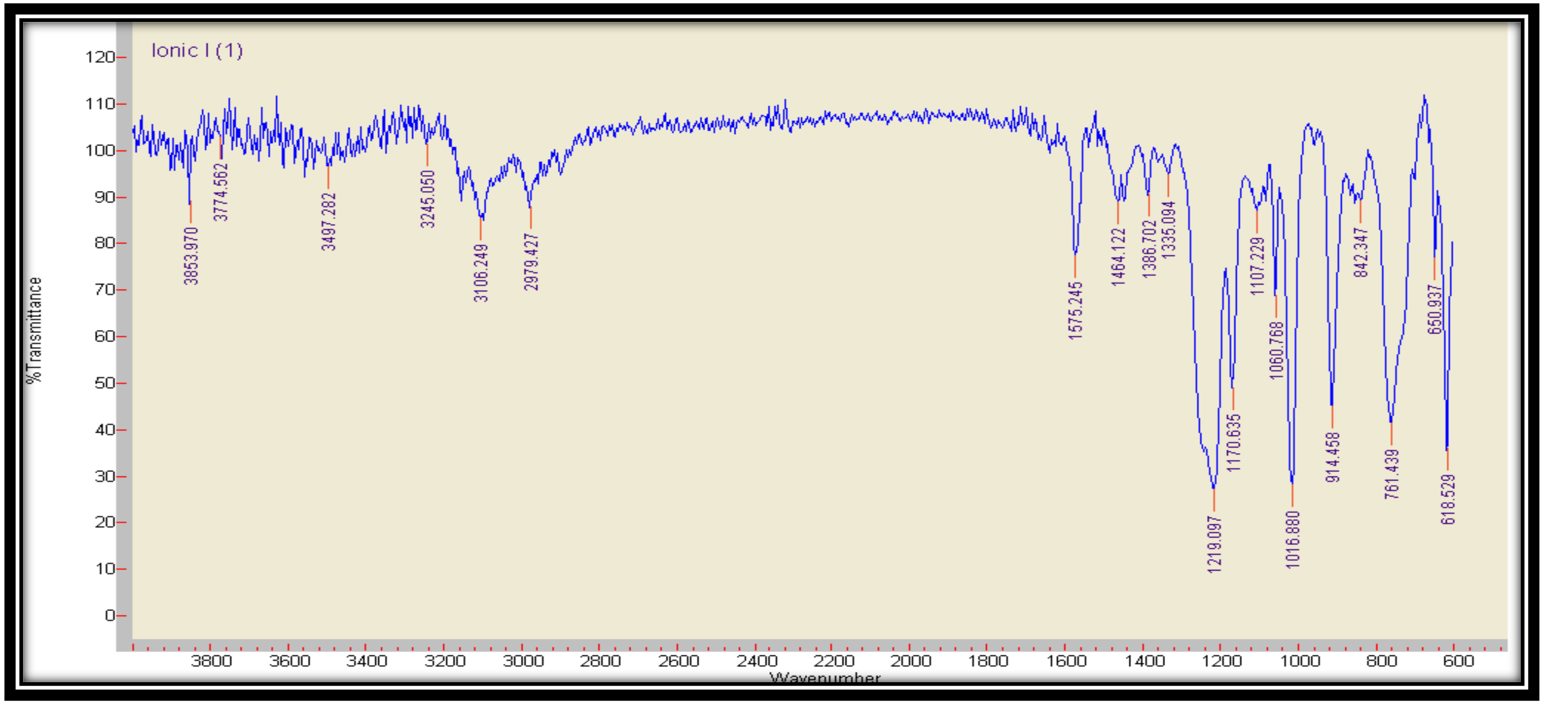

Figure A 7.1: FTIR-ATR Spectrum for IL standard [1] [EMIM][ESO_4]

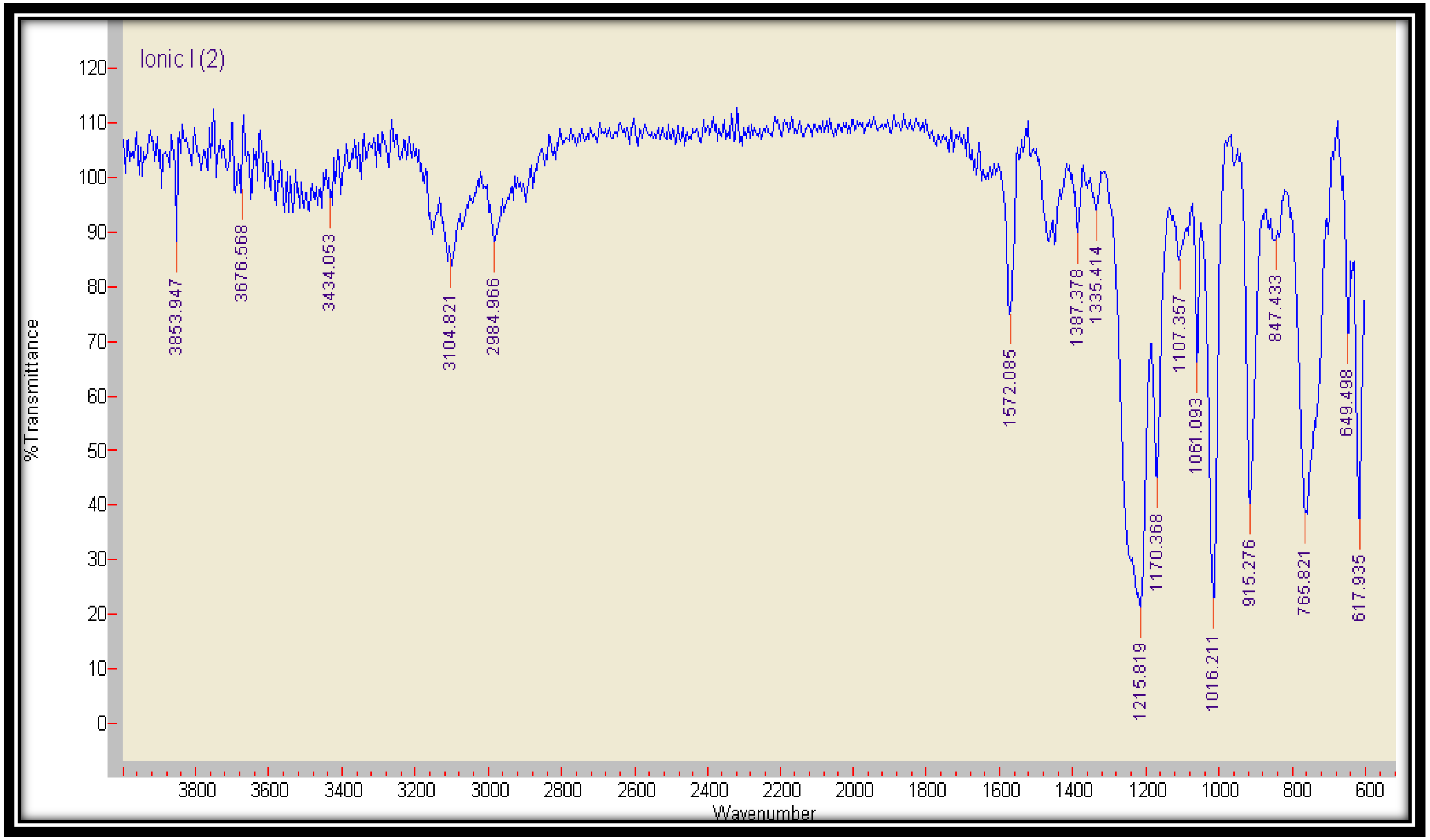

Figure A 7.2: FTIR-ATR Spectrum for synthesized IL [EMIM][ESO_4]

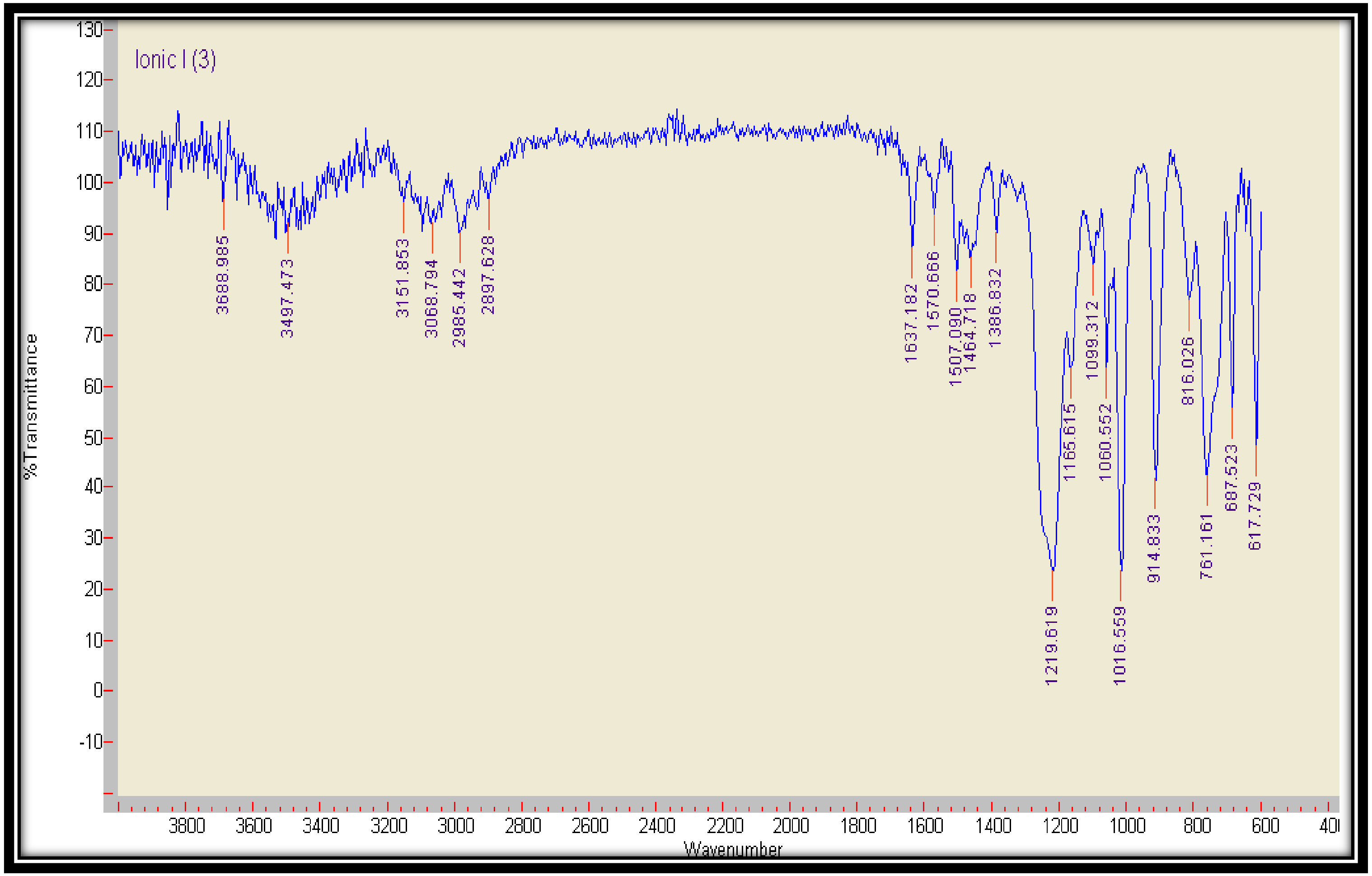

Figure A 7.3: FTIR-ATR Spectrum for IL standard [2] [EMIM][ESO_4]

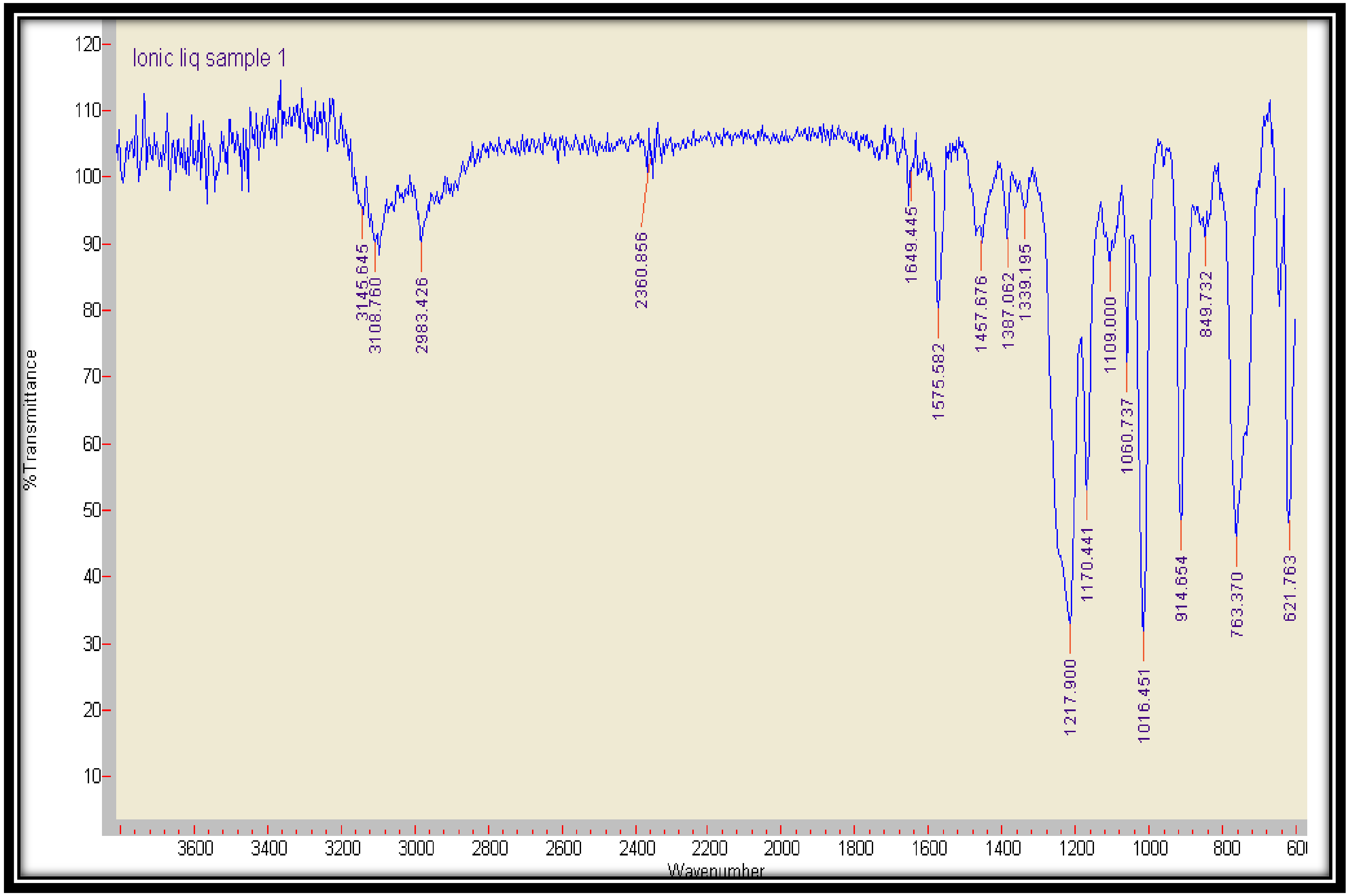

Figure A 7.4: FTIR-ATR Spectrum for IL regenerated once [EMIM][ESO_4]

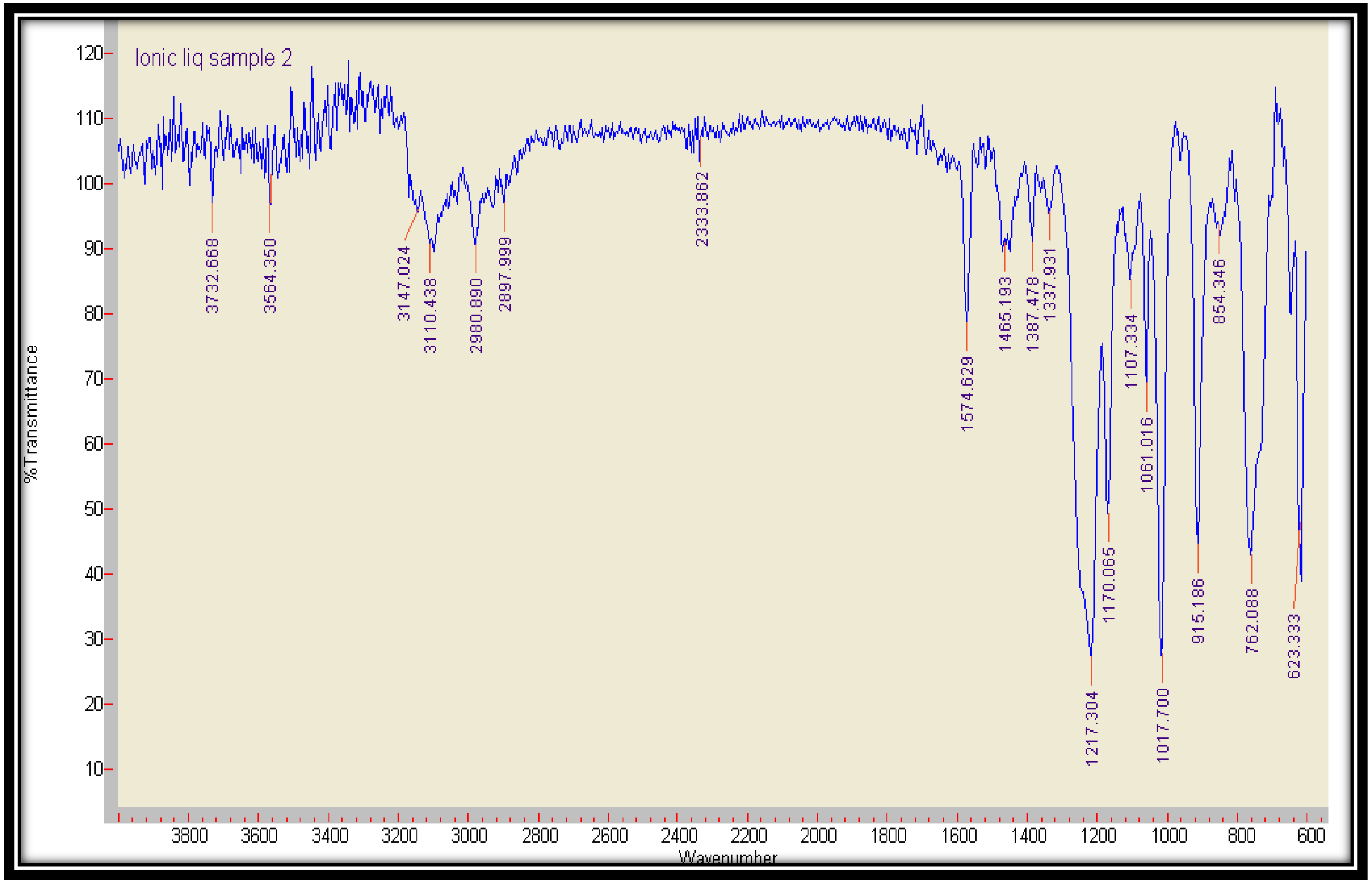

Figure A 7.5: FTIR-ATR Spectrum for IL regenerated twice [EMIM][ESO$_4$]

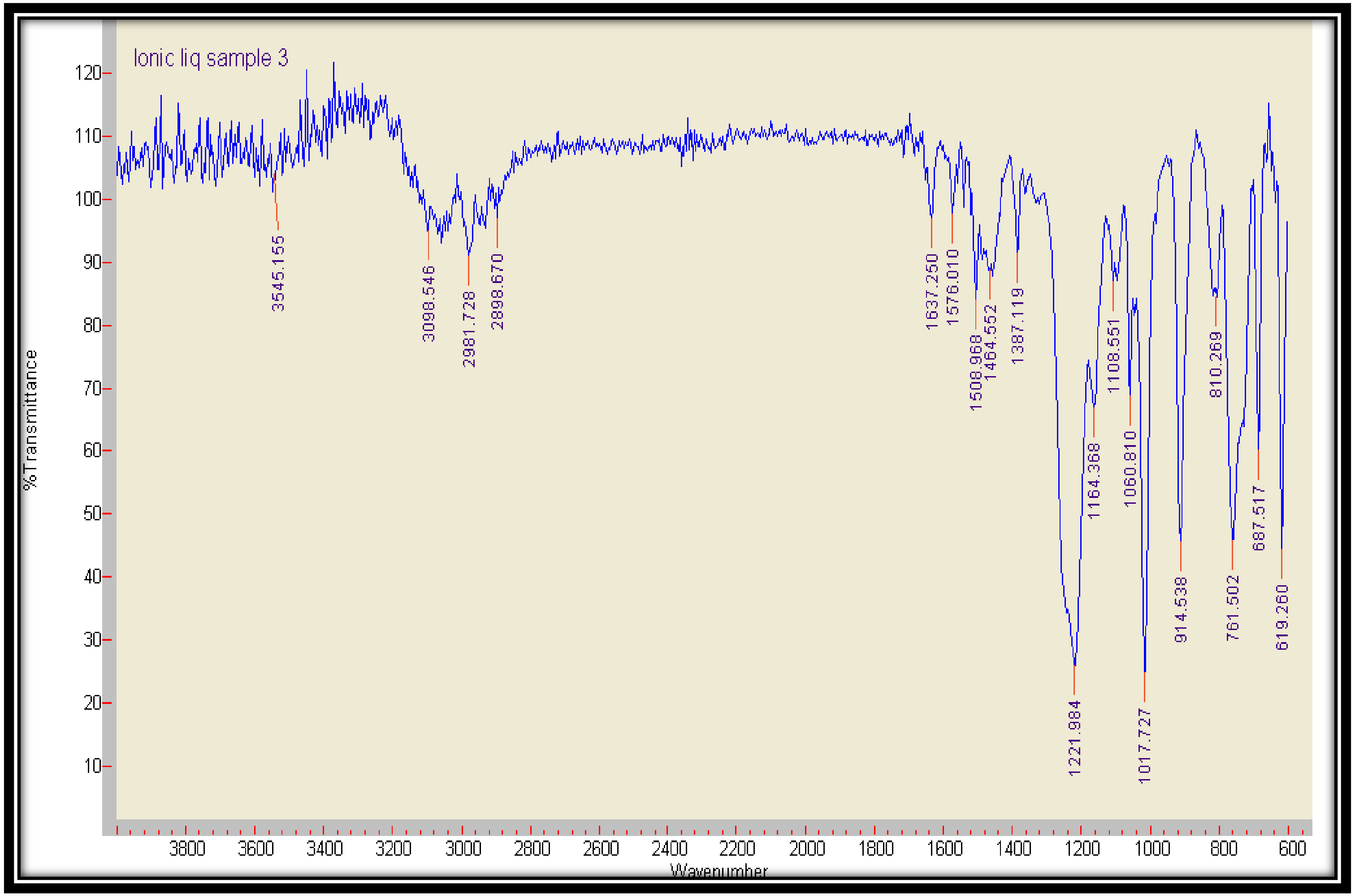

Figure A 7.6: FTIR-ATR Spectrum for IL regenerated thrice [EMIM][ESO$_4$]

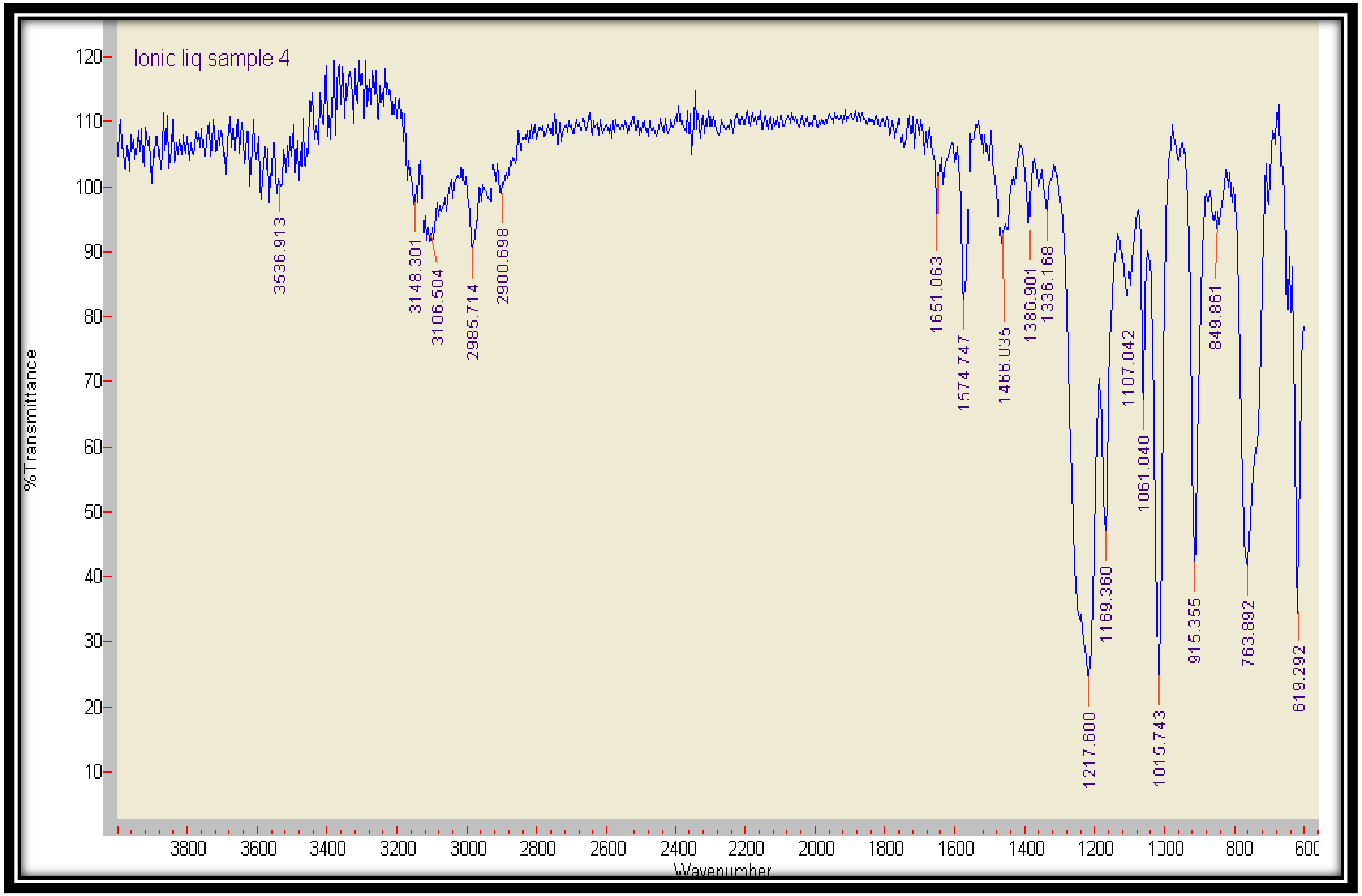

Figure A 7.7: FTIR-ATR Spectrum for IL regenerated four times [EMIM][ESO_4]

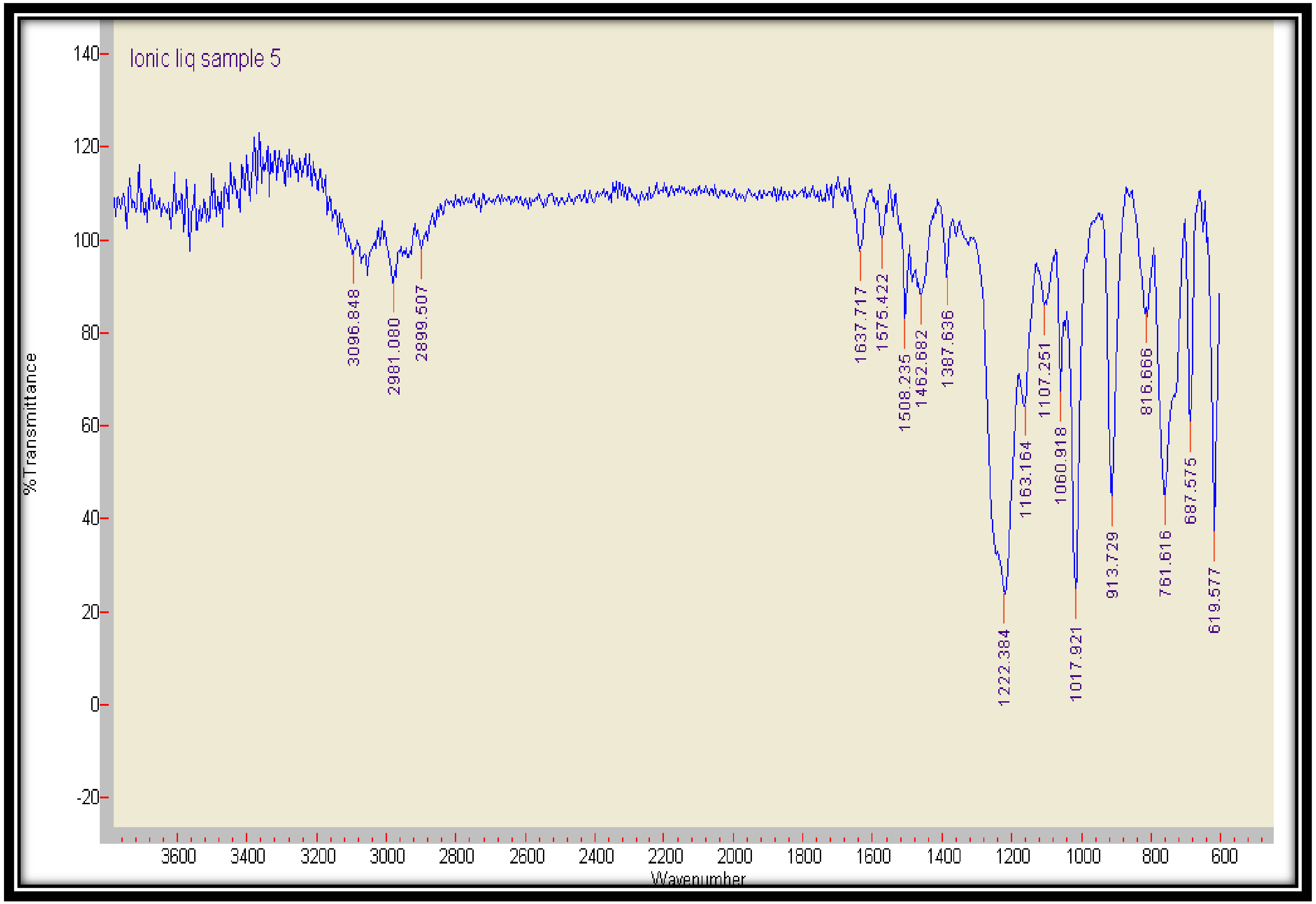

Figure A 7.8: FTIR-ATR Spectrum for synthesized IL [EMIM][ESO$_4$]

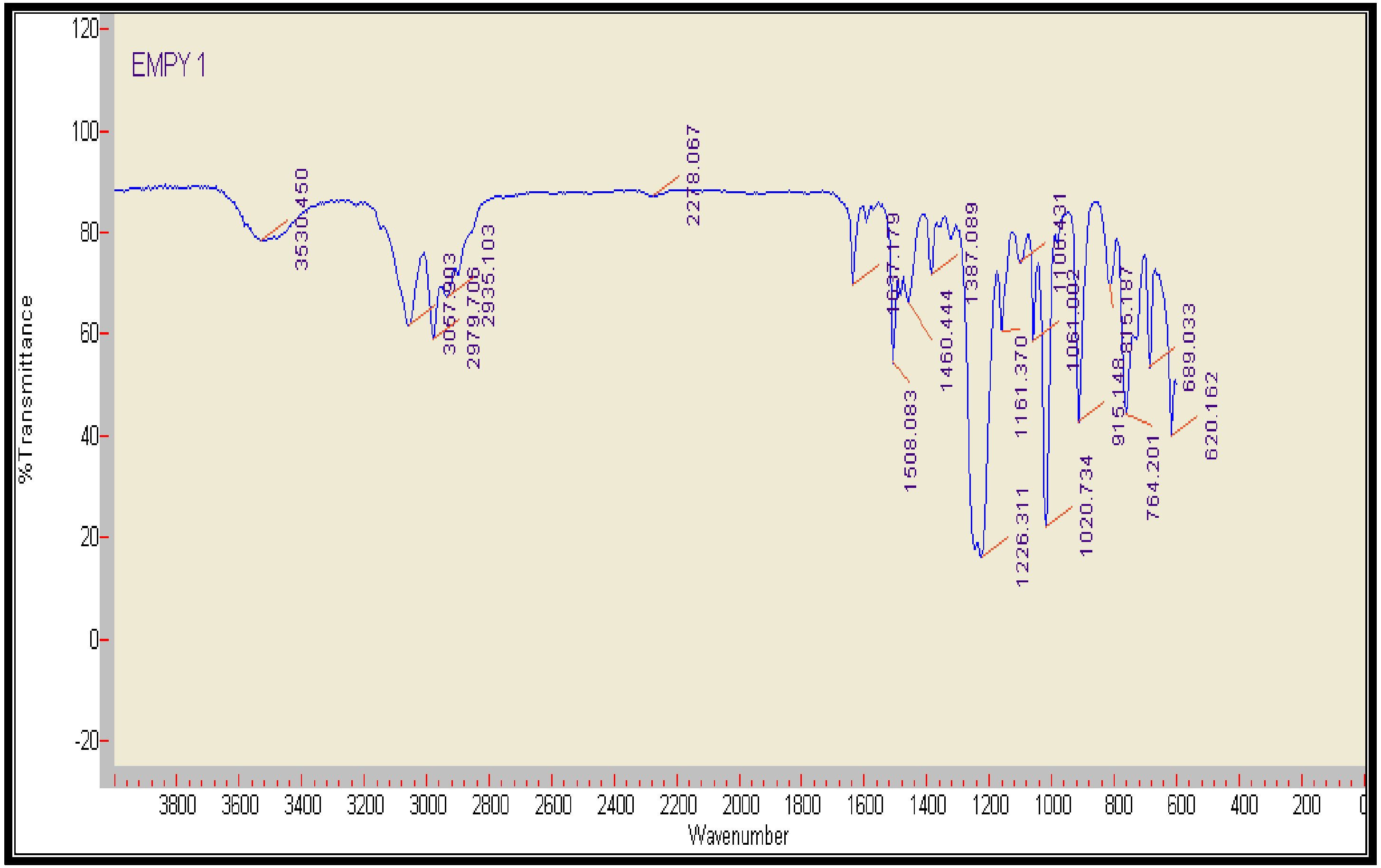

Figure A7.9 Infrared spectrum for the synthesized IL [EMpy][ESO$_4$

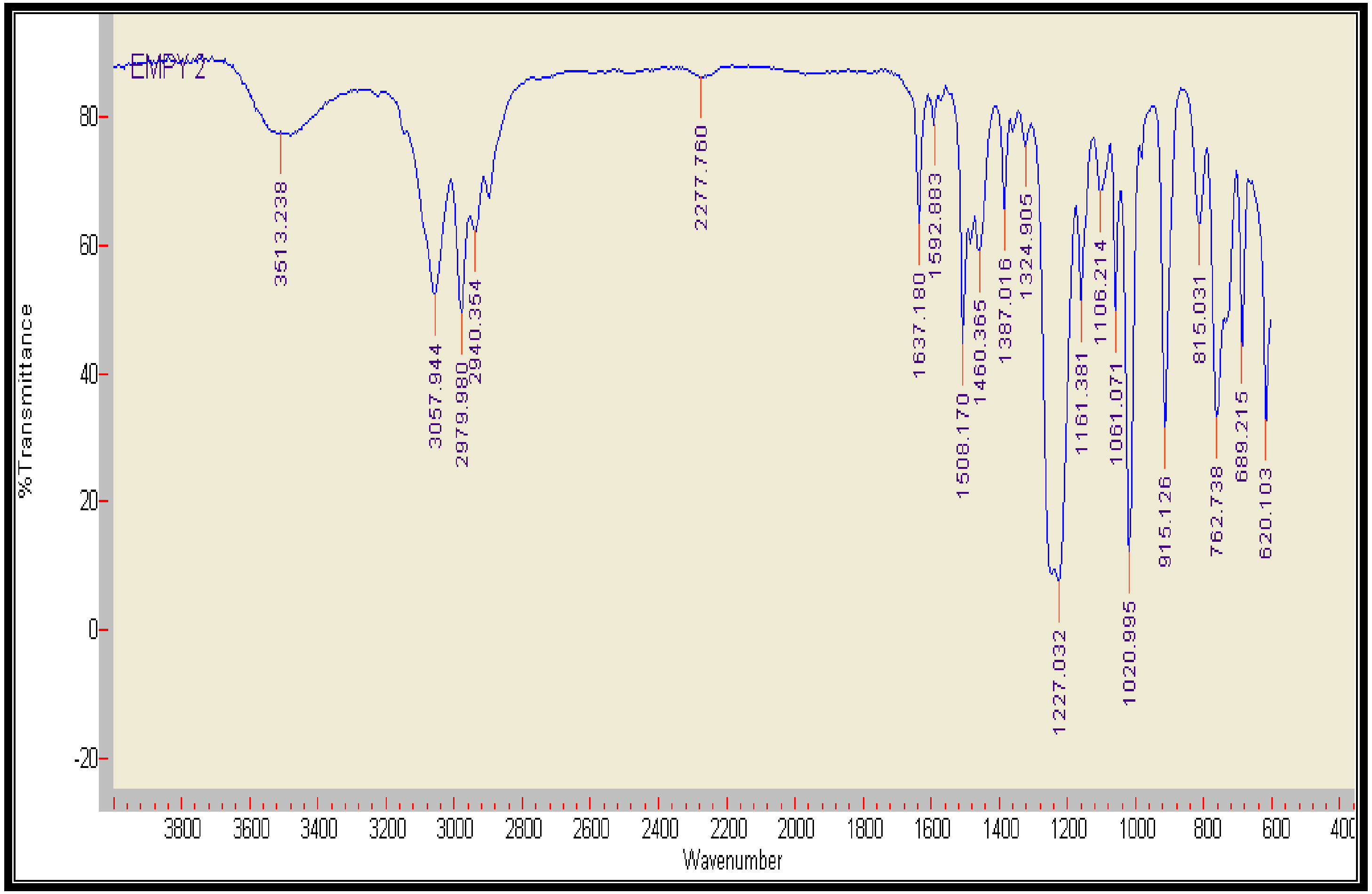

Figure A7.10 Infrared spectrum for the IL regenerated once [EMpy][ESO_4]

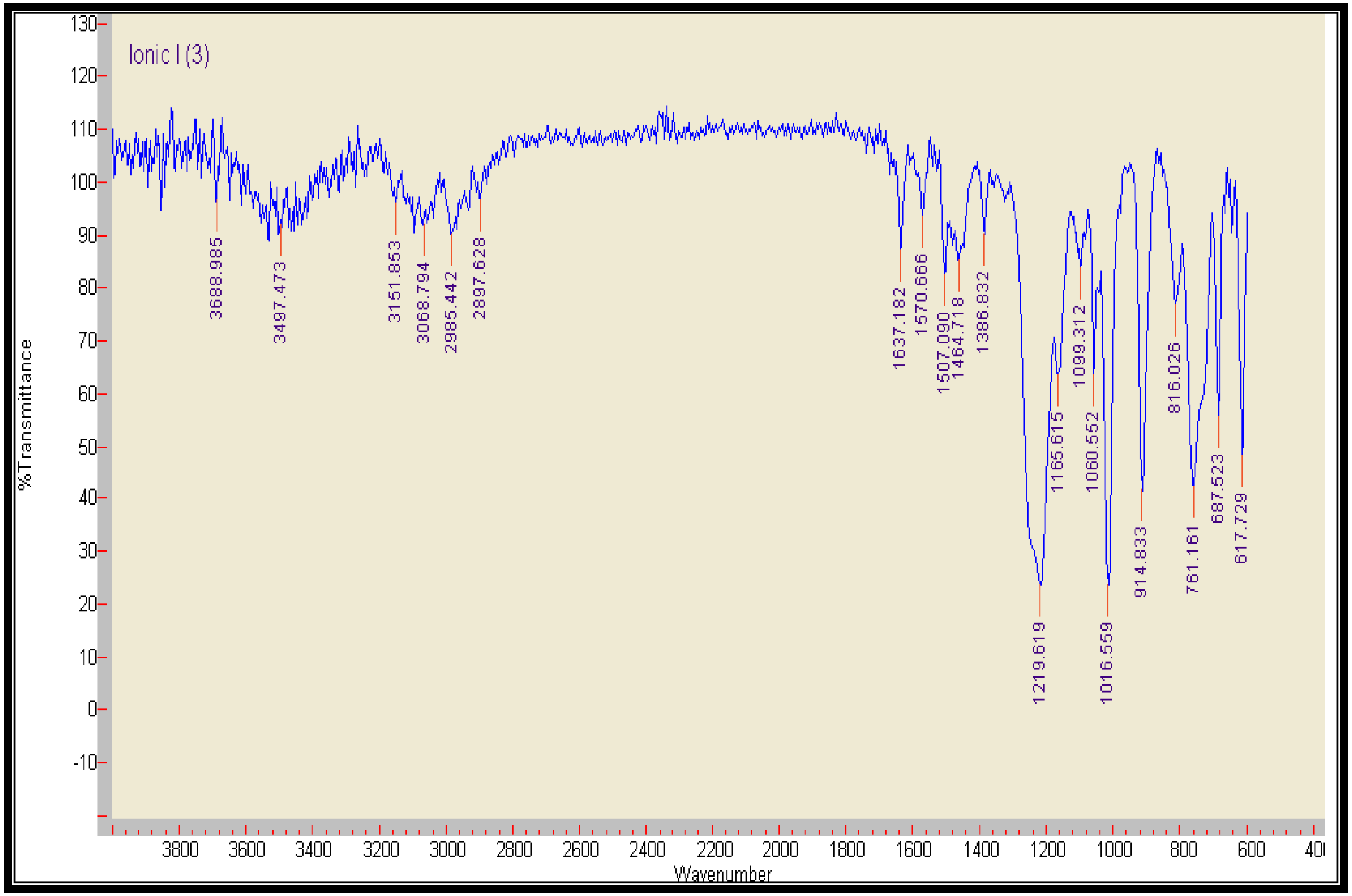

Figure A7.11 Infrared spectrum for the IL regenerated twice [EMpy][ESO$_4$]

Appendix 2: NMR Spectra for Ionic Liquids [EMIM][ESO_4] and [EMpy][ESO_4]

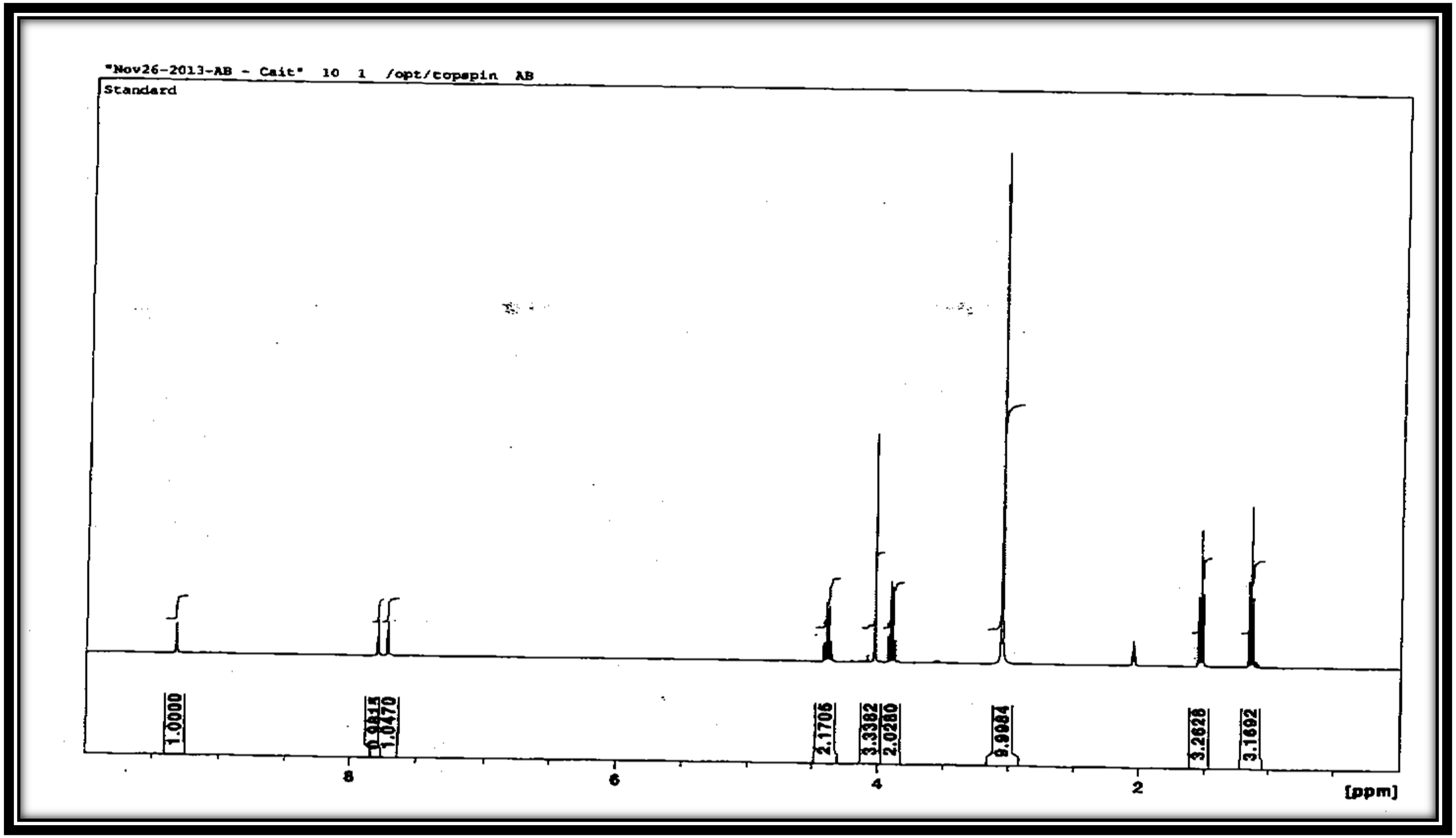

Figure A 7.12:^{1}H NMR spectrum for the IL standard [1] [EMIM][ESO_4]

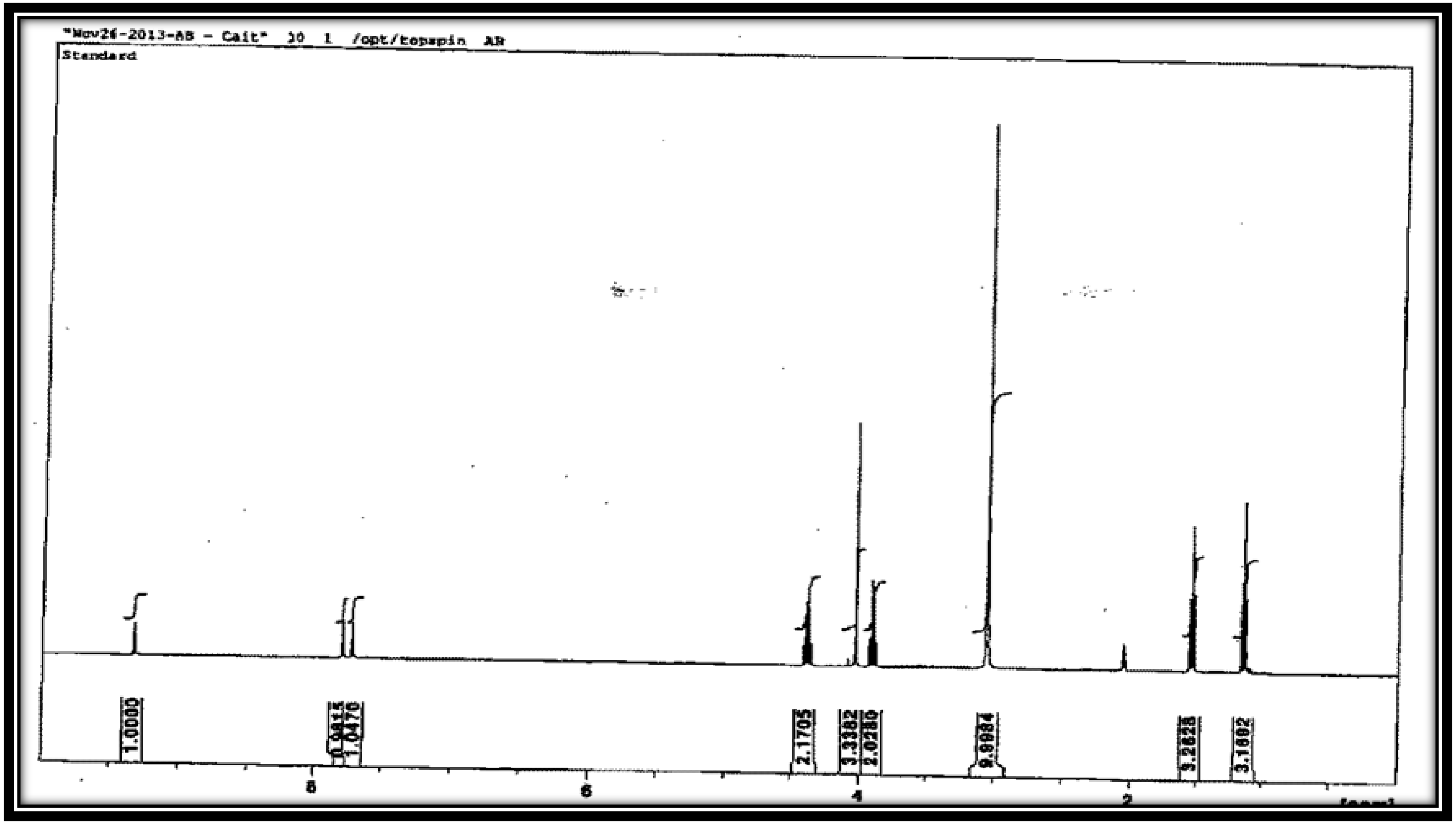

Figure A 7.13: ^{1}H NMR spectrum for the IL standard [2] [EMIM][ESO_4]

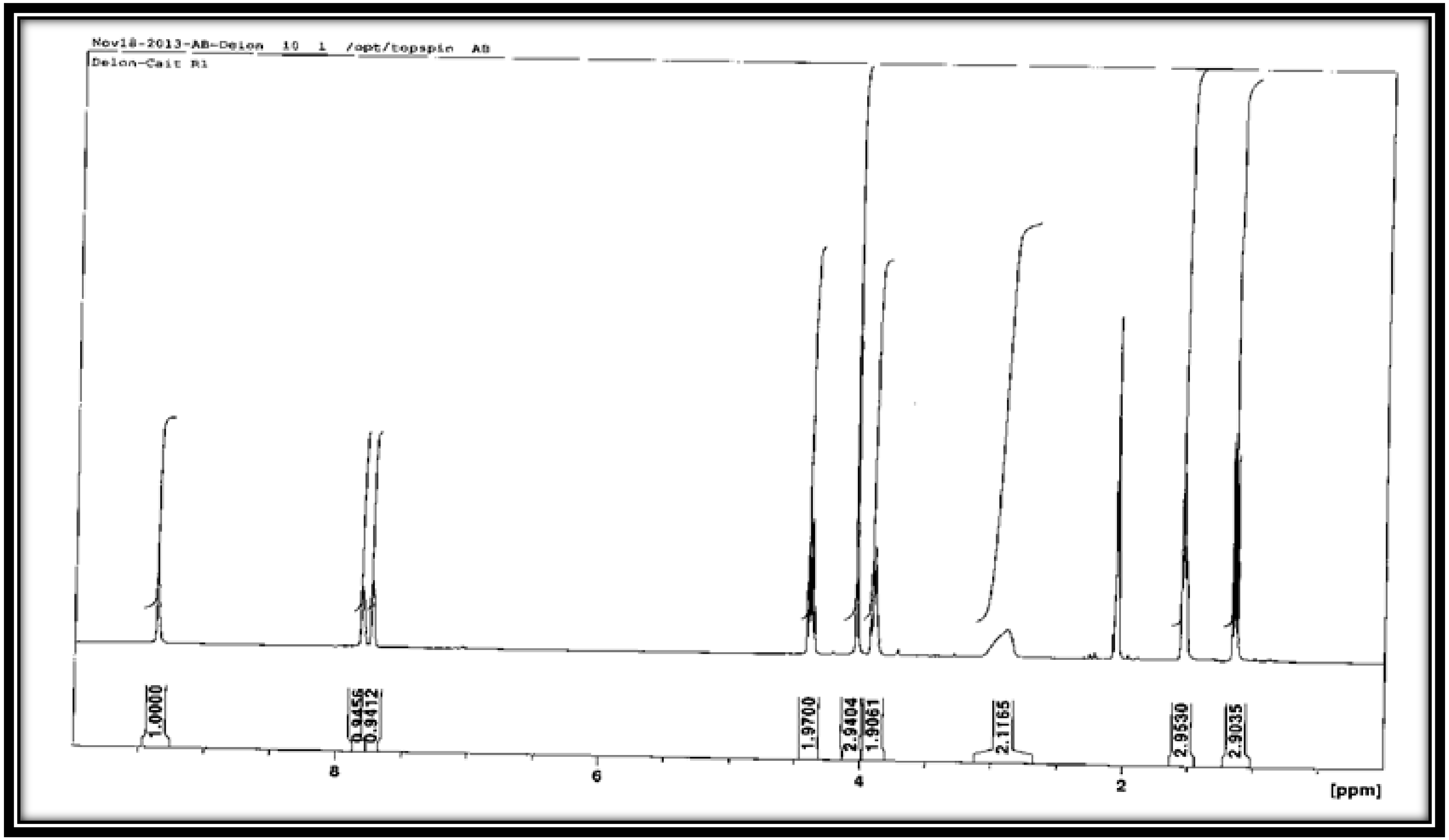

Figure A 7.14: ^{1}H NMR spectrum for the synthesized IL [EMIM][ESO$_4$]

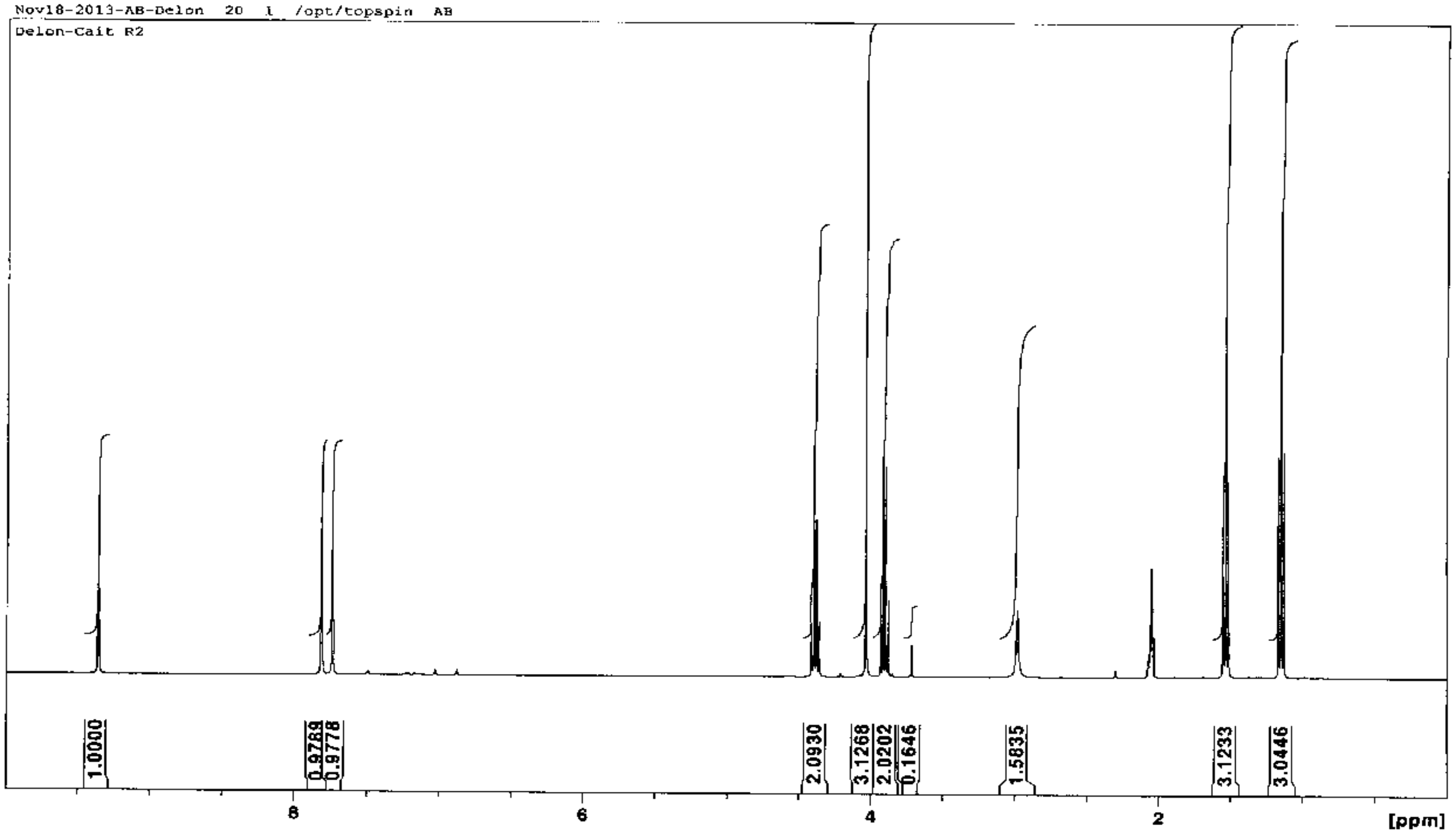

Figure A 7.15: ^{1}H NMR spectrum for the IL regenerated once [EMIM][ESO$_4$]

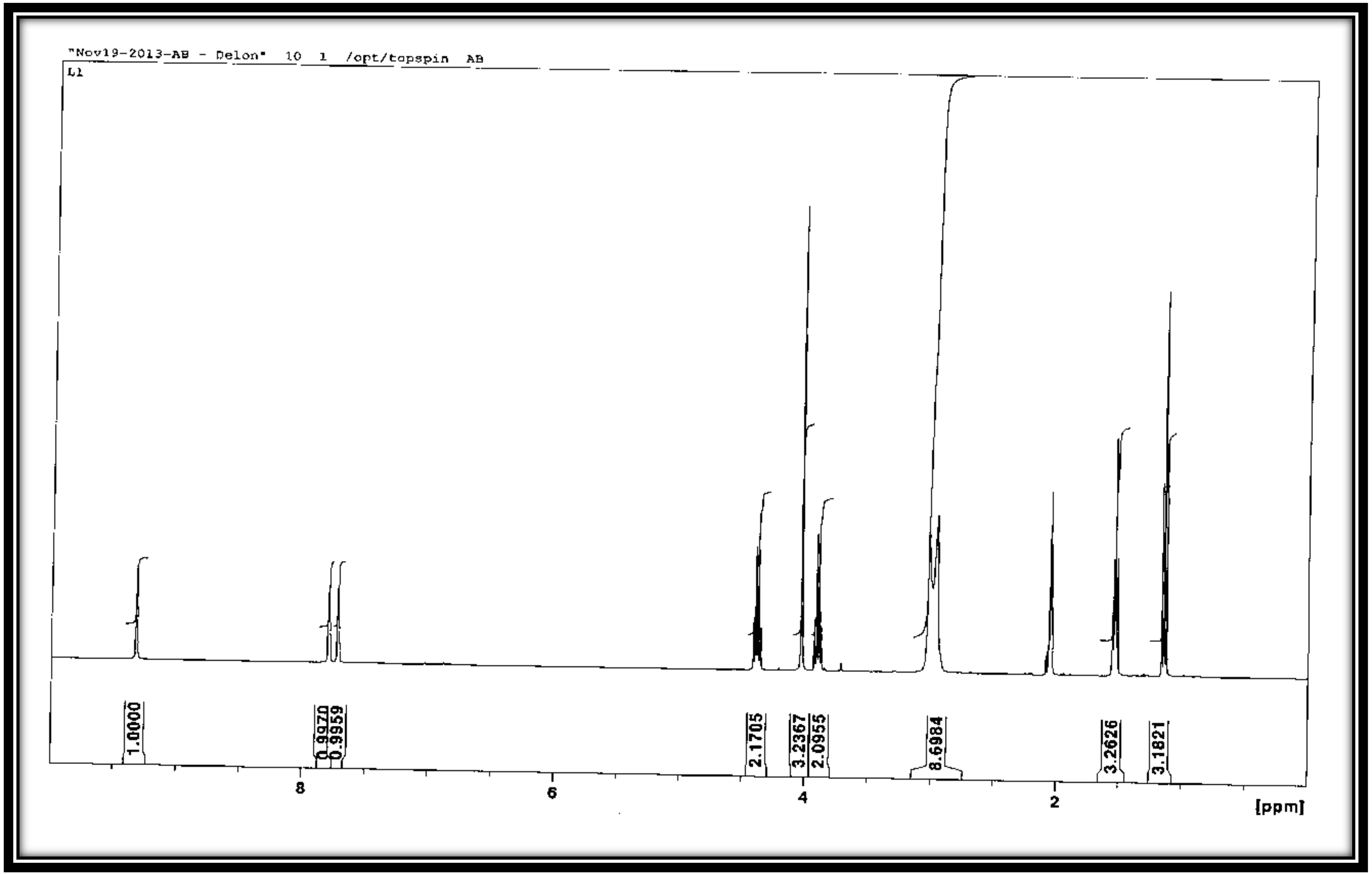

Figure A 7.16: ^{1}H NMR spectrum for the IL regenerated twice [EMIM][ESO$_4$]

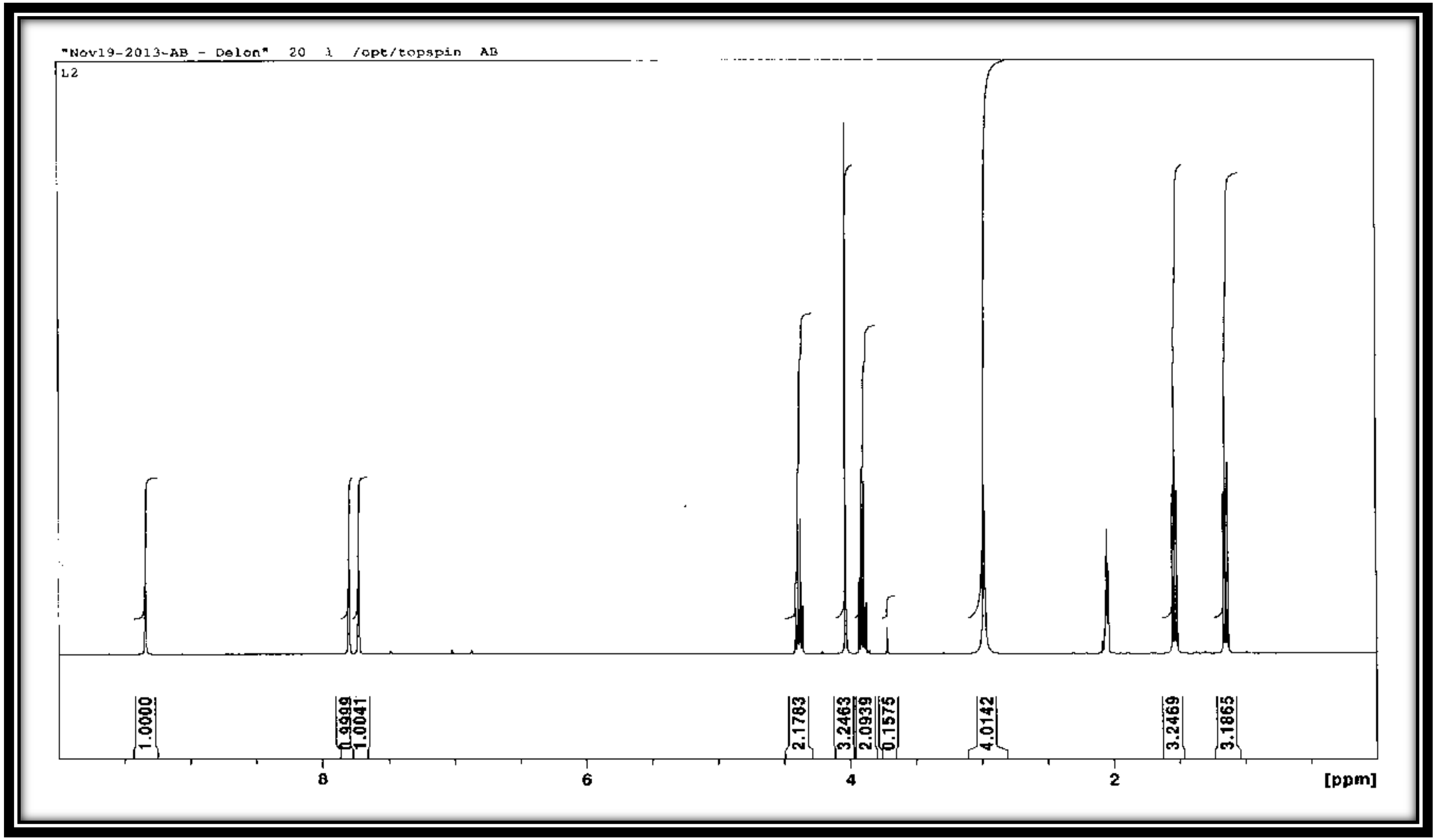

Figure A 7.17: ^{1}H NMR spectrum for the IL regenerated thrice [EMIM][ESO$_4$]

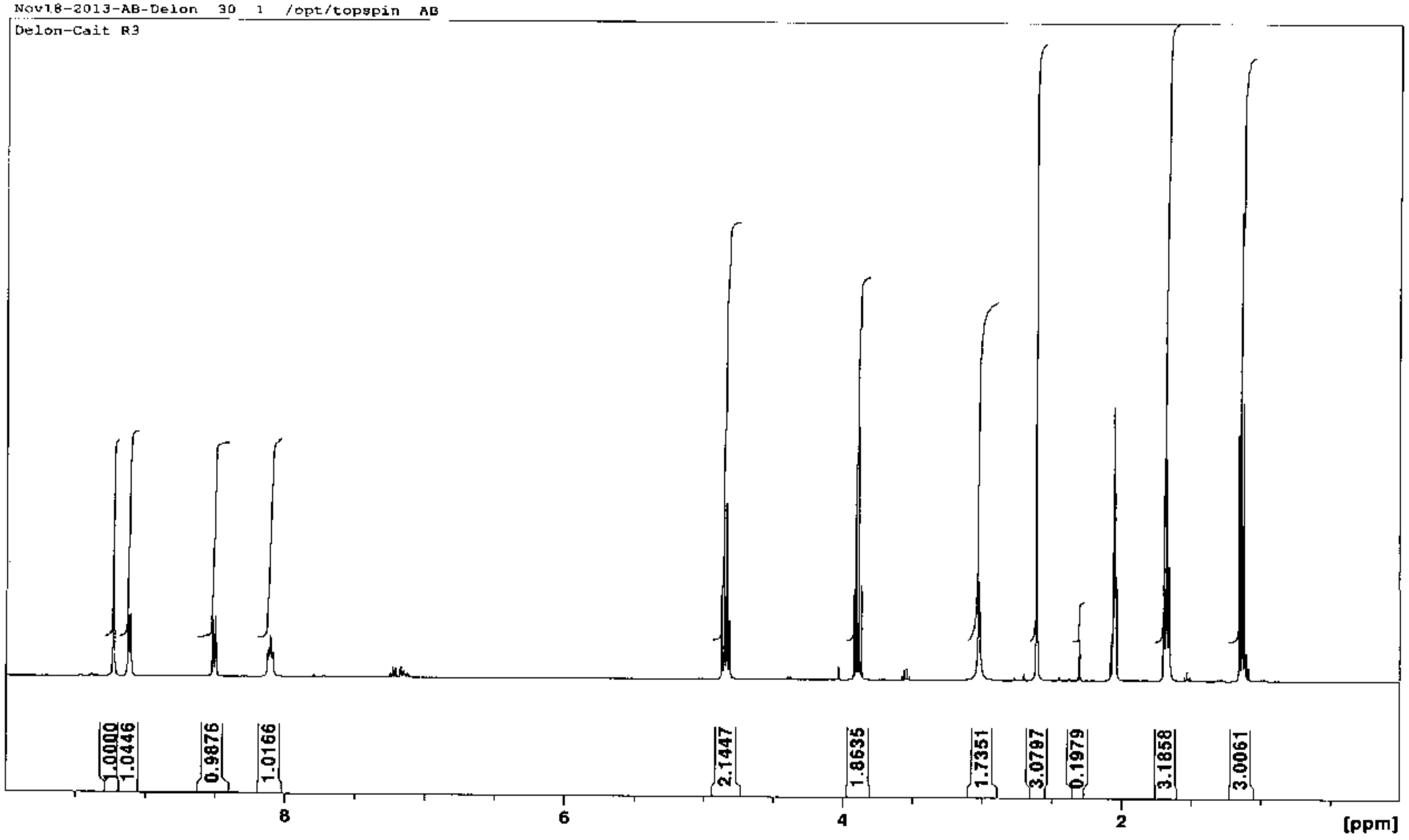

Figure A 7.18: ^{1}H NMR spectrum for the synthesized IL [EMpy][ESO$_4$]

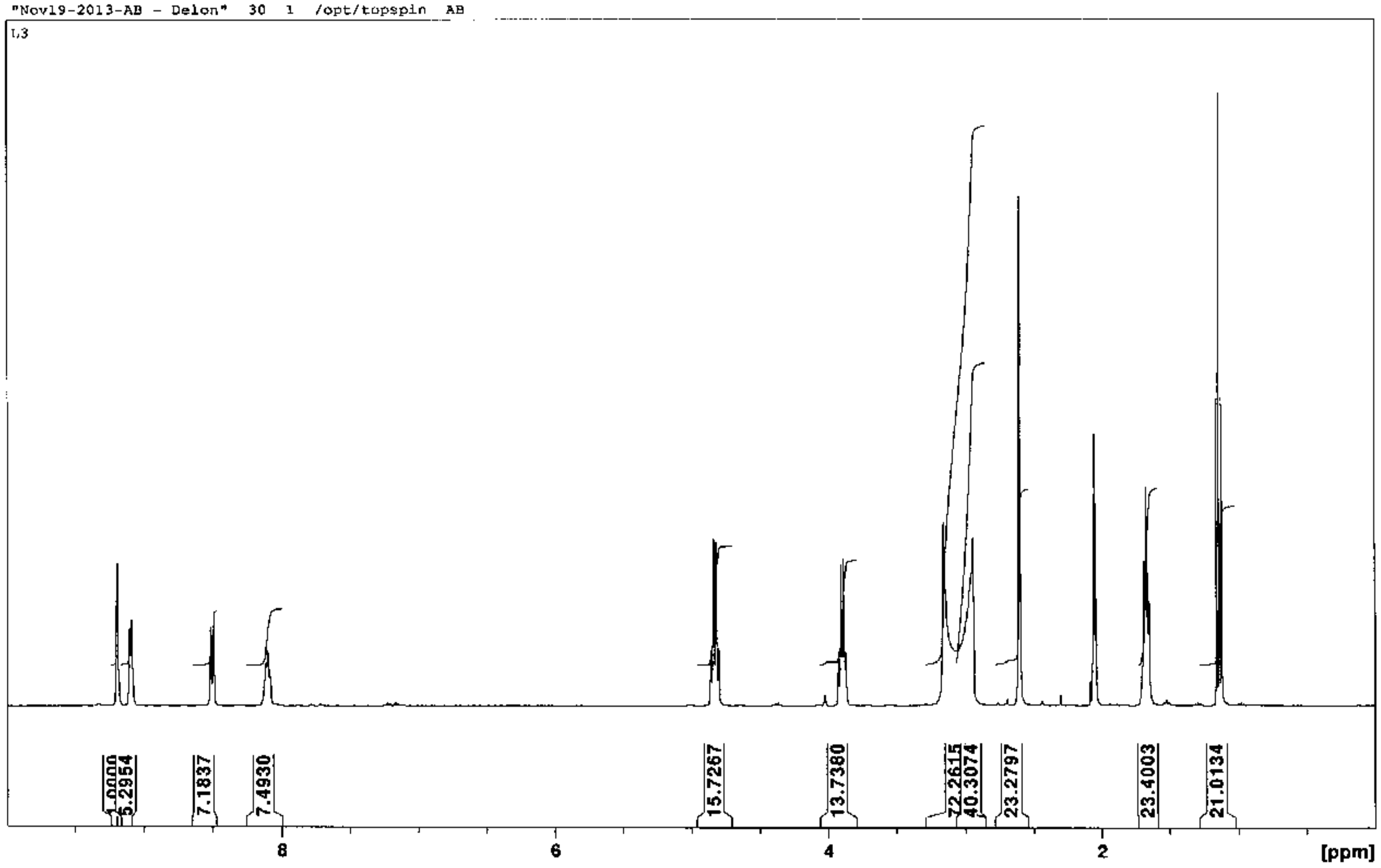

Figure A7.19: ^{1}H NMR spectrum for the IL regenerated once [EMpy][ESO$_4$]

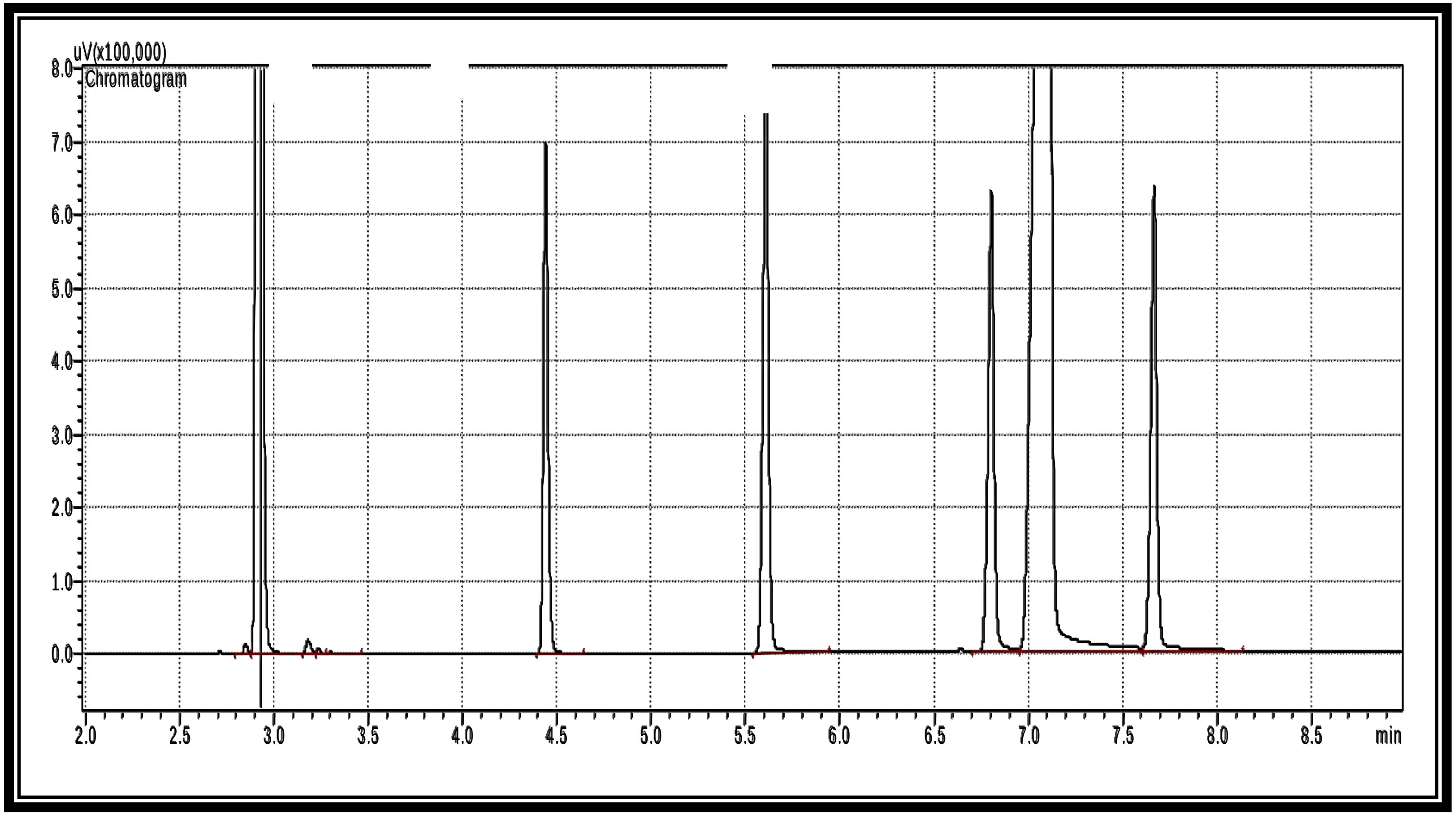

Figure A7.20: BTEX chromatogram for a 7.5 % (v/v) raffinate phase 1 = Benzene, 2 = Toluene, 3 = Ethylbenzene, 4 = o-Xylene

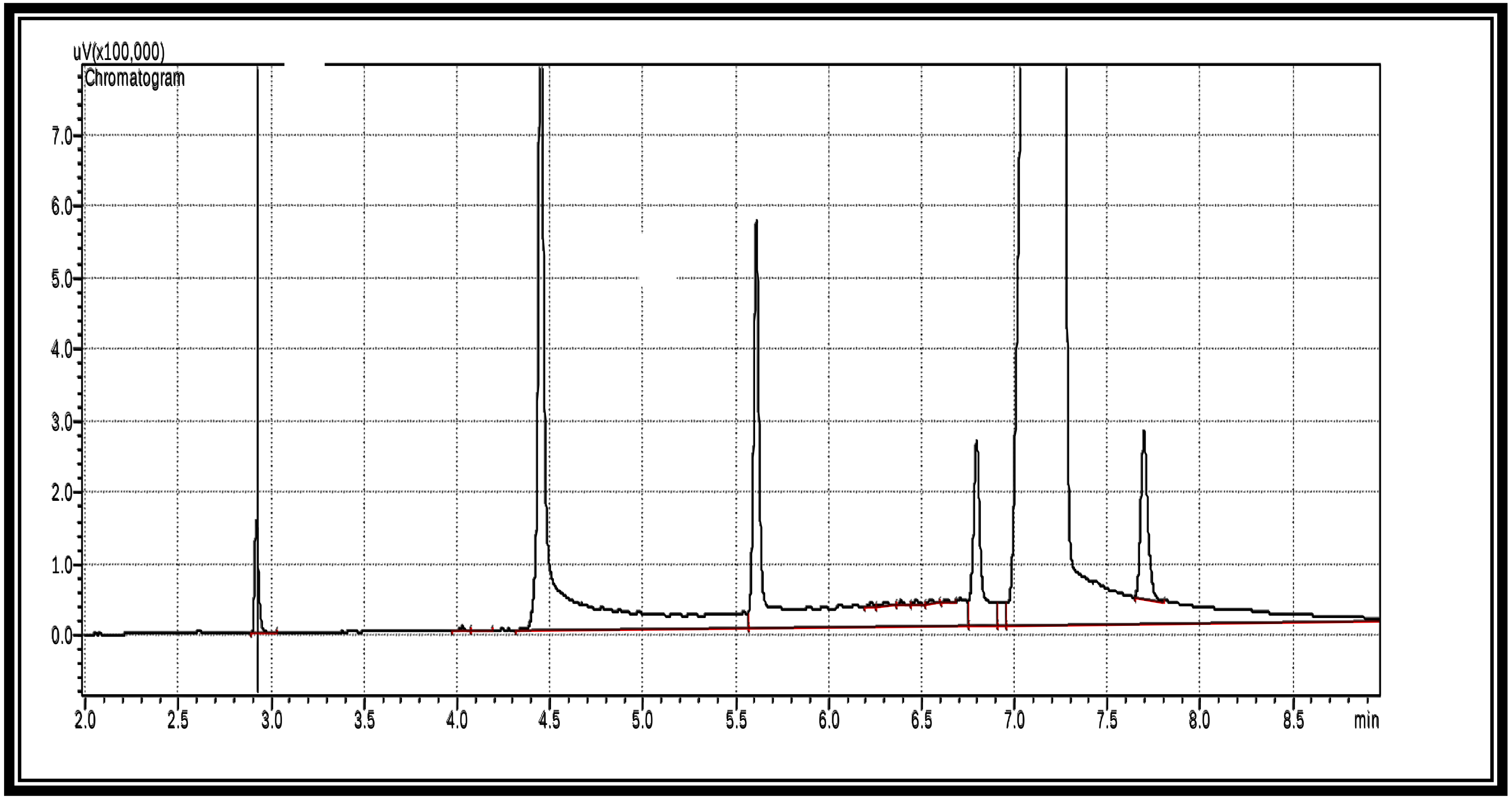

Figure A7.21: BTEX chromatogram for a 7.5 % (v/v) extract phase 1 = Benzene, 2 = Toluene, 3 = Ethylbenzene, 4 = o-Xylene 1= Benzene, 2 = Toluene, 3 = Ethylbenzene, 4 = o-Xylene

Table A7.1: BTEX results for the model mixtures using recycled once [EMIM][ESO$_4$

%Benzene	P/Area Std	P/Area[R]	% in [R]	P/Area[E]	% in [E]	% [R+E]	% Recovery
2.5	558806	392377	1.8	295767	0.7	2.5	100
5.0	1106865	747299	3.5	310233	0.7	4.2	83
7.5	1745653	1113543	5.1	684474	1.5	6.7	89
10.0	2272656	1467752	6.8	927421	2.0	8.8	88
%Toluene	**P/Area Std**	**P/Area[R]**	**% in [R]**	**P/Area[E]**	**% in [E]**	**% [R+E]**	**% Recovery**
0.0	0.0	412777	0	0	0	0	0
2.5	530696	882807	2.2	713386	0.7	2.9	117
5.0	1053671	1415959	4.6	873549	1.0	5.6	112
7.5	1655117	1841049	6.6	1007297	1.2	7.7	103
10.0	2169410	2365025	9.0	1866778	2.5	11.4	114

%E/Benzene	P/Area Std	P/Area[R]	% in [R]	P/Area[E]	% in [E]	% [R+E]	% Recovery
2.5	522505	482484	2.3	458408	0.5	2.8	113
5.0	1037949	1020580	4.7	731047	0.9	5.6	111
7.5	1649056	1473025	6.8	964072	1.1	7.9	105
10.0	2210234	1984950	9.1	1214563	1.4	10.5	105

%o-Xylene	P/Area Std	P/Area[R]	% in [R]	P/Area[E]	% in [E]	% [R+E]	% Recovery
2.5	645012	590256	2.4	346140	0.4	2.8	111
5.0	1147525	1296980	5.1	522017	0.5	5.6	113
7.5	1913568	1540389	6.0	756013	0.8	6.8	90
10.0	2655164	2158977	8.4	996663	1.0	9.4	94

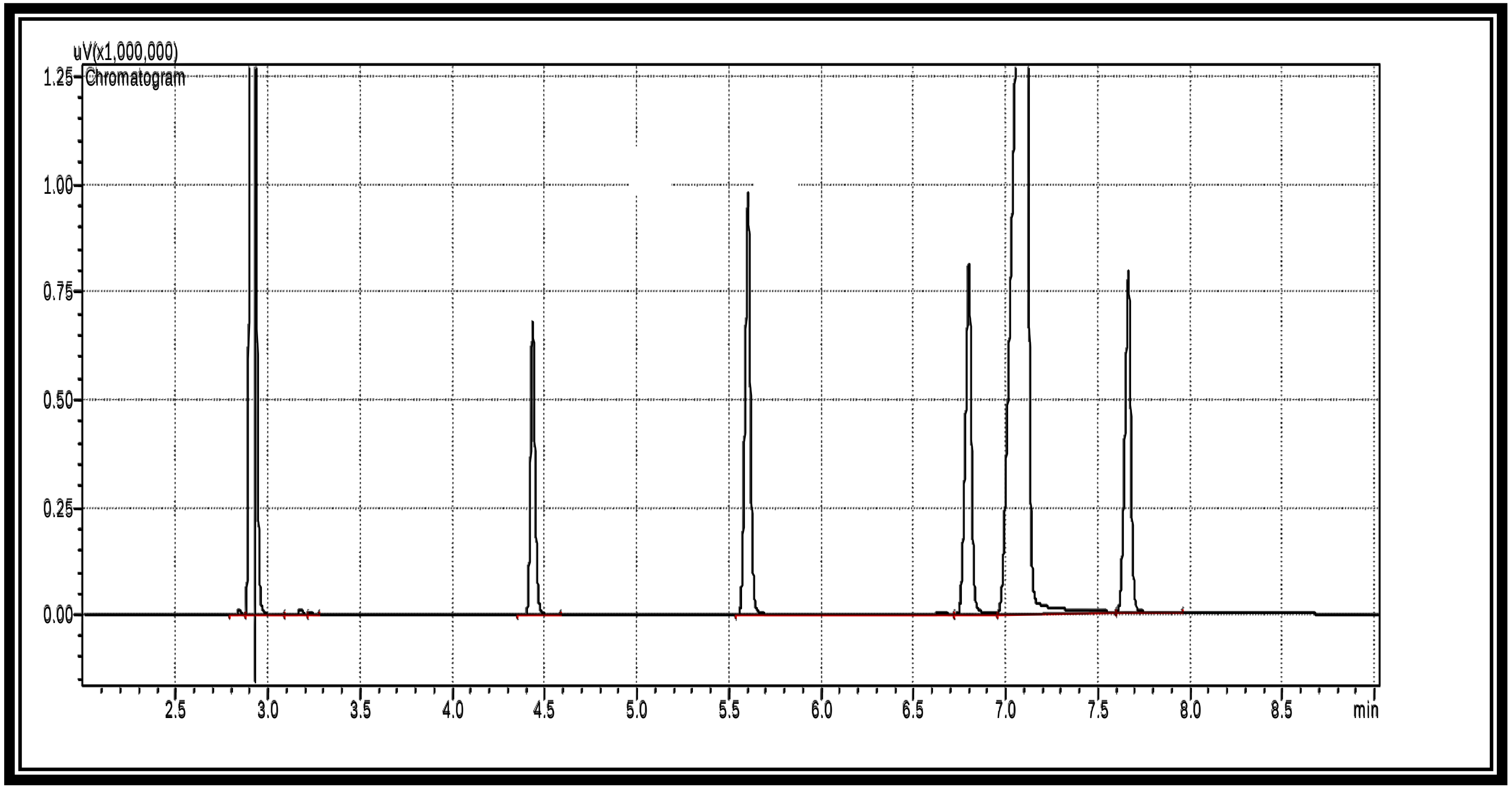

Figure A7.22: BTEX chromatogram for a 10 % (v/v) raffinate phase, 1 = Benzene, 2 = Toluene, 3 = Ethylbenzene, 4 = o-Xylene

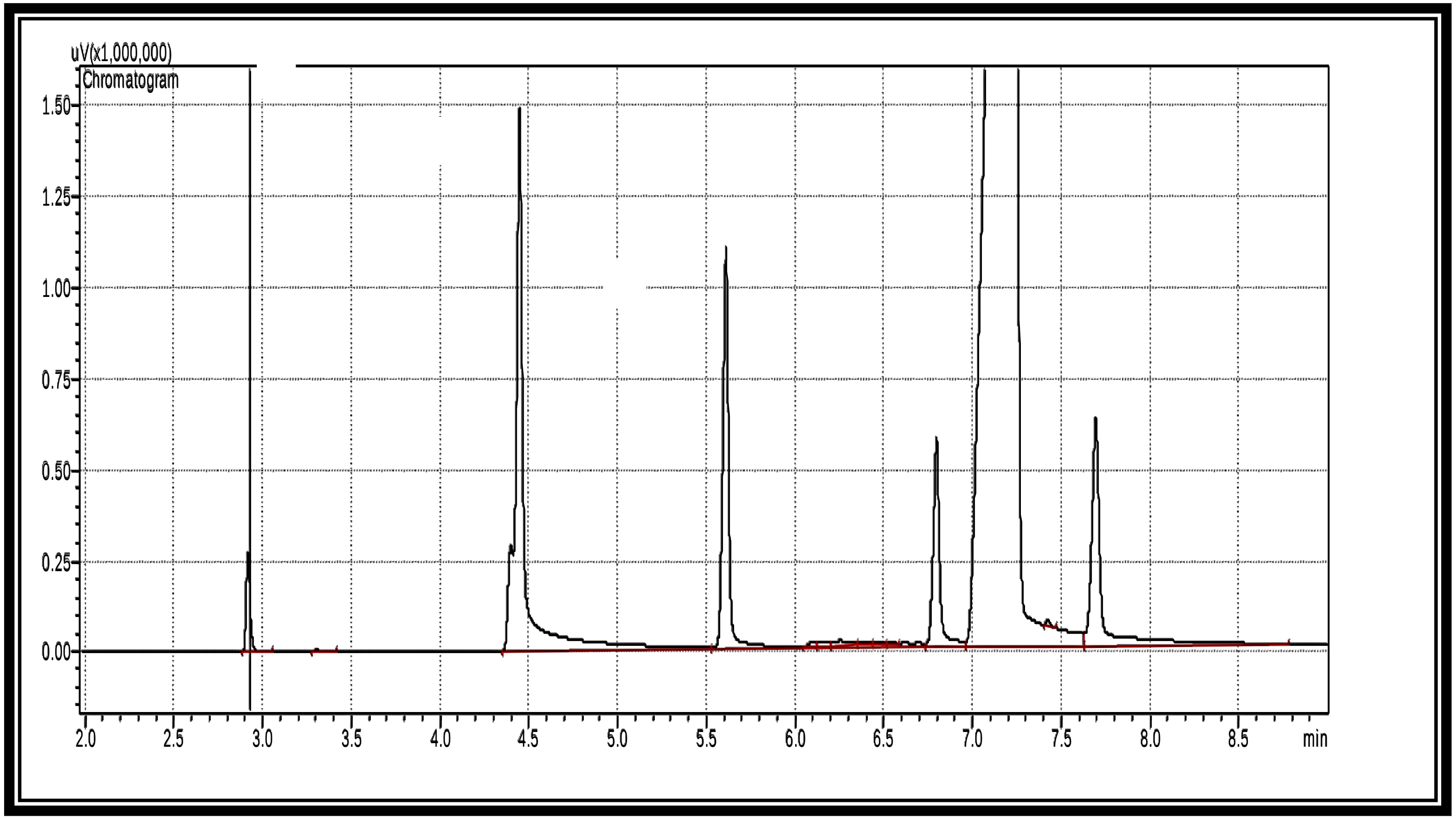

Figure A7.23: BTEX chromatogram for a 10 % (v/v) extract phase 1 = Benzene, 2 = Toluene, 3 = Ethylbenzene, 4 = o-Xylene

Table A7.2: Extractions of Model Mixtures using recycled once [EMpy][ESO$_4$]

%Benzene	P/Area Std	P/Area[R]	% in [R]	P/Area[E]	% in [E]	% [R+E]	% Recovery
2.5	558806	463907	2.1	201598	0.9	3.0	119
5.0	1106865	791893	3.5	426736	1.9	5.4	108
7.5	1745653	1185024	5.2	697938	3.1	8.3	111
10.0	2272656	1515964	6.7	714966	3.2	9.8	98

Toluene	P/Area Std	P/Area[R]	% in [R]	P/Area[E]	% in [E]	% [R+E]	% Recovery
0.0	0.0	362394	0	0	0	0	0
2.5	530696	713415	1.7	820144	1.0	2.6	104
5.0	1053671	1185246	3.8	1034287	1.2	5.0	100
7.5	1655117	1635282	5.9	1432206	1.7	7.5	100
10.0	2169410	2150344	8.2	3129254	3.6	11.8	118

E/Benzene	**P/Area Std**	**P/Area[R]**	**% in [R]**	**P/Area[E]**	**% in [E]**	**% [R+E]**	**% Recovery**
2.5	522505	397433	1.9	417475	0.5	2.4	96
5.0	1037949	847003	3.9	597463	0.7	4.6	93
7.5	1649056	1375378	6.3	797142	0.9	7.2	97
10.0	2210234	1881693	8.6	952153	1.1	9.7	97
%o-Xylene	**P/Area Std**	**P/Area[R]**	**% in [R]**	**P/Area[E]**	**% in [E]**	**% [R+E]**	**% Recovery**
2.5	645012	396547	1.7	251476	0.3	2.0	78
5.0	1147525	881006	3.5	402197	0.4	3.9	79
7.5	1913568	1429725	5.6	601289	0.6	6.2	83
10.0	2655164	1916515	7.4	740433	0.7	8.2	82

Appendix 5: Multi-Component Mixtures Extractions: BTEX +*n*-Hexane+ [BNMP][Br]/[MNMP][I]

Table A7.3: BTEX concentration in in the extract and raffinate Phases

Ionic Liquids	**Benzene**	**Raffinate Phase [R]**			**Extract Phase [E]**			**[R+E]**
	% (v/v)	P/Area	% (v/v)	% (v/v)	P/Area	% (v/v)	% (v/v)	% (v/v)
[BNMP][Br]	0.5	84195	0.2	48	135949	0.3	54	102
[BNMP][Br]	10.0	3811766	7.3	73	1365466	3.4	34	107
[MNMP][I]	10.0	2913362	5.9	59	1684049	3.9	39	98

Ionic Liquids	**Toluene**	**Raffinate Phase [R]**			**Extract Phase [E]**			[R+E]
	% (v/v)	P/Area	% (v/v)	% (v/v)	P/Area	% (v/v)	% (v/v)	% (v/v)
[BNMP][Br]	0.5	92747	0.4	87	55303	0.2	39	126
[BNMP][Br]	10.0	2402261	6.6	66	1019315	3.8	38	104
[MNMP][I]	10.0	2778394	6.0	60	984237	2.8	28	88

Ionic Liquids	**E/Benzene**	**Raffinate Phase [R]**			**Extract Phase [E]**			[R+E]
	% (v/v)	P/Area	% (v/v)	% (v/v)	P/Area	% (v/v)	% (v/v)	% (v/v)
[BNMP][Br]	0.5	106007	0.4	80	41192	0.2	44	124
[BNMP][Br]	10.0	2626238	6.3	63	803317	3.1	31	94
[MNMP][I]	10.0	3152734	7.2	72	738267	2.9	29	102

Ionic Liquids	**p-Xylene**	**Raffinate Phase [R]**			**Extract Phase [E]**			[R+E]
	% (v/v)	P/Area	% (v/v)	% (v/v)	P/Area	% (v/v)	% (v/v)	% (v/v)
[BNMP][Br]	0.5	105894	0.4	83	37703	0.2	43	126
[BNMP][Br]	10.0	2588522	6.2	62	772419	3.0	30	93
[MNMP][I]	10.0	3085653	7.1	71	734917	2.9	29	101

Ionic Liquids	**m-Xylene**	**Raffinate Phase [R]**			**Extract Phase [E]**			[R+E]
	% (v/v)	P/Area	% (v/v)	% (v/v)	P/Area	% (v/v)	% (v/v)	% (v/v)
[BNMP][Br]	0.5	112021	0.4	78	37519	0.2	43	121
[BNMP][Br]	10.0	2646693	6.3	63	817665	3.1	31	94
[MNMP][I]	10.0	4673418	8.2	82	803608	1.9	19	101

Ionic Liquids	**o-Xylene**	**Raffinate Phase [R]**			**Extract Phase [E]**			[R+E]
	% (v/v)	P/Area	% (v/v)	% (v/v)	P/Area	% (v/v)	% (v/v)	% (v/v)
[BNMP][Br]	0.5	101613	0.4	78	44566	0.2	44	122
[BNMP][Br]	10.0	2594653	6.1	61	858041	3.1	31	91
[MNMP][I]	10.0	3078713	6.9	69	808612	3.0	30	99

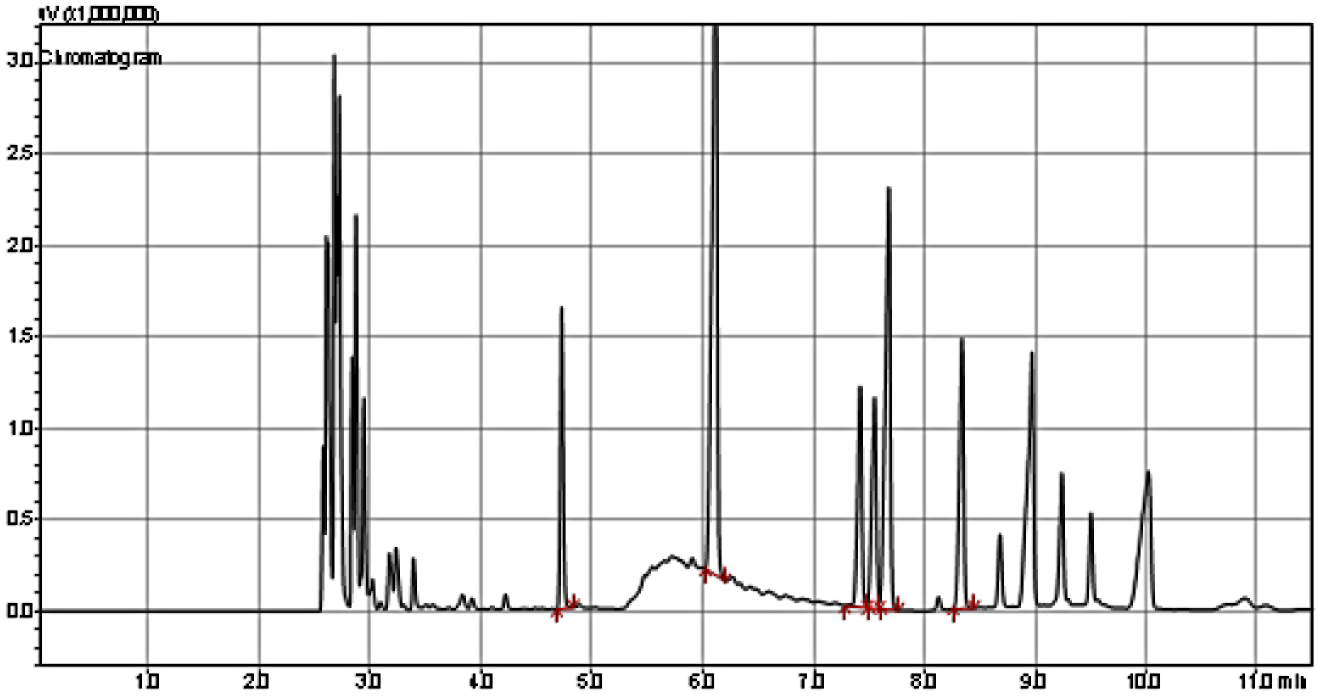

Figure A7.24: Chromatogram of Reformate Sample

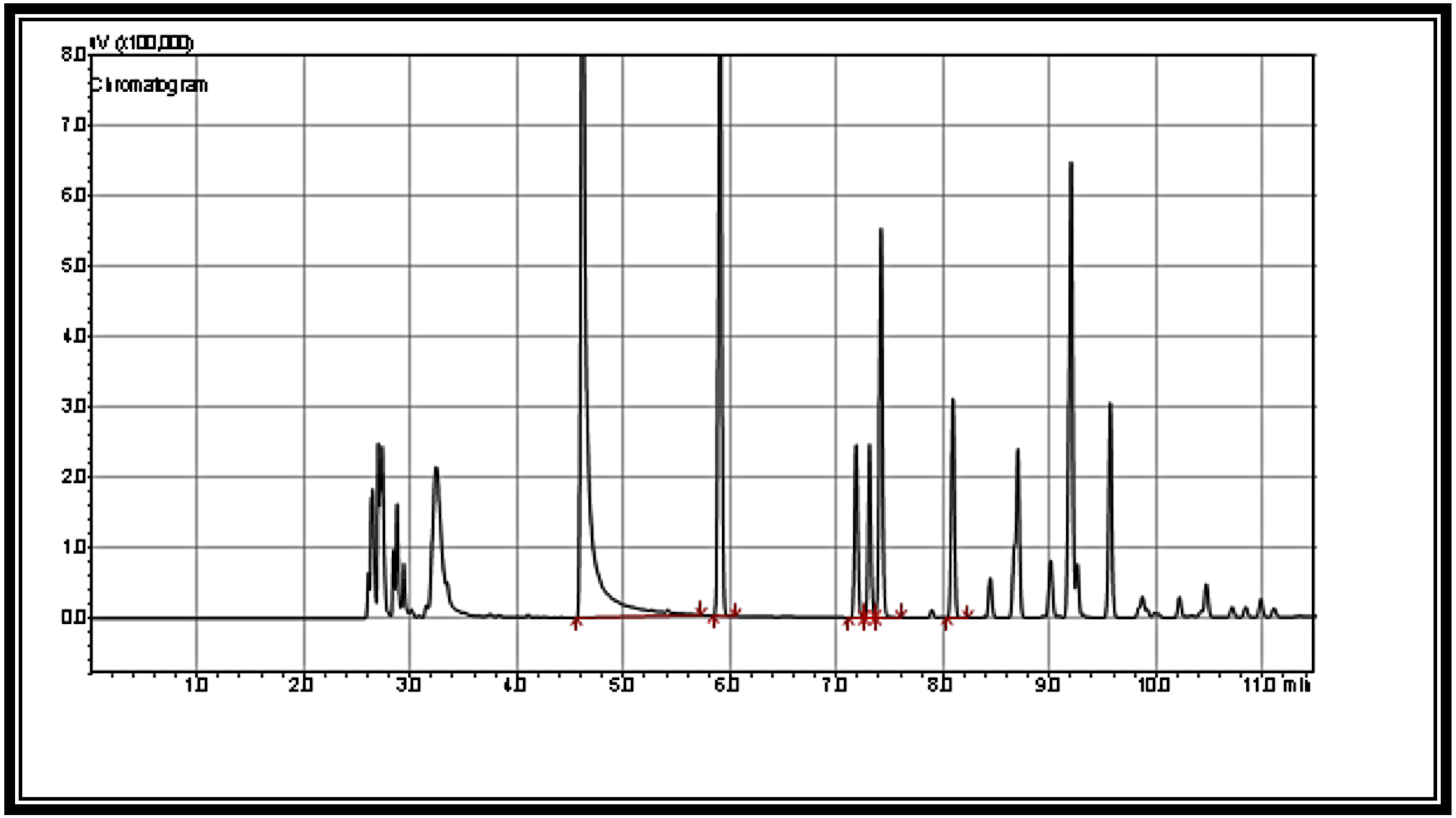

Figure A7.25: Extract Phase for Reformate Extraction using [BNMP]

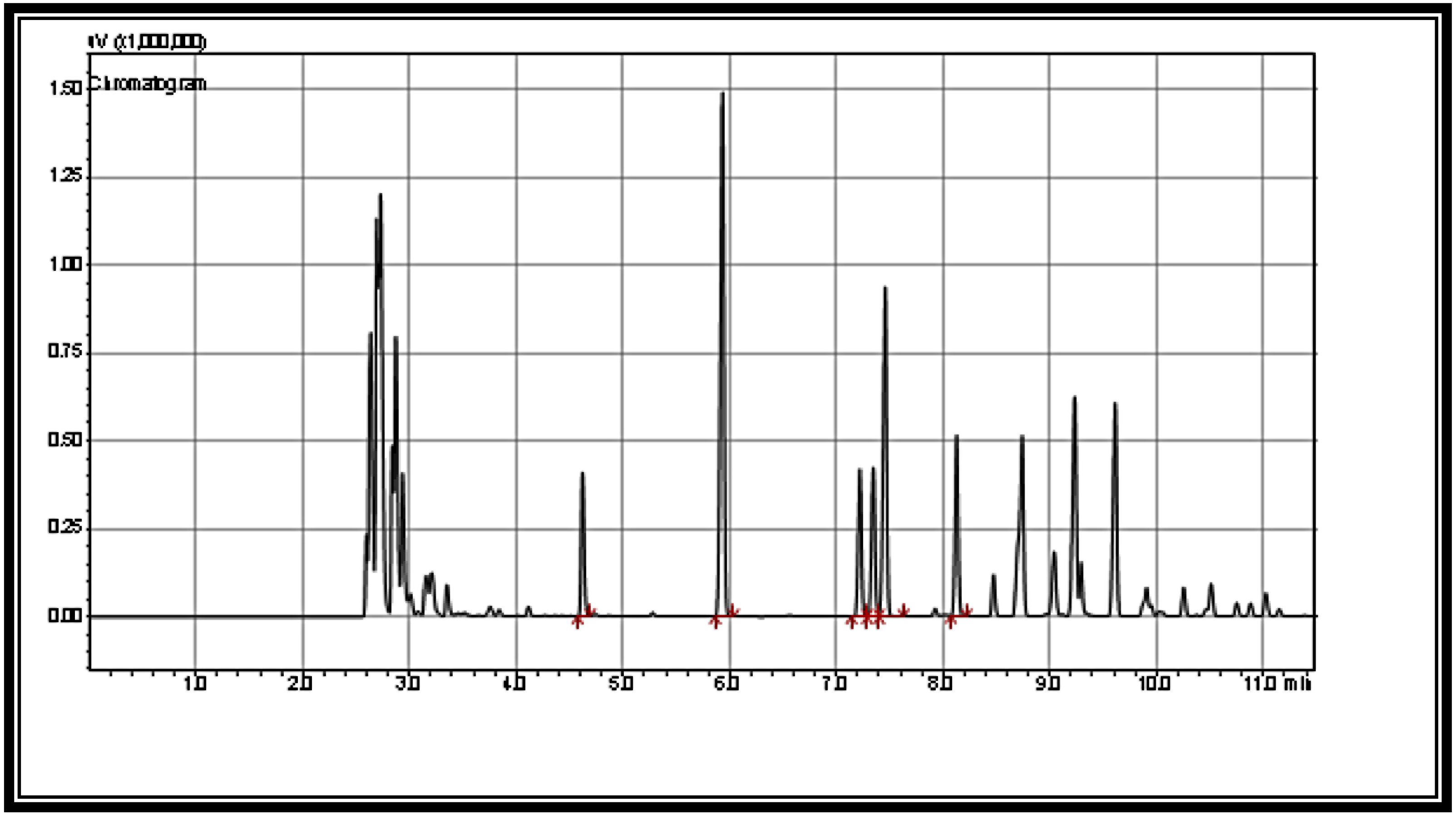

Figure A7.26: Raffinate Phase for Reformate Extraction using [BNMP]

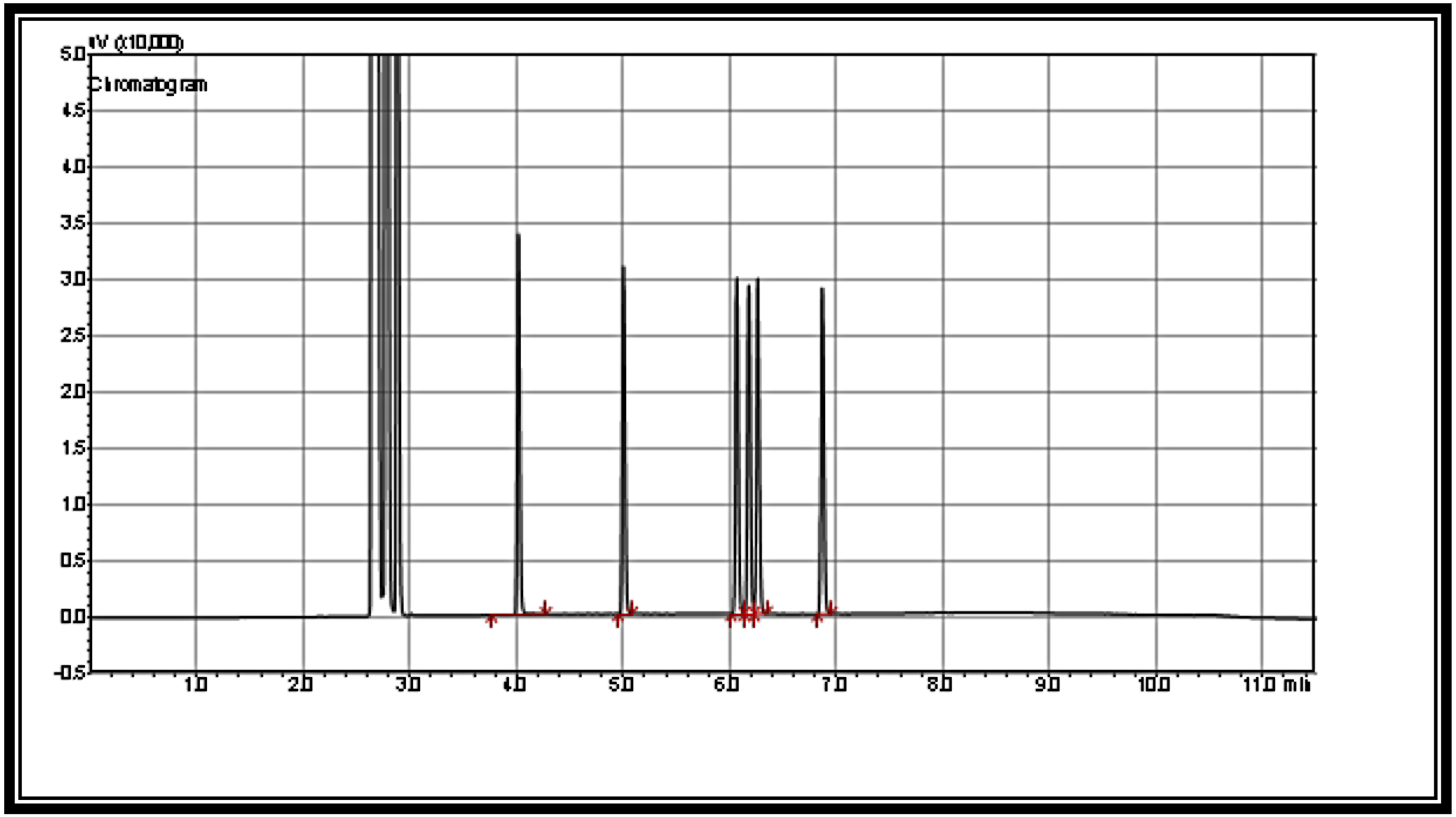

Figure A7.27: Chromatogram for a 0.5 % (v/v) BTEX Calibration Standard

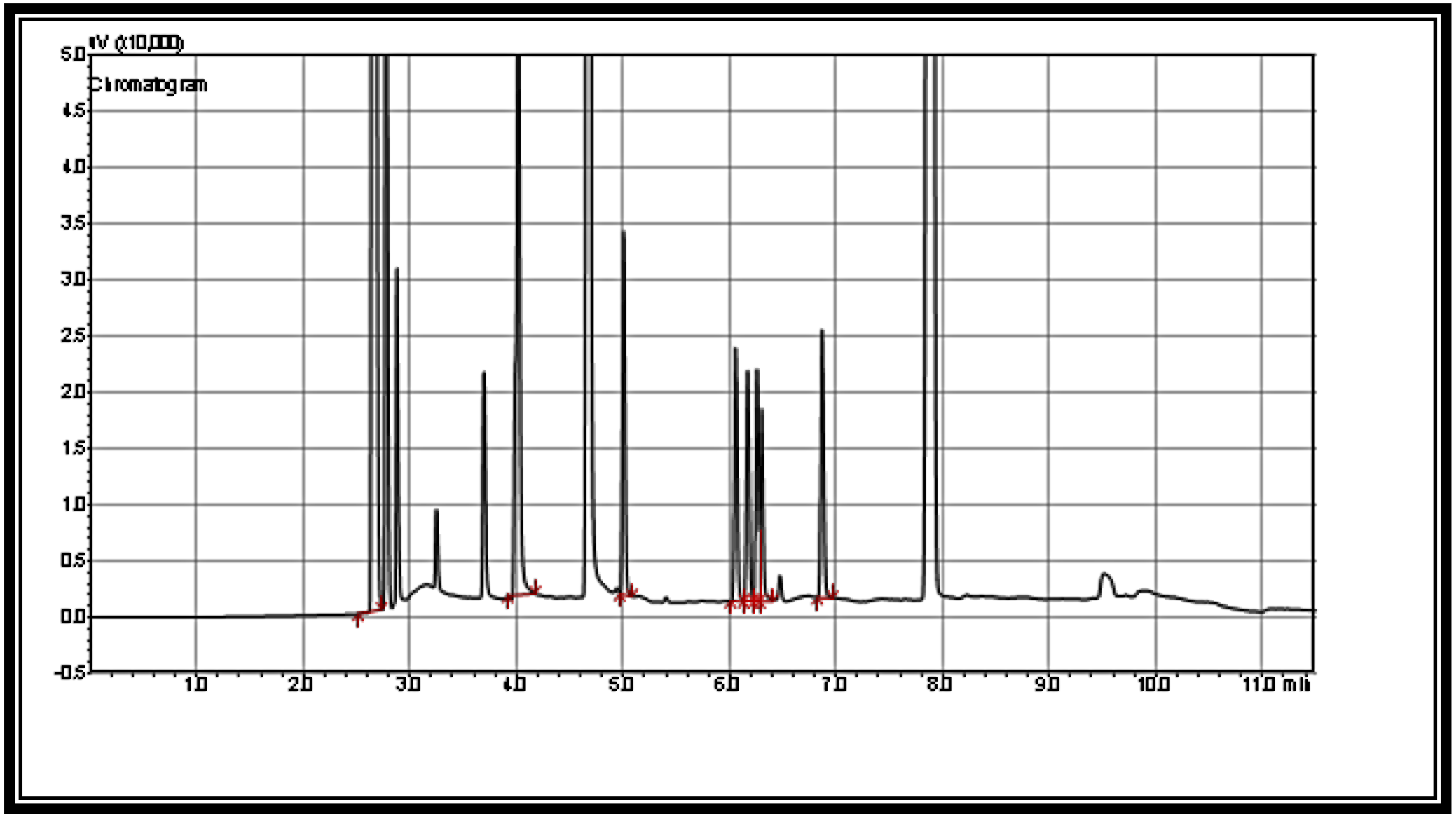

Figure A7.28: Extract Phase for a 0.5 % (v/v) model mixture extraction using [BNMP]

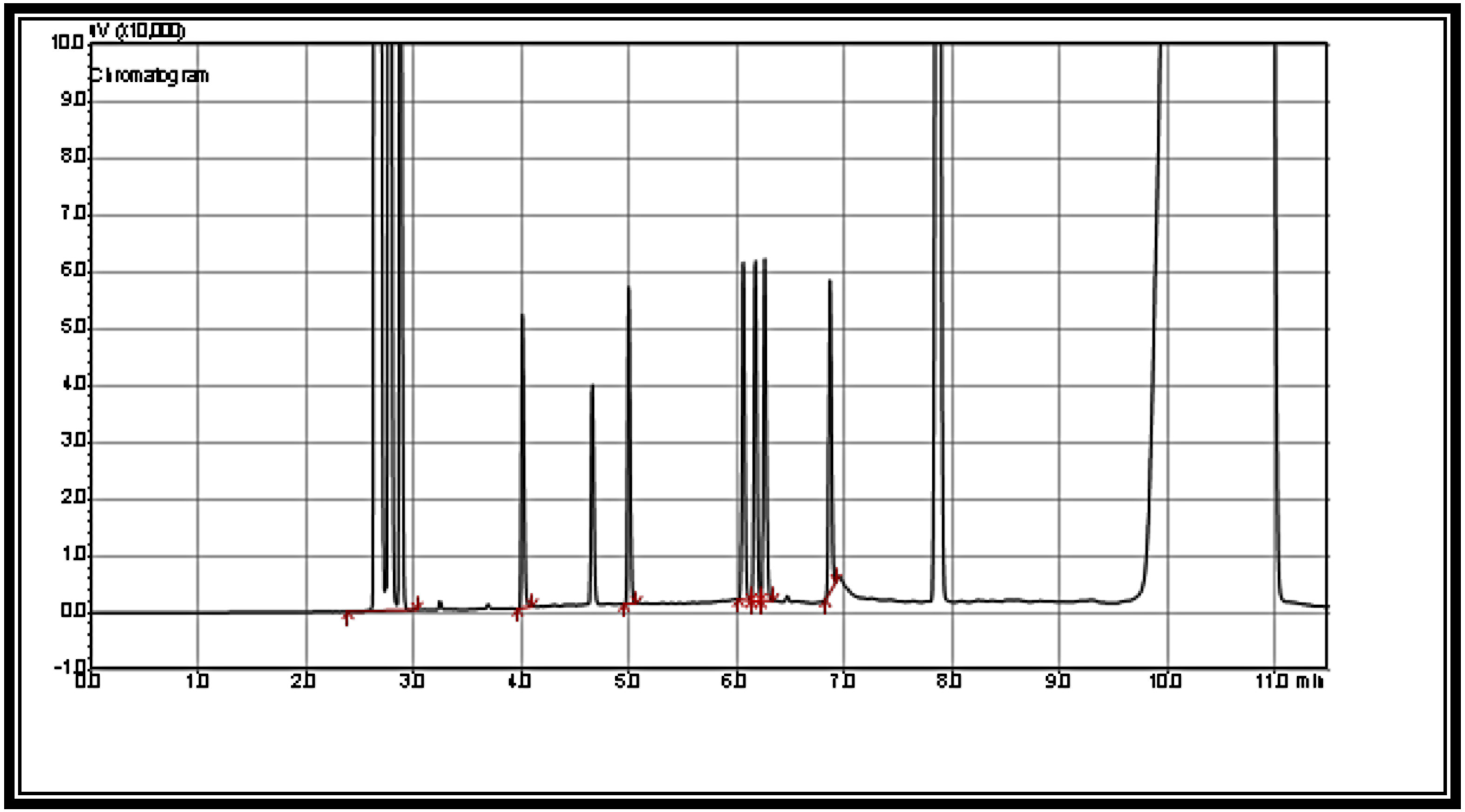

Figure A7. 29: Raffinate Phase for a 0.5 % (v/v) model mixture extraction using [BNMP]

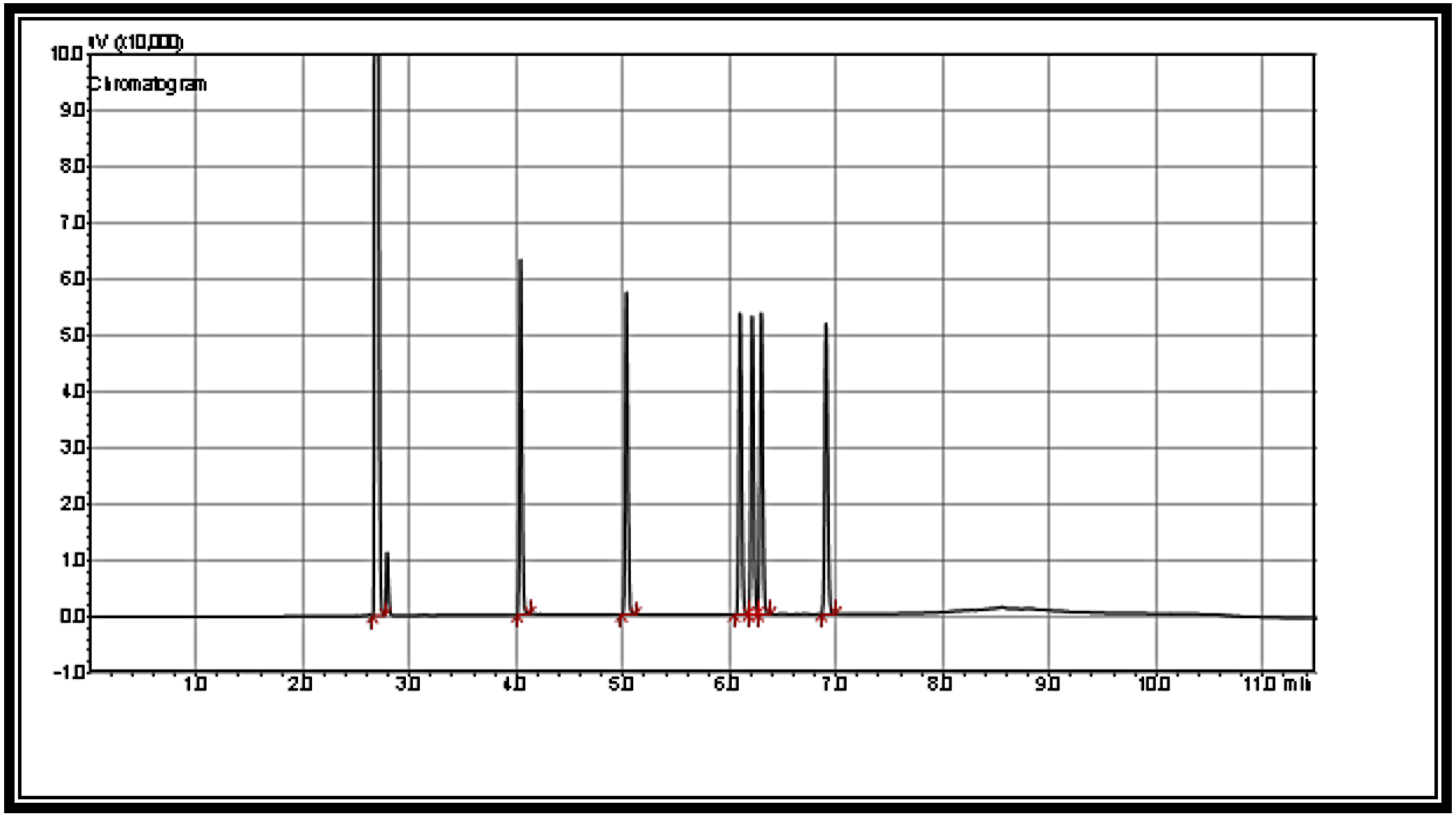

Figure A 7.30: Chromatogram for a 2.5 % (v/v) BTEX Calibration Standard

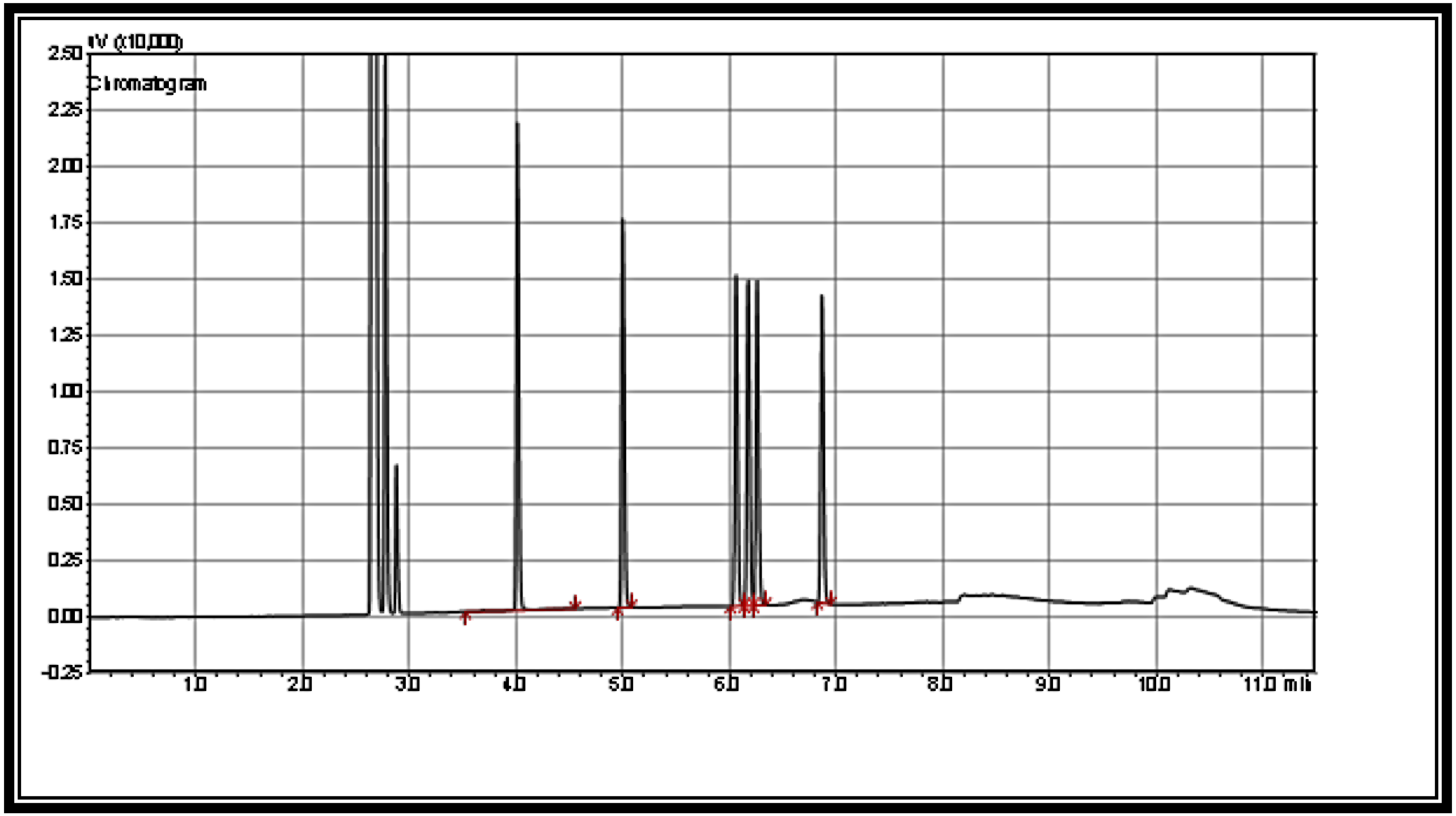

Figure A7.31: Chromatogram for a 5 % (v/v) BTEX Calibration Standard

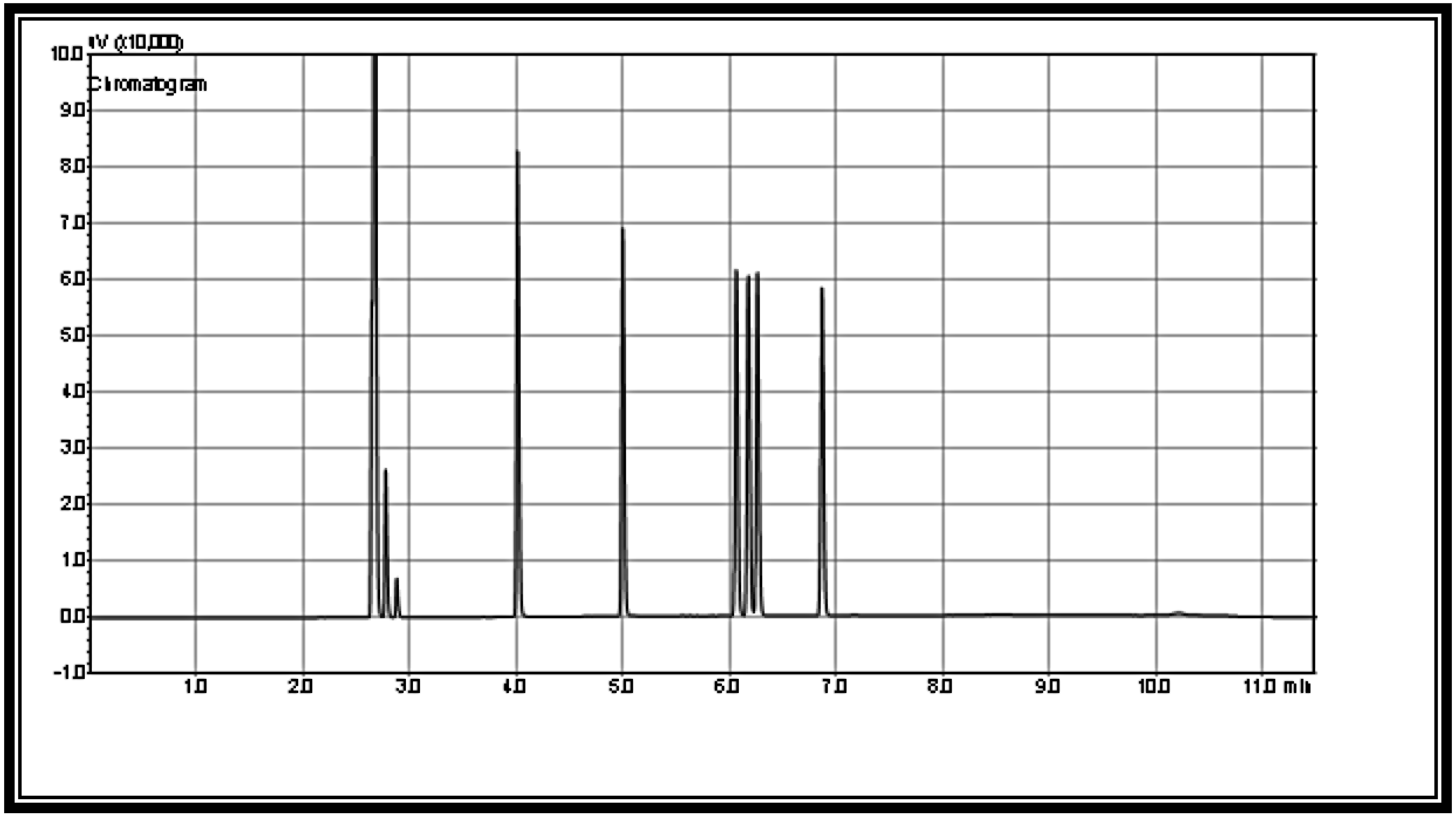

Figure A7.32: Chromatogram for a 10 % (v/v) BTEX Calibration Standard

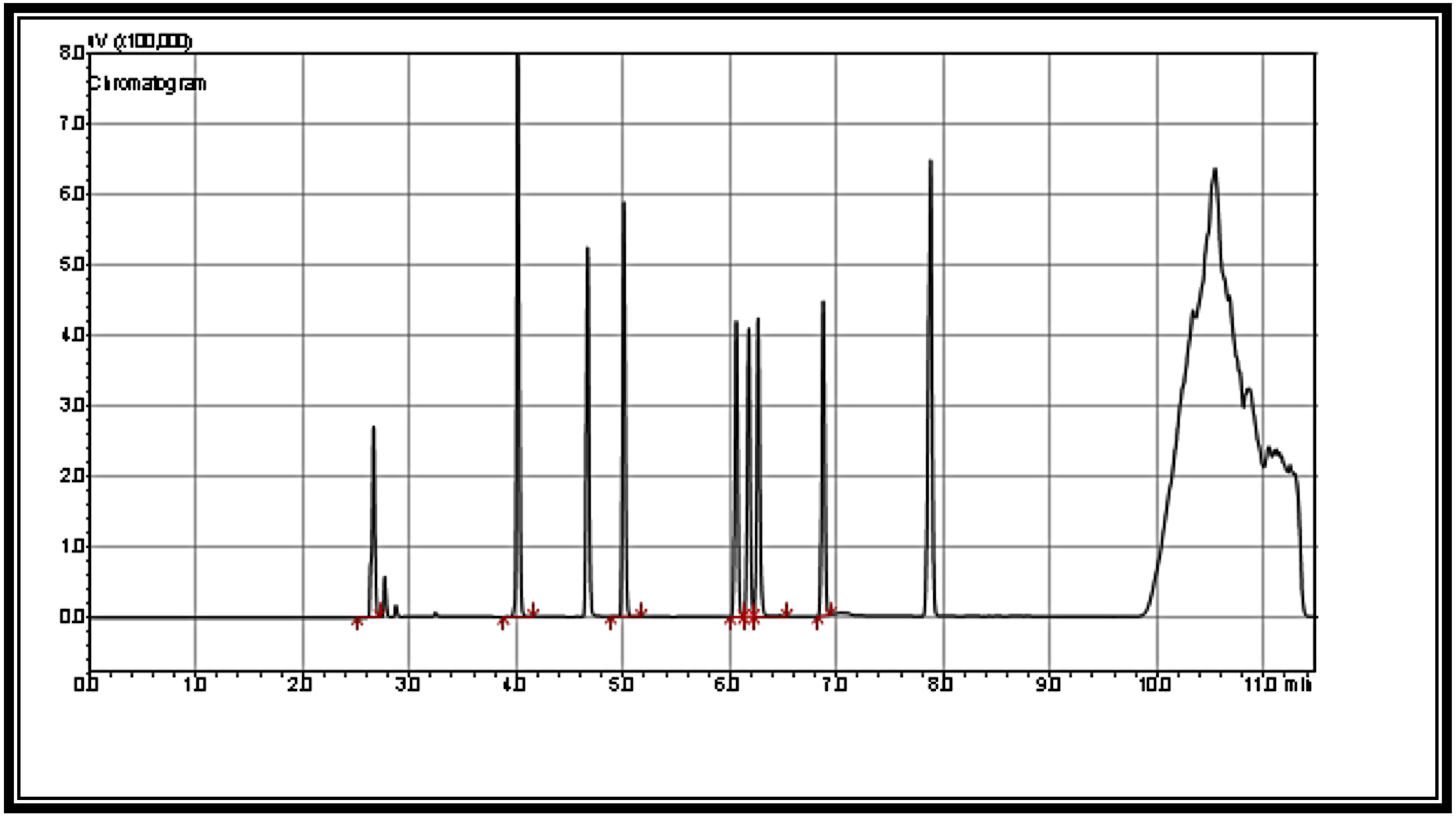

Figure A7.33: Extract Phase for a 10 % (v/v) model mixture extraction using [BNMP]

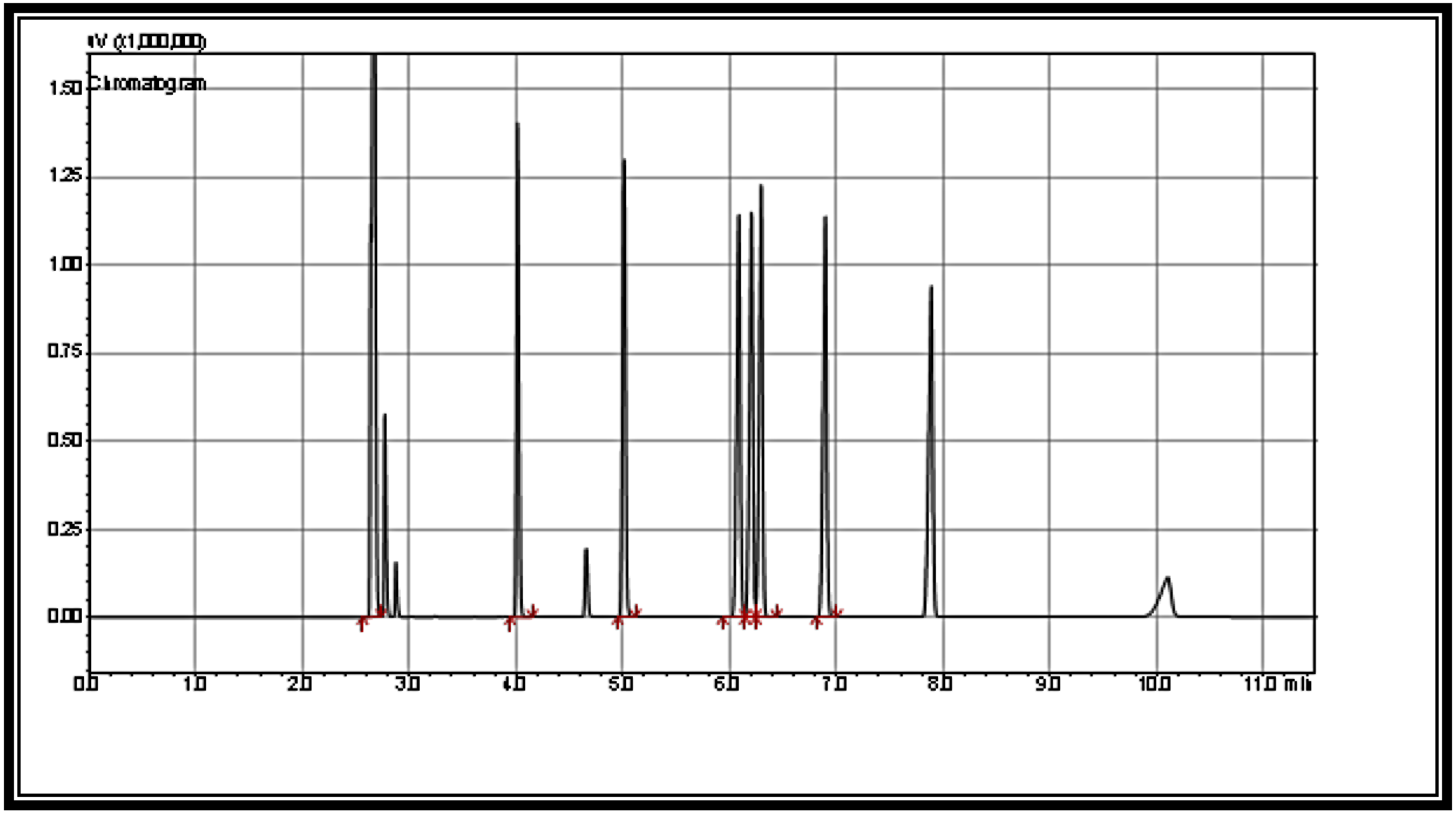

Figure A7.34: Raffinate Phase for a 10 % (v/v) model mixture extraction using [BNMP]

Appendix 6: **Chromatograms of reformate replicate samples**

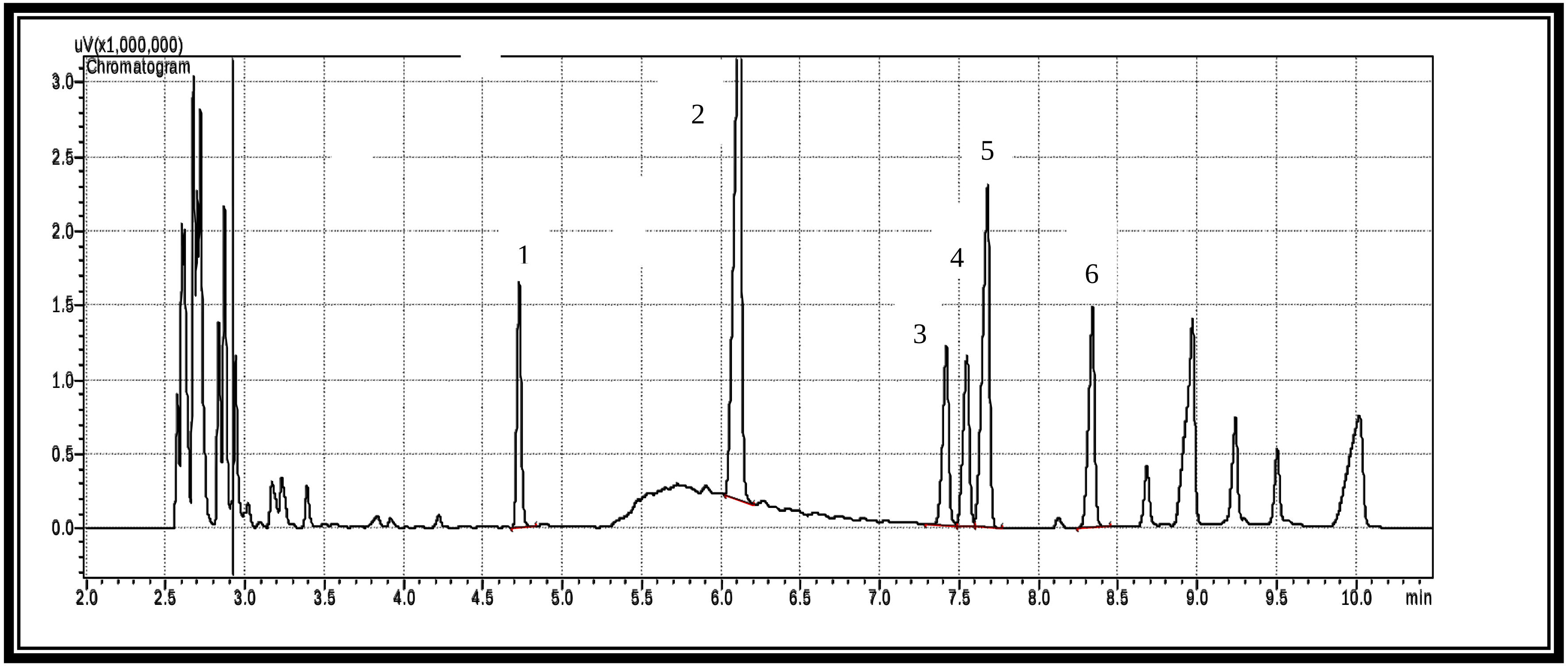

Figure A7.35: Chromatogram of reformate sample 1: 1 = Benzene, 2 = Toluene, 3 = Ethylbenzene, 4 = *p*-Xylene, 5 = *m*-Xylene, 6 = *o*-Xylene

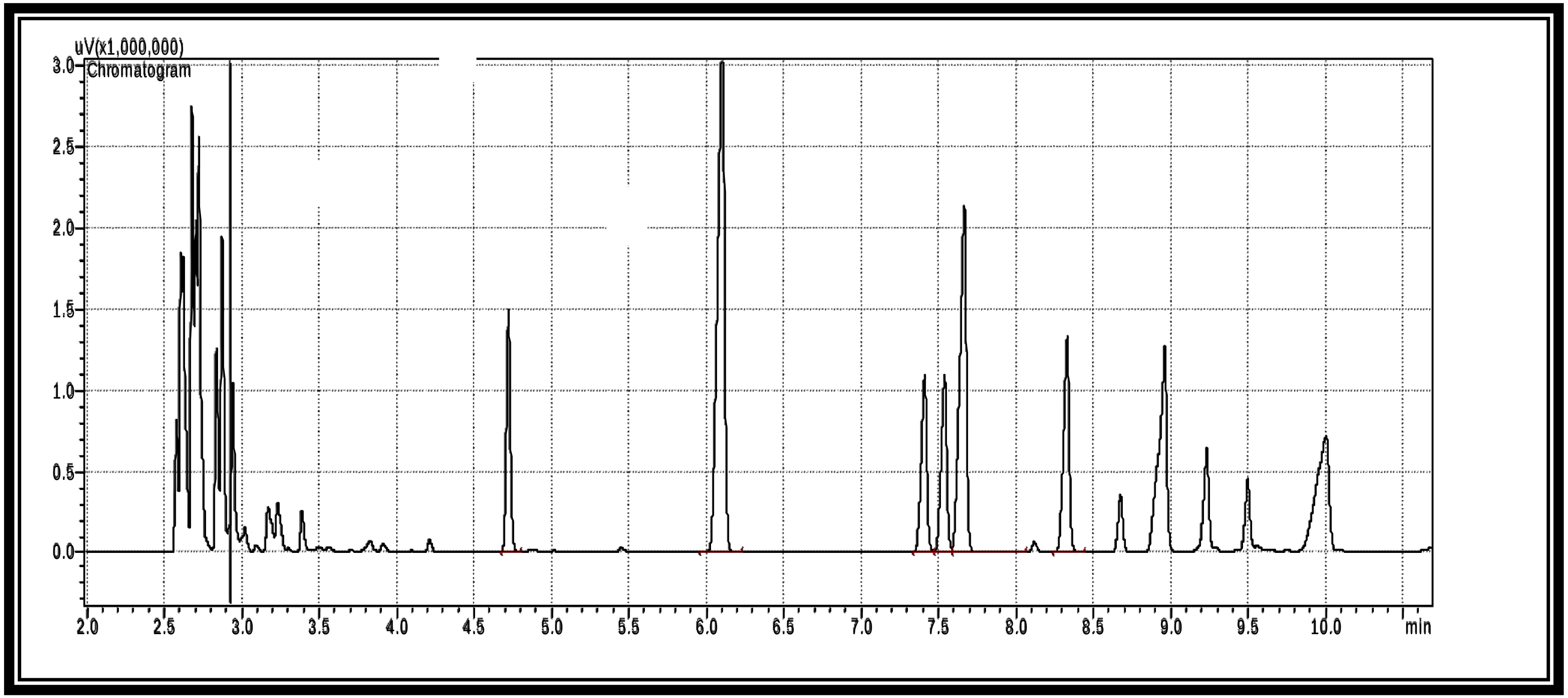

Figure A7.36: Chromatogram of reformate sample 2

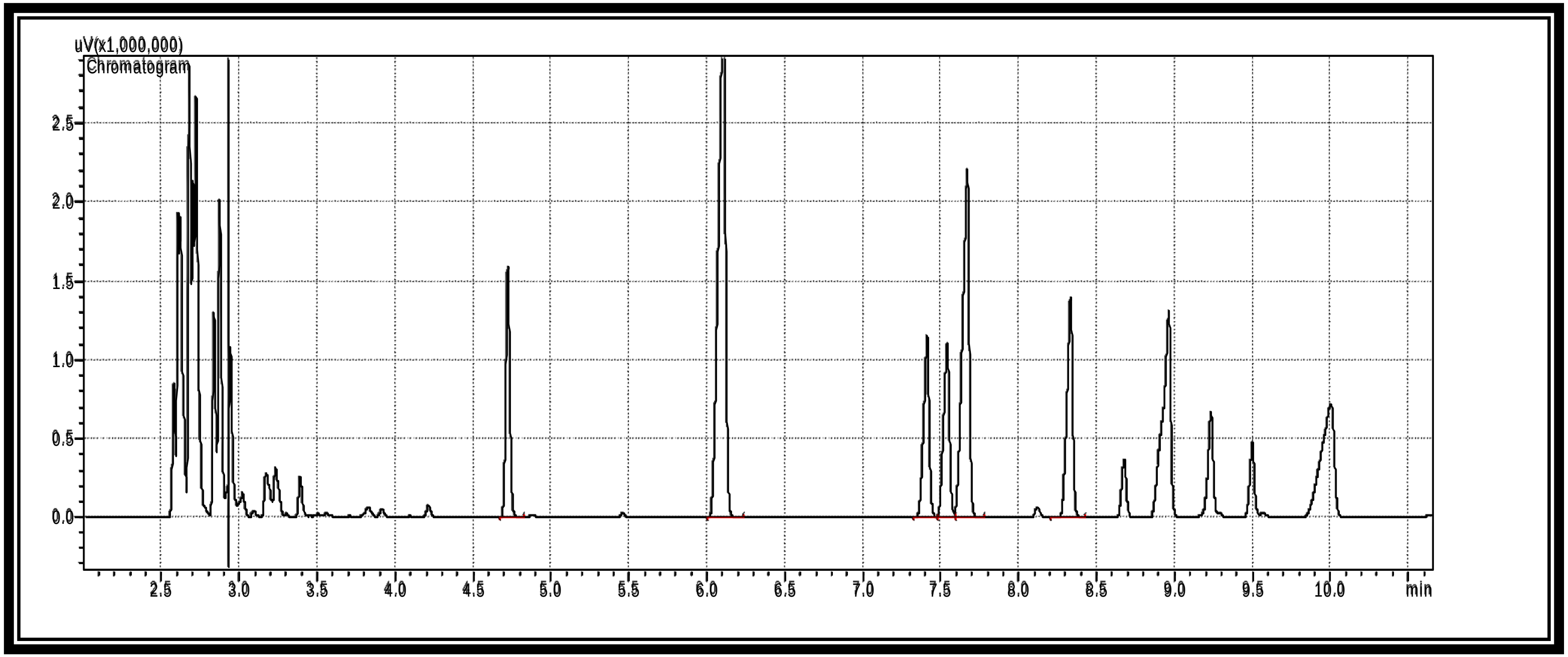

Figure A7.37: Chromatogram of reformate sample 3

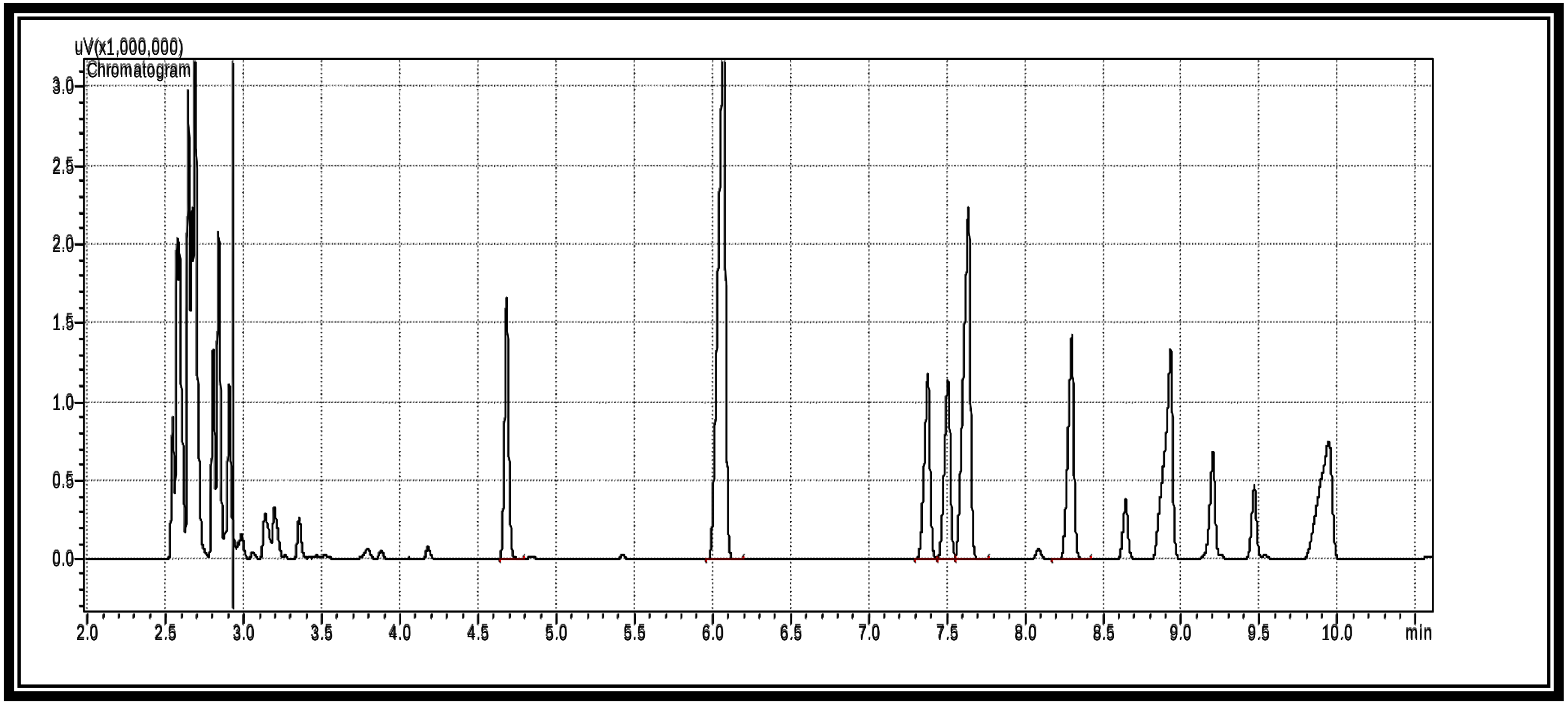

Figure A 7.38: Chromatogram of reformate sample 4

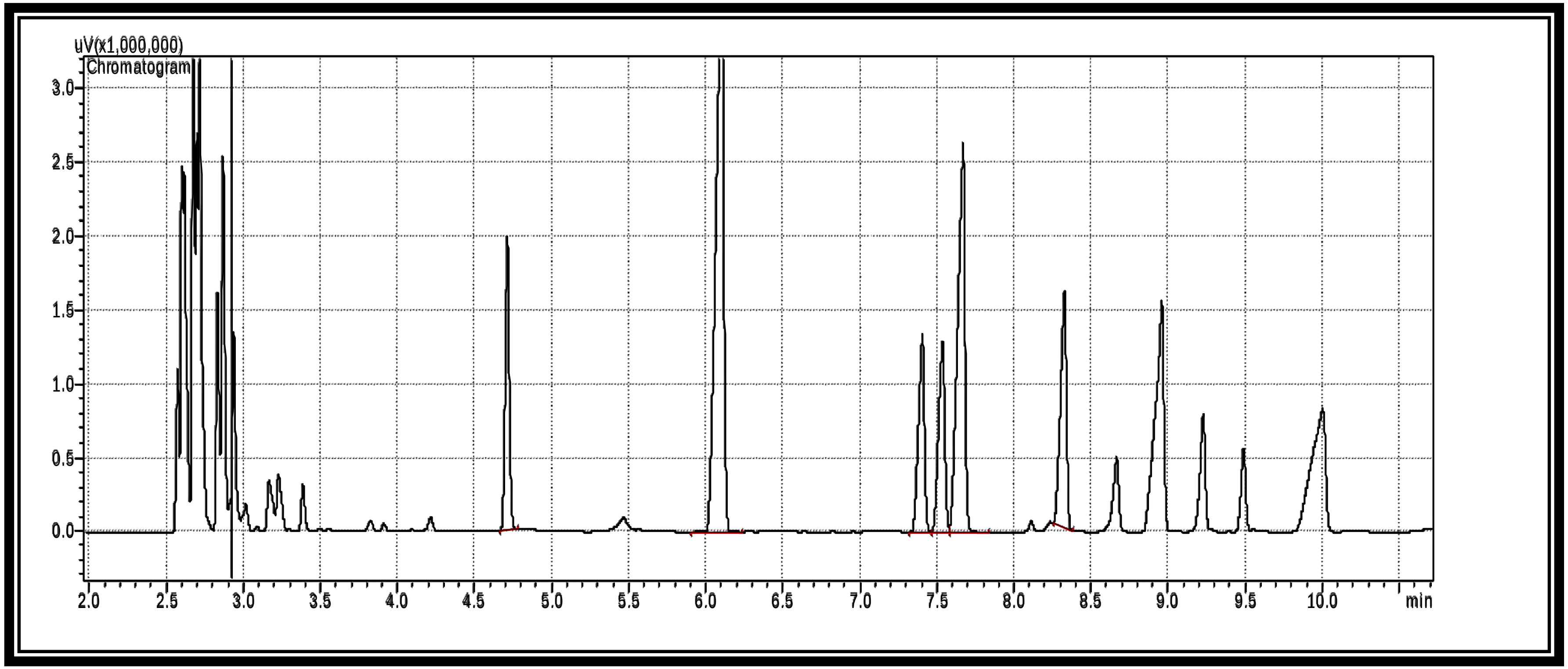

Figure A7.39: Chromatogram of reformate sample 5

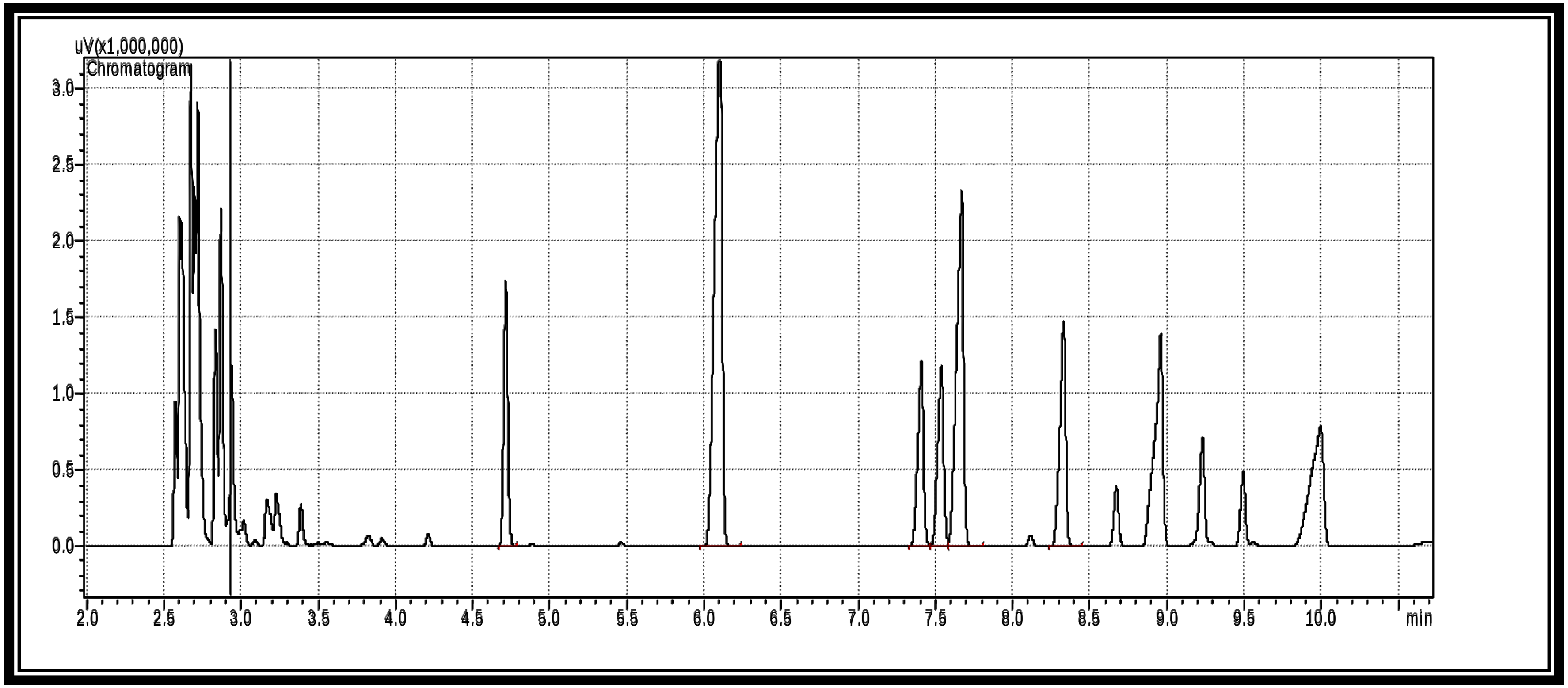

Figure A7.40: Chromatogram of reformate sample 6

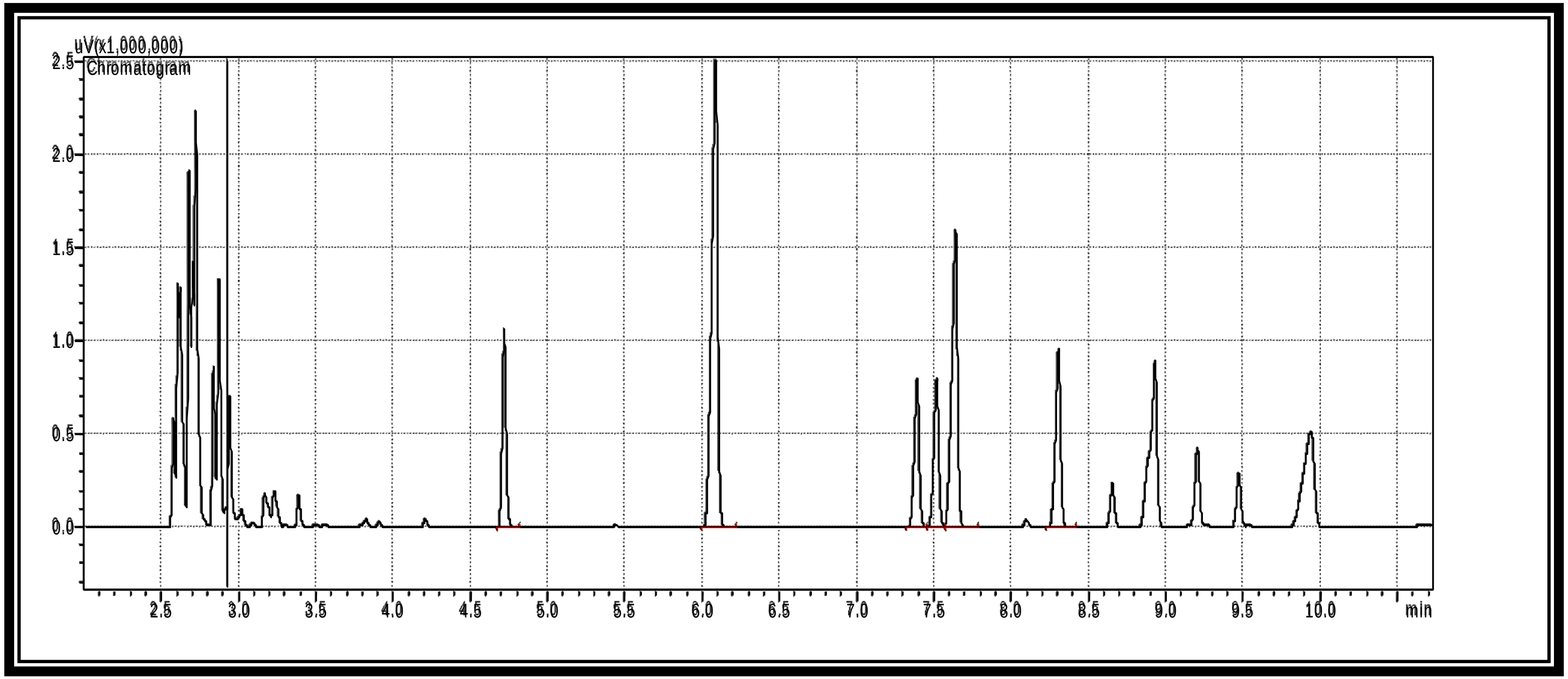

Figure A 7.41: Chromatogram of reformate sample 7

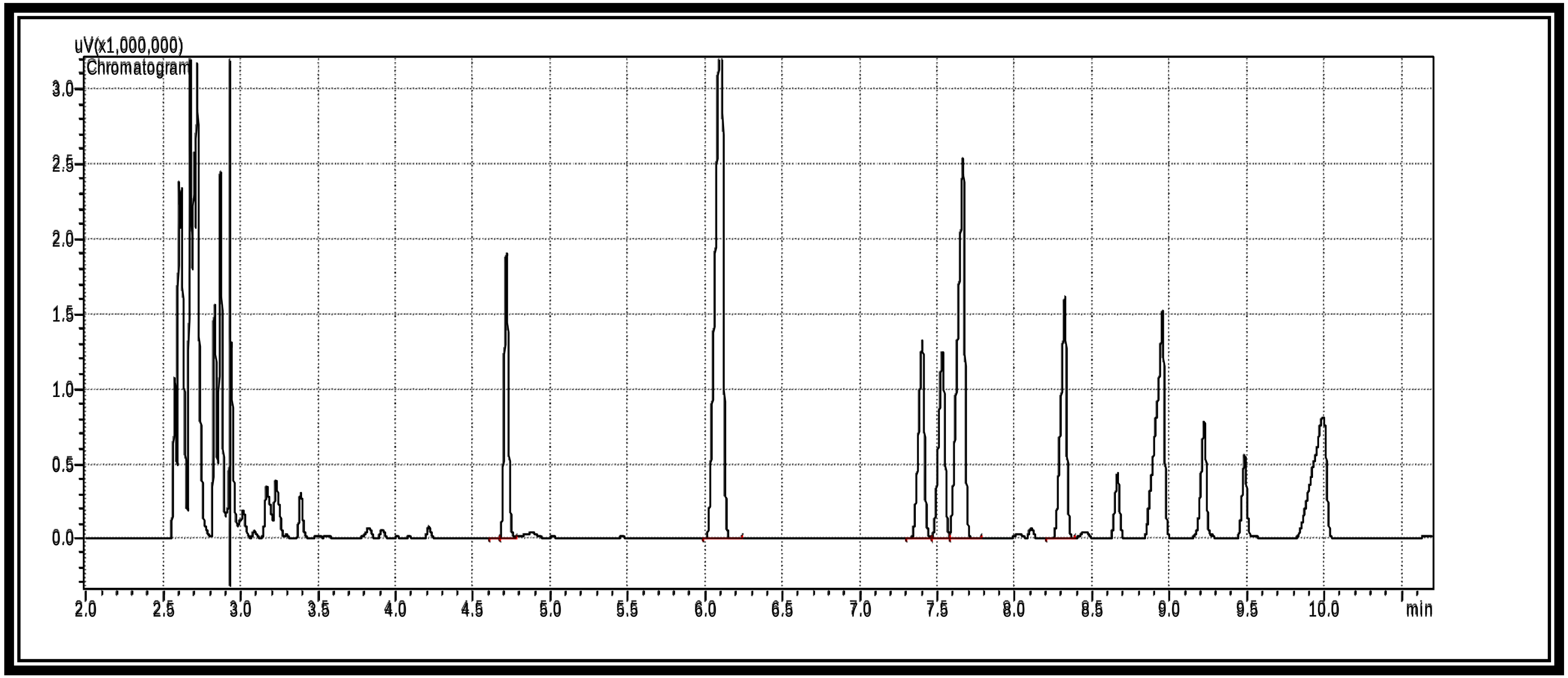

Figure A 7.43: Chromatogram of reformate sample 8

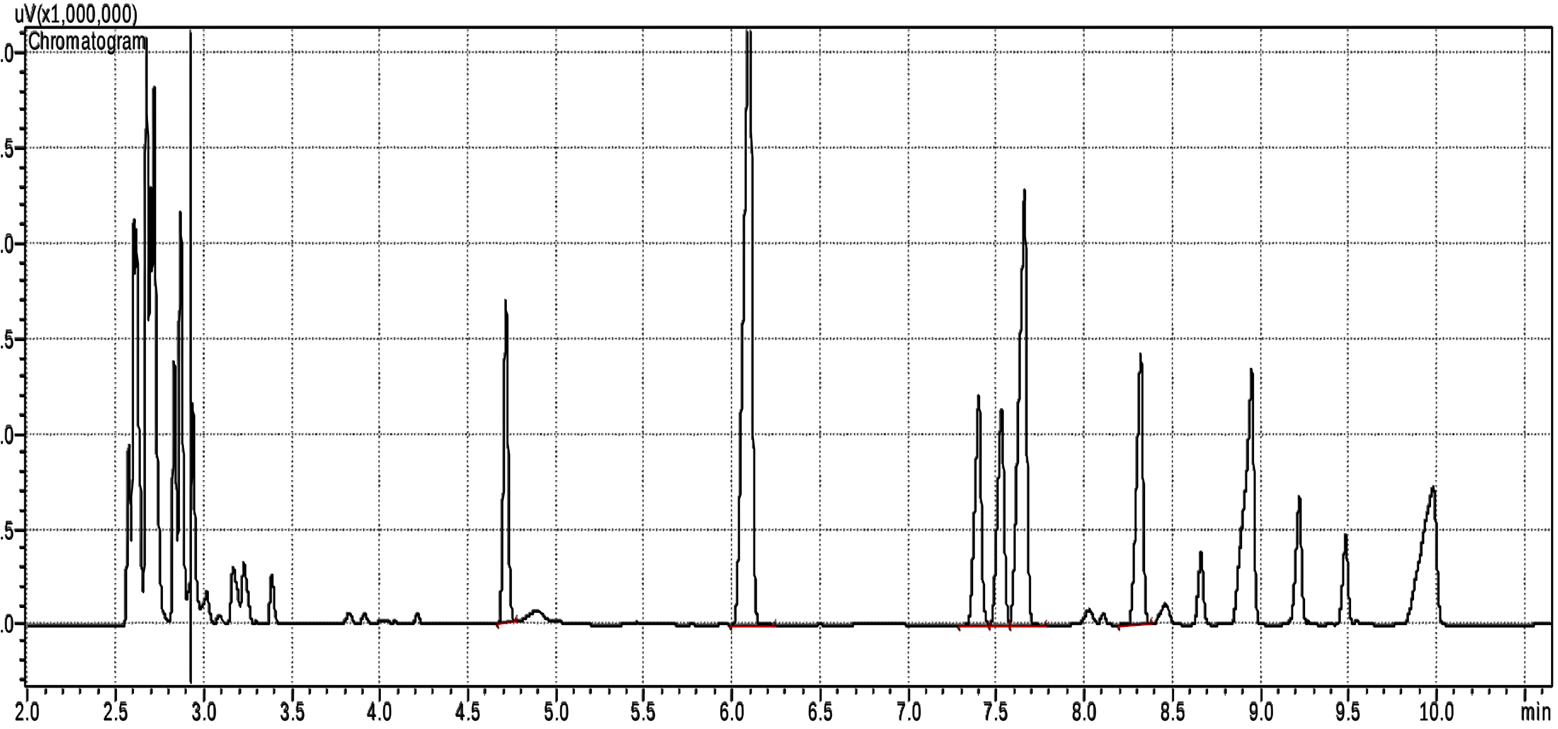

Figure A7.44: Chromatogram of reformate sample 9

Appendix 7 **Table A7.4:** Percent composition of Aromatic/Benzene/Heptane Mixture

BENZENE AND TOLUENE SEPARATIONS FROM HEPTANE USING [EMIM][ESO$_4$]								
EXTRACT PHASE AND RAFFINATE PHASE COMPARISON BY PEAK AREAS: CONCENTRATION RANGE 2.5 – 25%								
2.5% E	**P/Area**	**Vol%[E]**	**%Recovery[E]**	**P/Area**	**Vol%[R]**	**%Recovery[R]**	**Vol%[E+R]**	**%Recovery**
Heptane	162267	0.4	0.4	13442203	51.4	54		
Benzene	602058	1.4	56	287042	1.1	44	2.5	100
Toluene	369996	0.9	35	567078	2.2	87	3.0	122
Butanol	41285270	96.8		11837061	45.3			
Total	42629605	100.0		26133384	100.0			
5% E	**P/Area**	**Vol%[E]**	**%Recovery [E]**	**P/Area**	**Vol%[R]**	**%Recovery [R]**	**Vol%[E+R]**	**%Recovery**
Heptane	231193	0.5	0.5	14912551	52.6	58		
Benzene	1655998	3.4	68	711255	2.5	50	5.9	119
Toluene	767390	1.6	32	937956	3.3	66	4.9	98
Butanol	44650558	92.3		11806898	41.6			
Total	48381644	100.0		28368660	100.0			
5% E	**P/Area**	**Vol%[E]**	**%Recovery [E]**	**P/Area**	**Vol%[R]**	**%Recovery [R]**	**Vol%[E+R]**	**%Recovery**
Heptane	257366	0.5	0.6	13884787	50.3	56		
Benzene	1320480	2.8	56	611657	2.2	44	5.0	100
Toluene	761769	1.6	32	1035642	3.8	75	5.4	107
Butanol	44768271	95.0		12076638	43.7			
Total	47107886	100.0		27608724	100.0			

10% E	**P/Area**	**Vol%**	**%Recovery [E]**	**P/Area**	**Vol%[R]**	**%Recovery [R]**	**Vol%[E+R]**	**%Recovery**
Heptane	192866	0.4	0.5	13056160	47.3	59		
Benzene	3130548	6.1	61	1392175	5.0	50	11.1	111
Toluene	1391709	2.7	27	1794547	6.5	65	9.2	92
Butanol	47014302	90.9		11382078	41.2			
Total	51729425	100.0		27624960	100.0			
15% E	**P/Area**	**Vol%**	**%Recovery [E]**	**P/Area**	**Vol%[R]**	**%Recovery [R]**	**Vol%[E+R]**	**%Recovery**
Heptane	29259	0.3	0.4	11222019	43.1	62		
Benzene	868123	7.5	50	2050451	7.9	53	15.4	103
Toluene	430845	3.7	25	2697570	10.4	69	14.1	94
Butanol	10181437	88.5		10060818	38.6			
Total	11509664	100.0		26030858	100.0			
15% E	**P/Area**	**Vol%**	**%Recovery [E]**	**P/Area**	**Vol%[R]**	**%Recovery [R]**	**Vol%[E+R]**	**%Recovery**
Heptane	162853	0.3	0.5	11653981	41.4	59		
Benzene	2999905	5.8	39	2122874	7.5	50	13.3	89
Toluene	1905444	3.7	25	2810551	10.0	66	13.7	91
Butanol	46592135	90.2		11594925	41.1			
Total	51660337	100.0		28182331	100.0			
15% E	**P/Area**	**Vol%**	**%Recovery [E]**	**P/Area**	**Vol%[R]**	**%Recovery [R]**	**Vol%[E+R]**	**%Recovery**
Heptane	167653	0.3	0.5	10326621	41.7	60		
Benzene	3245301	6.3	42	1934124	7.8	52	14.1	94
Toluene	2063577	4.0	27	2420499	9.8	65	13.8	92
Butanol	45769362	89.3		10074761	40.7			
Total	51245893	100.0		24756005	100.0			

20% E	**P/Area**	**Vol%**	**%Recovery [E]**	**P/Area**	**Vol%[R]**	**%Recovery [R]**	**Vol%[E+R]**	**%Recovery**
Heptane	28396	0.2	0.4	10337852	37.5	63		
Benzene	1091806	9.6	48	2916158	10.6	53	20.2	101
Toluene	570628	5.0	25	3868087	14.0	70	19.0	95
Butanol	9696997	85.2		10438077	37.9			
Total	11387827	100.0		27560174	100.0			
New								
20% E	**P/Area**	**Vol%**	**%Recovery [E]**	**P/Area**	**Vol%[R]**	**%Recovery [R]**	**Vol%[E+R]**	**%Recovery**
Heptane	132098	0.3	0.4	9612698	36.4	61		
Benzene	4124094	8.3	41	2771928	10.5	52	18.8	94
Toluene	2526361	5.1	25	3616797	13.7	68	18.8	94
Butanol	42958273	86.4		10428255	39.5			
Total	49740826	100.0		26429678	100.0			
Old								
20% E	**P/Area**	**Vol%**	**%Recovery [E]**	**P/Area**	**Vol%[R]**	**%Recovery [R]**	**Vol%[E+R]**	**%Recovery**
Heptane	153624	0.3	0.5	9561571	37.3	62		
Benzene	3930463	7.0	35	2698425	10.5	53	17.5	88
Toluene	2431611	4.3	22	3413524	13.3	67	17.7	88
Butanol	49629833	88.4		9936515	38.8			
Total	56145531	100.0		25610035	100.0			

EXTRACT PHASE AND RAFFINATE PHASE COMPARISON BY PEAK AREAS: CONCENTRATION RANGE 2.5 – 10%								
2.5% E	**P/Area**	**Vol%[E]**	**%Recovery [E]**	**P/Area**	**Vol%[R]**	**%Recovery [R]**	**Vol%[E+R]**	**%Recovery**
Heptane	889796	1.9	2.1	13208804	55.6			
Benzene	1236914	2.7	108	308773	1.3	52	4.0	160
Toluene	431739	0.9	38	452930	1.9	76	2.8	114
Butanol	43443811	94.4		9797797	41.2			
Total	46002260	100.0		23768304	100.0			
5% E	**P/Area**	**Vol%[E]**	**%Recovery [E]**	**P/Area**	**Vol%[R]**	**%Recovery [R]**	**Vol%[E+R]**	**%Recovery**
Heptane	257064	0.6	0.6	12939723	53.4			
Benzene	1540830	3.5	70	627523	2.6	52	6.1	121
Toluene	655324	1.5	30	816756	3.4	67	4.8	97
Butanol	41878159	94.5		9848245	40.6			
Total	44331377	100.0		24232247	100.0			
7.5% E	**P/Area**	**Vol%[E]**	**%Recovery [E]**	**P/Area**	**Vol%[R]**	**%Recovery [R]**	**Vol%[E+R]**	**%Recovery**
Heptane	169401	0.4	0.5	13306417	52.0			
Benzene	1901162	4.6	61	1023931	4.0	53	8.6	114
Toluene	924556	2.2	30	1298607	5.1	68	7.3	97
Butanol	38664401	92.8		9956699	38.9			
Total	41659520	100.0		25585654	100.0			
10% E	**P/Area**	**Vol%[E]**	**%Recovery [E]**	**P/Area**	**Vol%[R]**	**%Recovery [R]**	**Vol%[E+R]**	**%Recovery**
Heptane	199134	0.5	0.5	13273880	49.6			
Benzene	2066043	5.1	51	1392735	5.2	52	10.3	103
Toluene	1209076	3.0	30	1830828	6.8	68	9.8	98
Butanol	36834227	91.4		10278891	38.4			
Total	40308480	100.0		26776334	100.0			