João Miguel Pinheiro Pinto Burguete Cardoso

Bachelor degree in Chemical and Biochemical Engineering

Extraction of safrole from essential oils with ionic liquids

Dissertation submitted in partial fulfillment
of the requirements for the degree of

Master of Science in
Chemical and Biochemical Engineering

Adviser: Ewa Bogel-Łukasik, Auxiliary Researcher,
Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa

Co-adviser: Urszula Domańska-Żelazna, Department of Physical Chemistry,
Faculty of Chemistry, Warsaw University of Technology

Examination Committee

Chairperson: Mário Fernando José Eusébio
Members: Luís Alexandre Almeida Fernandes Cobra Branco
Ewa Bogel-Łukasik

FACULDADE DE
CIÊNCIAS E TECNOLOGIA
UNIVERSIDADE NOVA DE LISBOA

March, 2017

Extraction of safrole from essential oils with ionic liquids

This document was created using the (pdf)LaTeX processor, based in the "unlthesis" template[1], developed at the Dep. Informática of FCT-NOVA [2].
[1] https://github.com/joaomlourenco/unlthesis [2] http://www.di.fct.unl.pt

Acknowledgements

I am grateful to FCT/UNL and the Physical Chemistry department at Warsaw University of Technology for providing me the opportunity to study abroad as well as their staff for its continuous collaboration on this research work. A very special thank you to Dr. Urszula Domańska-Żelazna and Dr. Ewa Bogel-Łukasik for all the support and guidance throughout the accomplishment of this work. I am also thankful to my parents and friends for all the support they have given me.

Abstract

In this study, new experimental results on liquid-liquid equilibria (LLE) in the binary systems of safrole, an organic aromatic compound and six diferent ionic liquids: trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide $[P_{6.6.6.14}][NTf_2]$, trihexyl(tetradecyl)phosphonium tricyanomethanide $[P_{6.6.6.14}][TCM]$, 1-dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[DoMIM]][NTf_2]$, octyltriethylammonium bis(trifluoromethylsulfonyl)imide $[N_{8.2.2.2}][NTf_2]$, 1-(2-methoxyethyl)-1-methylpiperidinium trifluorotris(perfluoroethyl)phosphate $[COC_2mPIP][FAP]$ and 1-(2-methoxyethyl)-1-methylpyrrolidinium trifluorotris(perfluoroethyl)phosphate $[COC_2mPYR][FAP]$ have been investigated. The experimental values presented have been determined using a dynamic method, which is based on disappearance of turbidity in slowly heated solution. All samples have been placed in a glass cell and sealed with a rotaflow needle valve at atmospheric pressure. The cells were immersed in a water bath. All mixtures were stirred and slowly heated to obtain homogenous system. In this work, the extraction performance of ionic liquids in the removal of compounds from sassafras oil has been studied. The investigated ionic liquids are phosphonium, imidazolium, ammonium, piperidinium and morpholinium based coupled with different anions. The anions are bis(trifluoromethylsulfonyl)imide $[NTf_2]$, tricyanomethanide [TCM], trifluorotris(perfluoroethyl)phosphate [FAP], dicyanamide [DCA], thiocyanate [SCN], tosylate [TOS], trifluoroacetate [TFA], ethylsulfate $[EtSO_4]$, methylsulfate $[CH_3SO_4]$ and acetate [AcO].

Mixtures with the supplied oil and each of the following ionic liquids: $[P_{6.6.6.14}][NTf_2]$, $[P_{6.6.6.14}][TCM]$, $[DoMIM][NTf_2]$ and $[N_{8.2.2.2}][NTf_2]$ were made. The mixtures were stirred while the composition was slowly varied, at room temperature. There were no miscibility gaps detected in any of the previously mentioned systems.

Keywords: Safrole, Sassafras oil, Ionic liquids, Liquid-Liquid Equilibria, Liquid-Liquid Extraction ...

Resumo

Neste estudo, novos resultados experimentais em equilíbrio líquido-líquido nos sistemas binários de safrol, um composto orgânico aromático e seis líquidos iónicos: trihexil(tetradecil)fosfónio bis(trifluorometilsulfonil)imida $[P_{6.6.6.14}][NTf_2]$, trihexil(tetradecil)fosfóniotricianometanida $[P_{6.6.6.14}][TCM]$, 1-Dodecil-3-metilimidazólio bis(trifluorometilsulfonil)imida $[DoMIM][NTf_2]$, Octiltrietilamónio bis(trifluorometilsulfonil)imida $[N_{8.2.2.2}][NTf_2]$, 1-(2-metóxietil)-1-metilpiperidina trifluorotris(perfluoroetil)fosfato $[COC_2mPIP][FAP]$ e 1-(2-metóxietil)-1-metilpirrolidínio $[COC_2mPYR][FAP]$ foram investigados. Os valores experimentais apresentados foram determinados usando um método dinâmico, baseado no desaparecimento de turvação em misturas lentamente aquecidas. Todas as amostras foram colocadas numa célula de vidro e seladas com uma válvula de agulha à pressão atmosférica. As células de vidro foram imersas num banho de água. Todas as misturas foram agitadas e lentamente aquecidas de forma a se obterem sistemas homogéneos. Neste trabalho, o desempenho de extração de líquidos iónicos na remoção de compostos do óleo de sassafrás foi estudado. Os líquidos iónicos investigados são baseados em fosfónio, imidazólio, amónio, piperidínio e morfolínio acoplados a diferentes anões. Os aniões são bis(trifluorometilsulfonil)imida $[NTf_2]$, tricianometanida [TCM], trifluorotris(perfluoroetil)fosfato [FAP], dicianamida [DCA], tiocianato [SCN], tosilato [TOS], trifluoroacetato [TFA], etilsulfato $[EtSO_4]$, metilsulfato $[CH_3SO_4]$ e acetato [AcO].

Misturas de óleo de sassafrás com cada um dos seguintes líquidos iónicos: $[P_{6.6.6.14}][NTf_2]$, $[P_{6.6.6.14}][TCM]$, $[DoMIM][NTf_2]$ e $[N_{8.2.2.2}][NTf_2]$ foram preparadas. As misturas foram agitadas enquanto a composição foi variada, à temperatura ambiente. Não foram detetadas lacunas de miscibilidade nos sistemas mencionados anteriormente.

Palavras-chave: Safrol, Óleo de sassafrás, Líquidos iónicos, Equílibrio líquido-líquido, Extração Líquido-Líquido ...

Contents

List of Figures

List of Tables

Chapter 1

Introduction

In this chapter, the motivation for realization of this work is presented and also the aims of the work are outlined.

This work was performed with collaboration with Warsaw University of Technology, Faculty of Chemistry, Warsaw, Poland, within the Erasmus program within the period of 20 of February 2016 to 20 of August 2016.

1.1 Motivation

This project will be focused on one of the methods currently used to obtain essential oils: solvent extraction. In the chemical industry, organic solvents are commonly used in a widespread of applications. However, these solvents have clear disadvantages since they are usually very flammable, toxic and quite volatile. Unlike organic solvents, the rising use of green solvents, such as ionic liquids, represent an alternative approach which should be explored. As such, this research is intended to investigate the efficiency of ionic liquids on the extraction of safrole from essential oils. If ionic liquids prove to be efficient, these solvents may minimize the environmental impact which expresses the concept of green chemistry.

1.2 Aim of the work

The research will be in the field of Physical Chemistry. The main purpose of this project will be the extraction of the highest amount of safrole from essential oils by means of different ionic liquids. If succeeded, ionic liquids could become an alternative method of extraction. Experiments regarding liquid-liquid equilibria will be performed with

different ionic liquids. With this in mind the aim of the work will englobe three main stages:

1. Data preparation for extraction from the oil, by choosing the oil depending on the safrole content and origin. It is intended to explore the extraction from essential oils that contain 80 % or higher content of safrole.
2. Solubility study with at least five different ionic liquids.
3. Performing safrole extraction with selected ionic liquids from essential oil.

Chapter 2

Theoretical Background

In this chapter, the aim is to present the theoretical information that serves as background for the future work.

2.1 Essential oils

A natural product is a chemical compound or substance produced by a living organism. Nowadays, these substances can be extracted from plants using a wide range of methods, depending on the properties of the compound of interest. At normal conditions of pressure and temperature, some compounds are in solid state, which makes them relatively easy to separate while others are in liquid state and are usually extracted from plants in a form of essential oil. The use of natural products from plants by mankind had an obscured beginning which dates back to the dawn of civilizations and it has become a field of interest to humans ever since. Plants containing essential oils have been used as remedies due to their healing properties for the treatment of diseases, religious ceremonies and for their pleasant fragrance [1] [2].

This display of interest by mankind was particularly pronounced in the Ancient Egypt, one of the earliest civilizations known to our actual days. Throughout History, countless physicians, alchemists and botanists have studied the properties of many of these plants and left records of their findings. However, the first systematic investigations of constituents from essential oils may be attributed to the French chemist M.J. Dumas. From then, much scientific progress was achieved, culminating an outstanding growth in our knowledge in the field of essential oils and their constituents when there were considerable advances in analytical methods, such as ultraviolet (UV) spectroscopy, chromatographic separation methods and nuclear magnetic resonance (NMR) spectroscopy in organic chemistry [2].

In the present times, the extraction of essential oils from plants is still a common practice because it provides a large array of chemicals to industry. In the present times, it has been reported an anual global production of 100 000 tons of volatile essential oils for food, flavor and fragrance industries, with a networth of about 1 billion US dollars [3]. This mass production of essential oils is achieved mostly by major cultivators and producers such as USA, Brazil, India and China [4]. Essential oils can be defined as very complex oily mixtures of volatile compounds, which can be isolated from a botanically defined plant raw material [3] [5]. Essential oils represent usually a small fraction of the plant composition (about 5% of the vegetal dry matter [5]. These odorant products could be biosynthesized as secondary metabolites in several plant organs such as fruits, bark, seeds, wood, leaves, herbs, flowers and roots [5]. The constituents of essential oils can be classified into distinct groups according to their chemical structures. Most of the components are mainly hydrocarbon terpenes (isoprenes) and terpenoids. Terpenes are a class of unsaturated hydrocarbons which can be classified into different subclasses: monoterpenes (10 carbon atoms) comprise more than 80% of essential oils composition and sesquiterpenes (15 carbon atoms) [5]. Terpenes are composed by building blocks of isoprene units (2-methyl-1,3-butadiene) which are represented by the general structural formula $(C_5H_8)_n$. Their chemical structure could be acyclic or even contain multiple cyclic structures.

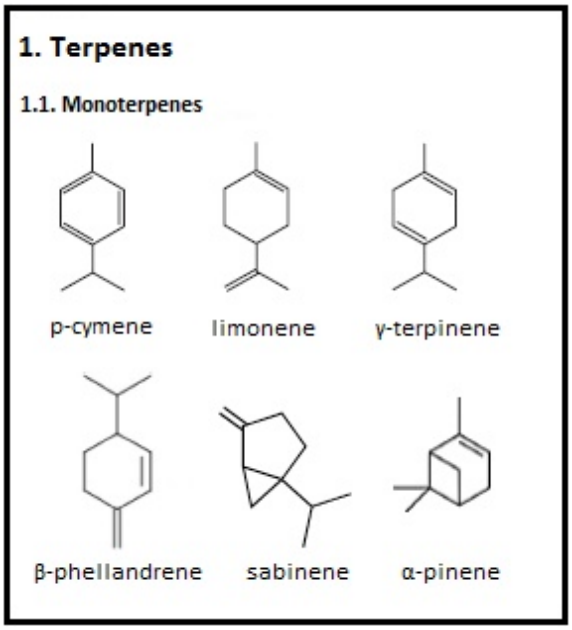

Figure 2.1: Examples of molecular structures of monoterpenes found in essential oils.

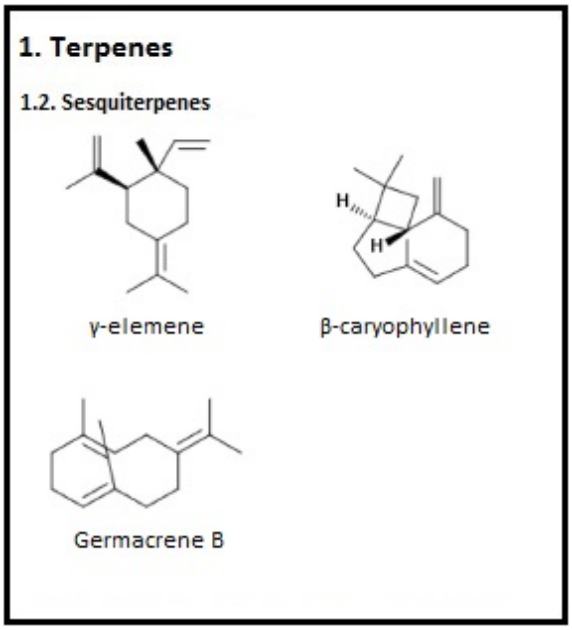

Figure 2.2: Examples of molecular structures of sesquiterpenes found in essential oils.

Terpenoids, also called isoprenoids, are oxygenated derivatives of hydrocarbon terpenes, which include aldehydes, esters, ethers, ketones, alcohols, phenols and acids [5] [6]. Another class of oxygenated compounds that are present in some particular cases are phenylpropanoids and their derivatives, which are found, for instance, in Sassafras or Cinnamon bark [5].

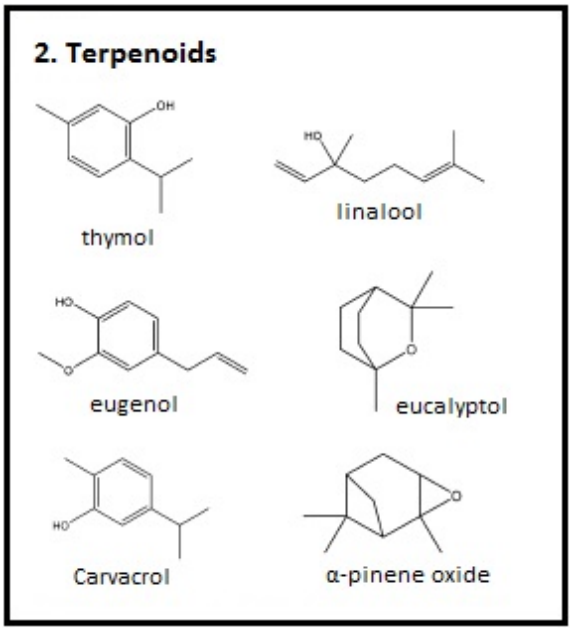

Figure 2.3: Examples of molecular structures of terpenoids found in essential oils[3].

Essential oils are generally lipophilic, soluble in organic solvents and immiscible with

water because these oils are hydrophobic and their density is often lower than that of water [5]. Essential oils are characterized by having two or three major components at significantly high concentrations (20-70%) and many other compounds present in trace amounts [7]. These major components usually determine the biological properties of the essential oils. However, this complex chemical composition of essential oils, usually containing about 20-60 components, results in a wide biological and antimicrobial properties (antifungal, antibacterial, antiviral, pest control, etc). Due to these interesting properties, they are included in the pharmaceutical composition of many dosage forms (ointments, creams, syrups, capsules, aerosols, etc) [5].

Table 2.1: Examples of essential oils and their applications [8].

Essential oils	Name of plant	Plant Parts	Application
Bergamot	*Citrus bergamia*	Fruit peel	Anxiety Agitation Stress Insomnia
Lemon	*Citrus limon*	Fruit peel	Insomnia
Sweet orange	*Citrus sinensis*	Fruit peel	Anxiety Agitation Stress Insomnia
Mandarin	*Citrus reticulata*	Fruit peel	Insomnia
Citronella	*Cymbopogon nardus*	Leaves	Fatigue
Petitgrain bigarade	*Citrus aurantium var. amara fol.*	Leaves	Anxiety Agitation Stress
Palmarosa	*Cymbopogon martinii*	Leaves	Anxiety Agitation Stress
Patchouli	*Pogostemon patchouli*	Leaves	Anxiety Agitation Stress
Geranium	*Pelargonium graveolens*	Entire plant	Anxiety Agitation Stress Fatigue
Lavender	*Lavandula augustifolia*	Entire plant	Anxiety Agitation Stress End-of-life agitation Insomnia Pain management
Ginger	*Zingiber officiale*	Roots	Fatigue Pain management
Orange blossom (neroli)	*Citrus aurantium var. amara*	Flowers	Fatigue Insomnia
Ylang ylang	*Cananga odorata*	Flowers	Insomnia

Table 2.2: Examples of essential oils components [9].

Essential oils	Plant botanical name	Major constituents
Cilantro	*Coriandrum sativum (immature leaves)*	Linalool
		E-2-decanal
Cinnamon	*Cinnamomum zeylandicum*	Trans-cinnamaldehyde
Clove (bud)	*Syzygium aromaticum*	Eugenol
		Eugenyl acetate
Coriander	*Coriandrum sativum (seeds)*	Linalool
		E-2-decanal
Oregano	*Origanum vulgare*	Carvacrol
		Thymol
		gamma-Terpinene
		p-Cymene
Rosemary	*Rosmarinus officinalis*	1,8-Cineole
		alpha-Pinene
		Bomyl acetate
		Camphor
Sage	*Salvia officinalis L.*	Camphor
		1,8-Cineole
		alpha-Pinene
		beta-Pinene
Thyme	*Thymus vulgaris*	Thymol
		p-Cymene
		gamma-Terpinene
		Carvacrol

2.2 Extraction Methods

As previously mentioned, mankind has started to try to extract essential oils from the many plants they could find in an early stage and have been developing new methods of extraction ever since. Nowadays, there are several extraction methods that may be used for that purpose. First of all, the methods of extraction may be classified into two categories: conventional/classical methods and advanced/innovative methods [5]. Efforts have been made during the last decades to improve the extraction efficiency (higher extraction yield and oil quality, decrease of extraction time and energy consumption) by means of new technologies, such as microwave and ultrasound). The techniques described below represent some of the methods commonly used nowadays while others are slight improvements of other methods.

2.2.1 Conventional/Classical methods

2.2.1.1 Hydrodistillation

Hydrodistillation is the oldest and most simple method of extraction of essential oils. Both the plant material and water are placed inside a vessel (alembic) and the whole is

heated up to boiling. The set up includes a heat source for the vessel, a condenser to condensate the essential oils and a decanter to separate them from water. During the heating, the molecules of oil and water form a heterogeneous mixture which is distilled simultaneously as if they were a single compound. This process is defined as a co-distillation which uses water vapour as solvent drive [5]. Most of the compounds in the oil are immiscible with water and thus, after condensation, they could be easily separated from each other by simple decantation. In a hydrodistillation by Clevenger system, the condensates are recycled through a cohobage system. For instance, this method is appropriate for the extraction from flower petals because it avoids compacting and clumping of plant material during the extraction. However, this method has plenty of disadvantages, such as: (i) overheating and loss of some polar compounds in the water removal, (ii) long extraction time (3-6 hours; 24 hours for rose petals), (iii) the prolonged contact with boiling water may cause chemical alterations of terpenic compounds (hydrolysis, cyclization, etc). An improvement to this technique was the turbodistillation, which enables the recycling of the aromatic water and thus, enhances the yield obtained [5]. This method allows the recovery of almost essential oils present in the vapor through the plate column. In addition, the presence of turbines helps to reduce distillation time. This technique is still being used in industrial scale due to its simplicity of installations (it does not need relatively expensive equipment), easiness of method implementing and its selectivity [5].

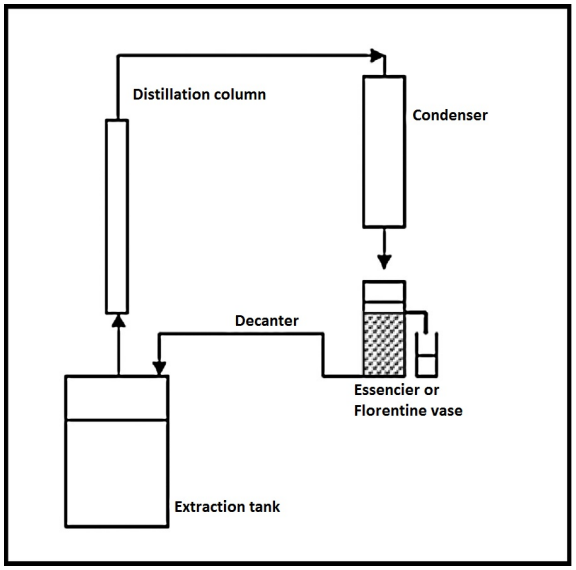

Figure 2.4: Hydrodistilation apparatus [5].

2.2.1.2 Entrainment by water steam

This technique is widely used for the extraction of essential oils. The same principle of hydrodistillation is applied, but in this case the plant and water do not have direct contact. Chemical alterations are reduced due to a shortened extraction time [5]. Variants of this

method are described below:

Vapor-hydrodistillation In this method, the extraction process is performed within an alembic, with the difference that the plant material is suspended on a system of perforated plate or grid above the water level, in order to avoid their direct contact. Then water vapours cross the plant material from the bottom up and carry the volatile compounds. Both the extraction duration and loss of polar molecules are reduced [5].

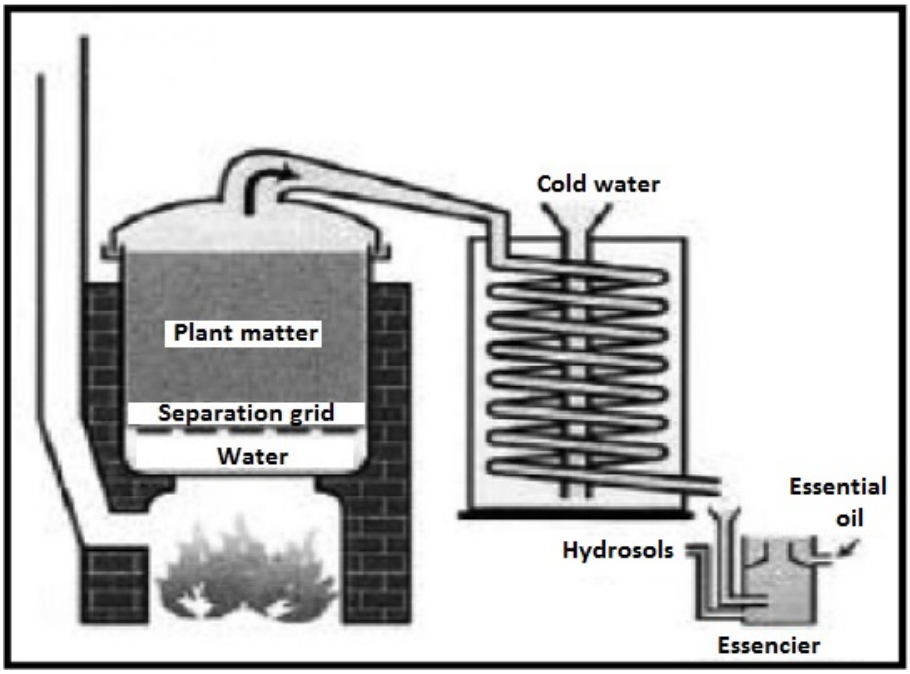

Figure 2.5: Vapour-Hydrodistilation apparatus [5].

Steam Distillation This technique is very similar to vapour-hydrodistillation, with the difference that the vapours are generated outside of the distillation alembic. The steam can be saturated or superheated [5]. Steam distillation is a widely used technique and it is often used in the literature as a reference to compare with other innovative techniques that are being investigated.

Table 2.3: Literature on Steam Distillation.

Plant source	Temperature(^oC)	Pressure (bar)	Reference
Ephedra sinica	100	1	[10]
Lavandula angustifolia	100	1	[11]
Nepeta persica	100	1	[12]
Origanum onites	100	1	[13]
Pogostemon cablin	100	1	[14]
Rosmarinus officinalis. L	100	1	[15]
Mentha piperita	125	1	[16]

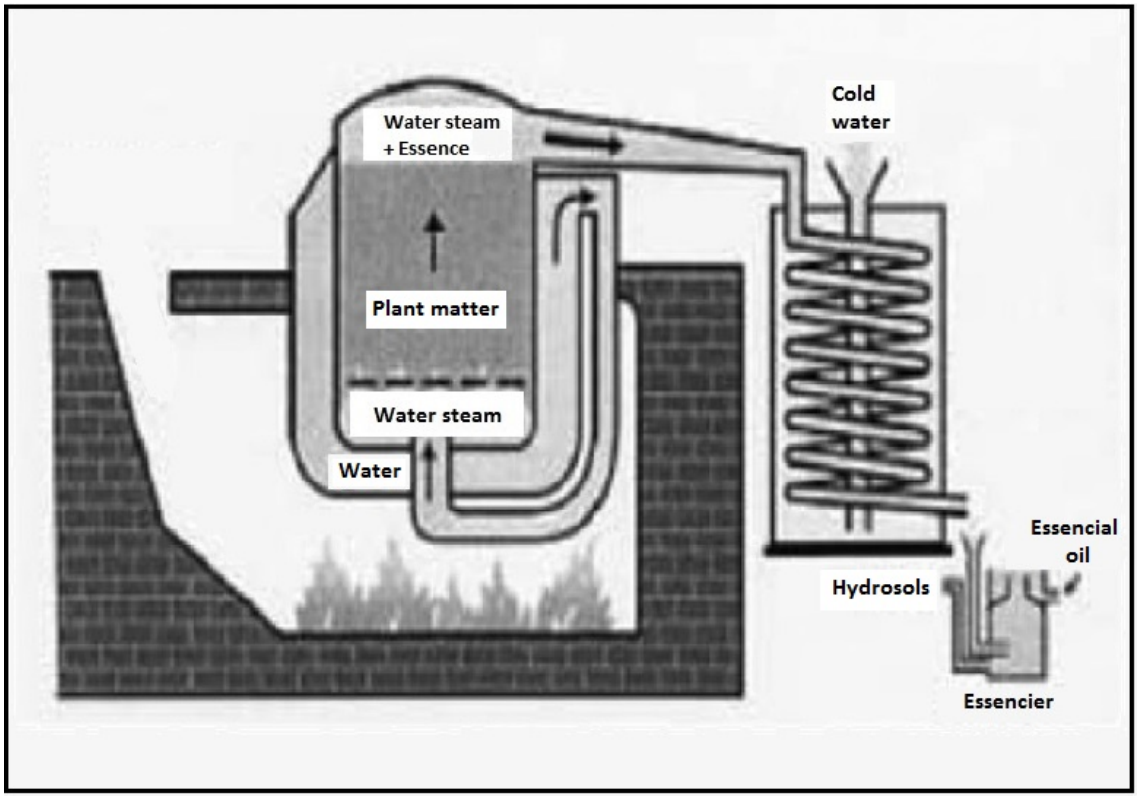

Figure 2.6: Steam Distillation apparatus [5].

Hydrodiffusion Another possible variant of vapour-hydrodistillation is named Hydrodiffusion and it consists on injecting steam from the top and the vapours flow downwards [5]. The condensation of the oil containing steam mixture occurs below a perforated tray on which the plant material is being heldl. The main advantages of this method are: a reduced steam consumption, a shorter distillation time and a better yield can be obtained when compared with steam distillation. The temperature and pressure conditions used for these variants are very similar: temperature near the water's boiling point and atmospheric pressure.

2.2.1.3 Organic Solvent Extraction

Organic solvent extraction is one of the most commonly used practices for the extraction of compounds from essential oils. The plant matter is macerated the desired compounds are dissolved in an organic solvent [5]. An advantage of this technique is a lower energy consumption than processes such as distillation or supercritical fluid extraction, while retaining the most volatile aliphatic chemicals [3]. Also, this method prevents chemical alterations of oil constituents caused by heat or pH shift in comparison with hydrodistillation. During hydrodistillation, some of the oil constituents are dissolved in the boiling water and reduce the pH considerably [5]. The combined effect of both heat and low

pH at which the fragrance constituents are subjected may cause chemical modifications, such as hydrolysis, deprotonations, hydrations or cyclizations [5]. On the other hand, a disadvantage of this method is that the extracts obtained may contain residues that compromise their safety. Therefore, this technique can not be used for food or pharmaceutical applications. However, a combination technology of organic solvents with low boiling point and steam distillation process (OS-SD) could avoid these problems [5].

The operating conditions of this method depend on the chosen solvent for the extraction, as the boiling point of each solvent differ from one another, at atmospheric pressure.

Table 2.4: Boiling Point of some of the most commonly used organic solvents.

Solvent	Boiling Point (^oC)
Acetone	56
Dichloromethane	57,2
Hexane	68
Ethanol	78,37

Currently, this technique is used in many cases as reference process for comparison between the standard traditional methods and the emerging developed extraction methods.

Table 2.5: Some examples of solvent extraction of essential oils.

Plant	Temperature(^oC)	Pressure (bar)	Reference
Agaricus bisporus L.	80	1	[17]
Eucalyptus loxophleba	90	1	[18]
Jasminum	78,4	1	[19]
Moringa oleifera	70	1	[20]
Origanum onites	68	1	[13]
Ricinus communis L.	68	1	[21]

2.2.1.4 Cold pressing

In this technique, the essential oils are released from the raw material by squeezing it mechanically at room temperature, followed by washing in cold running water. A watery emulsion is formed and then the oil is recovered by means of a centrifugation [5]. This method is particularly used for the extraction of essential oils from citrus fruit zest, which have applications in food and pharmaceutical industries [5].

2.2.2 Advanced/Innovative methods

With the advances in the technological and scientific field, new techniques have been under development in order to find suitable alternatives to the convential methods. As previously referred, an important disadvantage of conventional techniques is the high

applied temperatures at which the oil compounds are subjected. Consequently, the quality of the oils extracted is affected, particularly if the extraction time is long. The aim of these techniques is to reduce extraction times, energy consumption, solvent use and CO_2 emissions [5].

2.2.2.1 Supercritical fluid extraction (SCFE)

Supercritical Fluid Extraction has become a renowned extraction technique, particularly for food and pharmaceutical industries because the use of this technique prevents the presence of organic chemical residues in oil products. For fluids, the supercritical state is reached at specific conditions: critical pressure (Pc) and critical temperature (Tc). When those conditions are reached, some interesting properties can be observed, such as: density similar to that of liquids, high diffusivity and low viscosity [5].

This technique uses and recycles the fluid in repeated steps of compression/depression. The CO_2 supercritical state is reached by heating and high compression. It interacts with the raw plant material and, due to its high diffusitivity, it carries the compounds of interest. Then, there is a decompression step: the extract is routed to one or more separators, where the CO_2 is gradually decompressed (thus losing its solvent power) to separate the obtained extract from the fluid. The latter could be turned into a released gas and then could be recycled [5].

Carbon dioxide is generally used as the solvent for extraction due to its many advantages: the critical point is easy to obtain (low critical pressure (Pc = 72.9 atm) and low critical temperature (Tc = 31.2°C); practically harmless for plant essence compounds which are sensitive to heat; it is chemically inert, nontoxic and non flammable; available in high purity at relatively low cost; easy elimination of its traces from the obtained extract by simple depression and its polarity is similar to pentane which makes it suitable for extraction of lipophilic compounds [5].

However, it is a very expensive endeavour due to its equipments, installations and maintenance operation high costs.

2.2.2.2 Subcritical extraction

In this case, the fluid of choice, usually water or CO_2, is subjected to a pressure above the critical pressure (Pc) and temperature below the critical temperature (Tc), or conversely, in order to reach the subcritical state [5]. This technique is much less aggressive than hydrodistillation or steam distillation because it avoids the high temperatures at which the oil components are subjected.

2.2.2.3 Ultrasound assisted extraction (UAE)

This method combines the use of conventional/classical techniques (hydrodistillation and solvent extraction) with ultrasound technology. The plant matter is submerged in a solvent, such as water, while subjected to the mechanical vibrations caused by ultrasound,

which break the cell walls thus inducing the release of oil droplets [5]. In comparison with conventional/classical methods, UAE enhances the extraction efficiency, reduces extraction time and temperature required [5].

2.3 Safrole and Sassafras

Safrole (IUPAC name: 5-(2-propenyl)-1,3-benzodioxole; CAS 94-59-7) is an aromatic organic compound, colorless to slightly yellow liquid with the odor of sassafras [22]. A high amount of this particular oil can be found in plants such as sassafras trees but also in several others. It is present in tree trunks, roots, bark, branches and leaves of over 360 tree species [23]. It is insoluble in water and soluble in ethanol, chloroform and most common organic solvents [24]. It is reasonably anticipated to be a human carcinogen based on sufficient evidence of carcinogenicity from studies in experimental animals [25]. Minimal exposure to safrole may occur through the use of edible spices, such as nutmeg, which contain low levels of this compound [22].

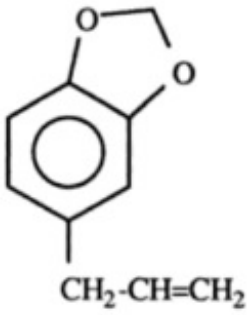

Figure 2.7: safrole

Some of the physical and chemical properties of safrole are listed in table 2.6.

Table 2.6: Some of the physical and chemical properties of safrole [24].

Properties	Information
Appearance	Colorless to slightly yellow, oily liquid
Molecular weight	162.18 g/mol
Melting point	11 °C
Boiling point	234.5°C
Specific gravity	1.092 - 1.101 at 25°C
Refractive index	1.5360 - 1.5385 at 20°C
Solubility	1:3 in 90% alcohol; insoluble in water; soluble in alcohol, ether, chloroform and most common organic solvents

Sassafras is a genus in the family Lauraceae and consists of three species: *Sassafras albidum* is native from eastern North America while the other two (*Sassafras tzumu* and *Sassafras randaiense*) are found in eastern Asia [26]. Sassafras oil (CAS 8006-80-2) can be

extracted from the root bark and wood of *Sassafras albidum* tree. The oil obtained from the root bark, entire root or root wood of sassafras tree by different methods. However, according to literature, it is known that the root bark contains up to 9% oil while the entire root contains only 1.0 - 2.0% oil and the root wood contains less than 1.0% oil [27].

The sassafras oil extracted from the root bark by organic solvent extraction, with hexane and chloroform as solvents, contained about 85% of safrole and the others are minor compounds such as terpenes and terpenoids [28]. It has also been reported that sassafras oil obtained by steam distillation had about 80% safrole and by hydrodistillation contained 82.82% safrole [28] [27]. Safrole can also be found as a minor constituent of oils from several spices, including nutmeg and black pepper. The oil extracted from Nutmeg seeds (Myristica fragrans Houtt.) contains 4.28% safrole and black pepper spice has about 1% safrole [29] [30]. Nowadays, the main purpose of sassafras oil is the isolation of safrole to be used by chemical industry. The safrole extract is then converted by the chemical industry into two commercial derivatives: heliotropin, which is normally used as a fragrance fixer in perfumery or as a flavouring agent; and piperonal butoxide (PBO), a vital component of pyrethroid insecticides. PBO is a key component in bio insecticides and acts as a synergist of natural pyrethrum [31]. The future of the natural pyrethrum industry is linked to the continued availability of PBO [31]. However, it is also the precursor used in the production of ecstasy, a well-known psychoactive drug commonly consumed as a recreational drug [23].

2.4 Ionic liquids

Ionic liquids are a class of salt-like materials which are liquid at unusually low temperatures. Ionic liquids use the boiling point of water as reference and are officially defined: "Ionic liquids are ionic compounds which are liquid below 100 ºC" with a melting temperature below the boiling point of water [32].

Ionic liquids can be composed by a wide variety of cations and anions. Ionic liquids are composed by poorly coordinated ions: usually a large organic nitrogen-containing cation (imidazolium, pyrrolidinium, ...) coupled with relatively small organic or inorganic anions (Cl^-, PF_6^-, BF_4^-, ...) [32]. Ionic liquids have poorly coordinated ions because at least one of them has a delocalized charge preventing the formation of a stable crystal lattice.

Since ionic liquids were widely considered as an alternative solvent, they have been used in many fields including extraction, replacing the commonly used environmentally hazardous volatile organic solvents in chemical industry.

Their negligible vapour pressure is the main reason that renders them useful in green chemistry. In addition, they can be easily recovered and produce minimum volatile organic compounds emissions if no organic solvents are used to recycle them [33].

The application of ionic liquids for extraction processes is promising because of their of unique combination of physicochemical characteristics: wide liquid range and electrochemical window, low flammability, extremely low vapour pressure and high thermal

stability [34]. The possibility to manipulate the cations and/or anions in order to obtain a certain set of properties allows for the design of these solvents to exhibit selective solubility for specific components in fluid mixtures, being potentially useful for a large range of applications [34]. These characteristics allow ionic liquids to serve as excellent alternative solvents for extraction purposes and as potential green solvents for industrial purposes [33]. Unsaturated organic compounds, particularly aromatic compounds, tend to be soluble in ionic liquids whereas saturated organic compounds are generally immiscible with ionic liquids [35]. Although aromatics exhibit a large solubility in ionic liquids, a miscibility gap is usually observed [35]. According to literature, one exception is, for instance, the fact that the ionic liquid $[P_{6.6.6.14}][NTf_2]$ has complete miscibility with benzene [36].

The interactions between ionic liquids and different compounds can be studied by means of activity coefficients at infinite dilution (γ_{13}^{∞}). Activity coefficients at infinite dilution, also referred to as limiting activity coefficient, is the limiting value of the activity coefficient of a solute when its concentration tends towards zero. In those conditions, each solute molecule is surrounded only by solvent molecules, therefore, only solute-solvent interactions take place [37]. It provide useful information about the possibility of use of an IL in separation processes: selectivities and capacities at infinite dilution for different systems can be obtained directly from activity coefficients [38]:

1. Selectivity: $S_{12}^{\infty} = \gamma_{13}^{\infty}/\gamma_{23}^{\infty}$
2. Capacity: $k_2^{\infty} = 1/\gamma_{13}^{\infty}$

The lower the values of γ_{13}^{∞} , the stronger are the interaction between solvent and solute[38]. A valid and commonly used method is inverse gas chromatography, which is especially suitable for ionic liquids due to their low volatility [39].

Chapter 3

Experimental Section

3.1 Materials

Safrole was purchased from Sigma Aldrich. It was stored over freshly activated 5 Å molecular sieves of type 522 (Roth) for approximately 24 hours prior the experiments in order to remove water impurities. Sassafras oil was purchased from BOC Sciences. According to the supplier, Sassafras oil from this supplier contains 71% safrole in weight. The ionic liquids $[P_{6.6.6.14}][NTf_2]$, $[DoMIM]][NTf_2]$ and $[N_{8.2.2.2}][NTf_2]$, were purchased from Iolitec. As for $[P_{6.6.6.14}][TCM]$, $[COC_2mPIP][FAP]$ and $[COC_2mPYR][FAP]$, these were purchased from Merck. The ionic liquids mentioned were purified by subjecting them to a very low pressure at a temperature of 343 K for at least 8 hours with stirring and then placed in a vacuum oven under the same conditions overnight. The Karl Fischer analysis revealed that water content was around 300 ppm, specifically $[P_{6.6.6.14}][NTf_2]$ 290 ppm, $[DoMIM]][NTf_2]$ 296 ppm, $[N_{8.2.2.2}][NTf_2]$ 300 ppm, $[P_{6.6.6.14}][TCM]$ 298 ppm, $[COC_2mPIP][FAP]$ 300 ppm and $[COC_2mPYR][FAP]$ 295 ppm.

Table 3.1: Names, Supplier and purity of the original materials used in this study

Compound	Supplier	Mass fraction purity	CAS number
Safrole	Sigma-Aldrich	≥ 0.97	94-59-7
Sassafras oil	BOC Sciences	0.71	8006-80-2

Table 3.2: Name, abbreviation and structure of investigated ionic liquids

Name	Abbreviation
Trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide	$[P_{6.6.6.14}][NTf_2]$
Trihexyltetradecylphosphonium tricyanomethanide	$[P_{6.6.6.14}][TCM]$
1-Dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	$[DoMIM]][NTf_2]$
Octyltriethylammonium bis(trifluoromethylsulfonyl)imide	$[N_{8.2.2.2}][NTf_2]$
1-(2-methoxyethyl)-1-methylpiperidinium trifluorotris(perfluoroethyl)phosphate	$[COC_2mPIP][FAP]$
1-ethyl-3-methylimidazolium dicyanamide	[EMIM][DCA]
1-ethyl-3-methylimidazolium thiocyanate	[EMIM][SCN]
1-ethyl-3-methylimidazolium tosylate	[EMIM][TOS]
1-ethyl-3-methylimidazolium trifluoroacetate	[EMIM][TFA]
1-ethyl-3-methylimidazolium ethylsulfate	[EMIM][$EtSO_4$]
1-butyl-3-methylimidazolium tetrafluoroborate	[BMIM][BF_4]
1-butyl-3-methylimidazolium methylsulfate	[BMIM][CH_3SO_4]
1-butyl-3-methylimidazolium acetate	[BMIM][AcO]
ethylmethylmorpholinium acetate	[EMMo][AcO]

3.2 Differential scanning calorimetry

This method was used to measure the basic thermal properties of safrole, i.e temperature and enthalpy of fusion and crystallization. The analysis of pure safrole was conducted using a Mettler Toledo DSC 1 STARe System equipped with a nitrogen cooling system. A droplet of pure safrole was sealed in a 40 µl aluminum crucible with pin. The sample was subjected to a initial temperature of -130ºC at a heating rate of 5 ºC.min^{-1} until 30 ºC, then cooled at the same rate and reheated. All data was collected and processed using STARe software.

3.3 Binary Liquid-liquid equilibria measurements

In order to estimate which ionic liquids were potentially more suitable for the extraction of safrole from the oil, activity coefficients at infinite dilution of organic solutes in different ionic liquids were consulted. Although there is no record of previous experimental work on the subject regarding safrole, activity coefficient values at infinite dilution for other organic compounds with specific characteristics were selected from literature: gamma infinity of benzene was selected due to its aromatic ring and gamma infinity of 1,4-dioxane was selected due to its carbon-oxygen bonding. Both of these characteristics are present in the safrole molecule. Six ionic liquids were chosen on the criteria of smaller activity coefficient at infinite dilution. In this work, the cloud point method for safrole(1) + ionic liquid(2) binary systems was used. However, some experimental data with the following ionic liquids: $[N_{8.2.2.2}][NTf_2]$, $[COC_2mPIP][FAP]$ and $[COC_2mPYR][FAP]$ were not investigated as these binary systems required a very high temperature, specially at very low concentration of these ionic liquids. Only experimental data at temperature below 368 K were investigated in this study.

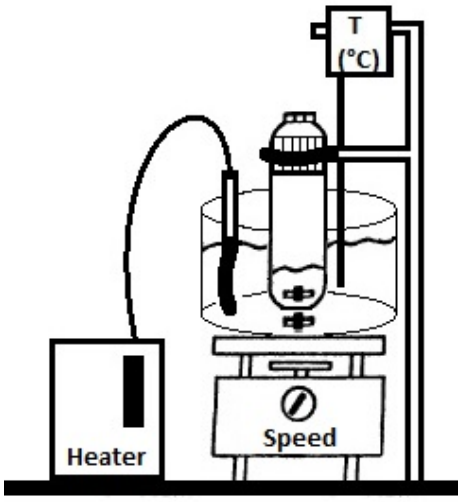

Figure 3.1: Experimental setup for liquid-liquid equilibria.

3.4 GC analysis

All the experiments to determine safrole by this technique were performed using a PerkinElmer® Clarus® 580 gas chromatograph and all data were collected and processed using TotalChrom Workstation software. Firstly, a calibration curve for the compound safrole was prepared so that the quantification of safrole extracted from the oil could be done afterwards. This calibration curve may be consulted from appendix B. Multiple samples were prepared with different amounts in order to obtain a proper calibration curve. All samples were injected by autosampler and measured at least three times. The conditions used are described in table 3.3.

Table 3.3: Operating conditions in the GC for the compositional analysis of sassafras oil and safrole

Element	Characteristic	Description
Column	Type	PerkinElmer Elite-5 (5% diphenyl / 95% dimethyl polysiloxane) 30 m length, 0.53 mm internal diameter, 1.5 µm film thickness PerkinElmer Elite-WAX (Polyethylene Glycol) 30 m length, 0.53 mm internal diameter, 1 µm film thickness
	Flow	3 $cm^3.min^{-1}$ for 35 min
	Carrier gas	Helium
Oven	Temperature	423.15 K for 35 min
Injector	Injection volume	10^{-4} cm^3
	Split ratio	7:1
	Temperature	473.15 K
Detector	Type	Flame Ionization Detector (FID)
	Temperature	493.15 K

3.5 GC/MS analysis

Experiments to confirm the safrole content in sassafras oil were performed. The samples were injected manually into a PerkinElmer® Clarus® 560 mass spectrometer via a PerkinElmer® Clarus® 580 gas chromatograph. All data were collected and processed using Turbomass GC/MS software and the conditions used are described in table 3.4.

Table 3.4: Operating conditions in the GC/MS for the compositional analysis of sassafras oil and safrole

Element	Characteristic	Description
Column	Type	PerkinElmer Elite-5MS (5% diphenyl / 95% dimethyl polysiloxane) 30 m length, 0.25 mm internal diameter, 0.25 µm film thickness
	Flow	1 $cm^3.min^{-1}$
	Carrier gas	Helium
Oven	Temperature	473.15 K for 1 min; then gradient: 10 $K.min^{-1}$ until 573.15 K and held for 10 min
Injector	Split ratio	49:1
	Temperature	523.15 K

3.6 CNMR and HNMR analysis

Nuclear magnetic resonance (NMR) of safrole and sassafras oil were performed in order to confirm the presence of safrole in the oil. These analysis were performed on a Varian NMR System 500 MHz spectrometer at 25ºC. Both samples were diluted in deuterated chloroform (CDCl3) at 1:3 ratio (v/v).

3.7 Extraction

The liquid-liquid extraction experiments were carried out at T = 298.15 K by preparation of immiscible mixtures of 2 cm^3 of sassafras oil and 2 cm^3 of ionic liquids. Mixtures were placed into a jacketed glass cell with a volume of 10 cm^3, together with a coated magnetic stirring bar, and closed to avoid losses of substances by evaporation or absorption of moisture from the atmosphere. The jackets were connected to a thermostat bath (LAUDA Alpha A12) which was set to maintain a constant temperature of 298.15 K in the vessels. The mixtures were stirred using the magnetic stirrer for at least 3 h to reach the thermodynamic equilibrium and then allowed to settle overnight to guarantee that the equilibrium state was reached completely. After phase separation, approximately 0.1 cm^3 samples from both phases in equilibrium (a denser ionic liquid rich phase at the bottom and a less dense oil phase on the top) were taken using single use syringes, without disturbance of the interface. Samples of the phase were placed in a sample vial and sealed with a septum cap. Acetone (1 cm^3) was added to the samples to avoid phase splitting and to maintain a homogeneous mixture. Since ionic liquids have a negligible vapour pressure, they can not be analyzed by GC and, consequently, only components from the oil were analyzed.

The capillary column of the gas chromatograph was protected with a pre-column to prevent the non-volatile ionic liquid from reaching the column. The data were collected and processed using TotalChrom Workstation software. The extraction of safrole from sassafras oil was attempted with both ionic liquids and organic solvents. Firstly, it was necessary to observe if the most promising ionic liquids: $[P_{6.6.6.14}][NTf_2]$, $[P_{6.6.6.14}][TCM]$, $[DoMIM]][NTf_2]$ and $[N_{8.2.2.2}][NTf_2]$ formed two separated liquid phases with the oil so that the extraction was feasible. The ionic liquids previously mentioned were promising because they presented a significantly narrow miscibility gap with safrole. Then, the same procedure was followed with other ionic liquids mentioned in table 3.2 and also with different classes of organic solvents such as alcohols, amines, ketones, ethers and alkanes.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Differential scanning calorimetry

Firstly, DSC analysis of safrole was performed. Values of temperature and enthalpy of fusion (T_{fus} and ΔH_{fus}) as well as temperature and enthalpy of crystallization were obtained. The melting temperature of safrole obtained by DSC was 9.6 ºC and the enthalpy of fusion was 139.51 J.g^{-1}. Both parameters were obtained by the average of the resulting values during cooling and heating of the sample. According to literature, safrole has a melting point of 11.2 ºC, although it has been reported to melt at 7-8 ºC for crude isolates [40]. The temperature of crystallization obtained by this method was -63.38 ºC and the enthalpy of crystallization was 110.78 J.g^{-1}.

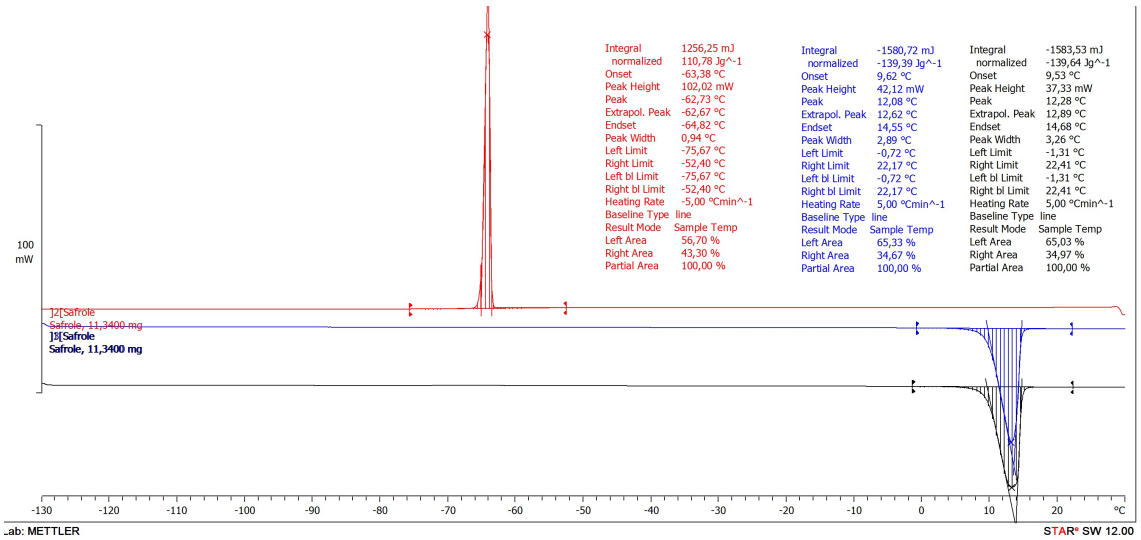

Figure 4.1: DSC analysis results for pure safrole.

4.2 Binary Liquid-liquid equilibria measurements

LLE phase diagrams for the investigated safrole(1) + ionic liquid(2) binary systems are presented in figure 4.2 and all the data points are presented in tables A.1 and A.2. Based on the measured binary systems data, some observations regarding the choice of ionic liquids used for extraction can be made. Firstly, in all cases, the miscibility gap was located at the safrole rich region (higher than 0.5 molar fraction). It was also noticed that there is a significative difference of the width of some miscibility gaps. Both systems $[P_{6.6.6.14}][NTf_2]$ and $[P_{6.6.6.14}][TCM]$ presented a very similar behaviour and the most narrow miscibility gaps.$[DoMIM]][NTf_2]$ had a slightly wider miscibility gap than those previously mentioned, but it was miscible over a wide region. As for $[N_{8.2.2.2}][NTf_2]$, $[COC_2mPIP][FAP]$ and $[COC_2mPYR][FAP]$ these presented very large miscibility gaps and the maximum of the binodal curves were not obtained for this work. . The maximum of the binodal curves and corresponding composition are presented in table A.3.

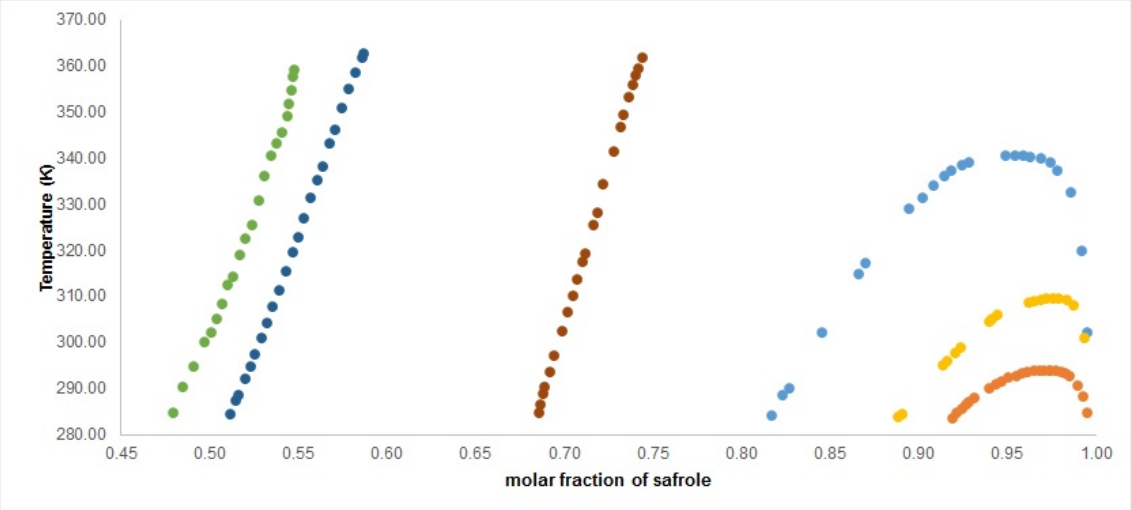

Figure 4.2: Binary LLE phase diagrams for safrole with different ionic: $[P_{6.6.6.14}][NTf_2]$ (orange); $[P_{6.6.6.14}][TCM]$ (yellow); $[DoMIM]][NTf_2]$ (blue); $[N_{8.2.2.2}][NTf_2]$ (brown); $[COC_2mPIP][FAP]$ (dark blue) and $[COC_2mPYR][FAP]$ (green).

4.3 GC analysis

The samples of safrole and sassafras oil were prepared and the analysis were performed under the conditions described in table 3.3. Firstly, both pure and diluted samples of safrole were analysed. Acetone was used to dilute the samples.

Then both pure and diluted samples of sassafras oil were tested.

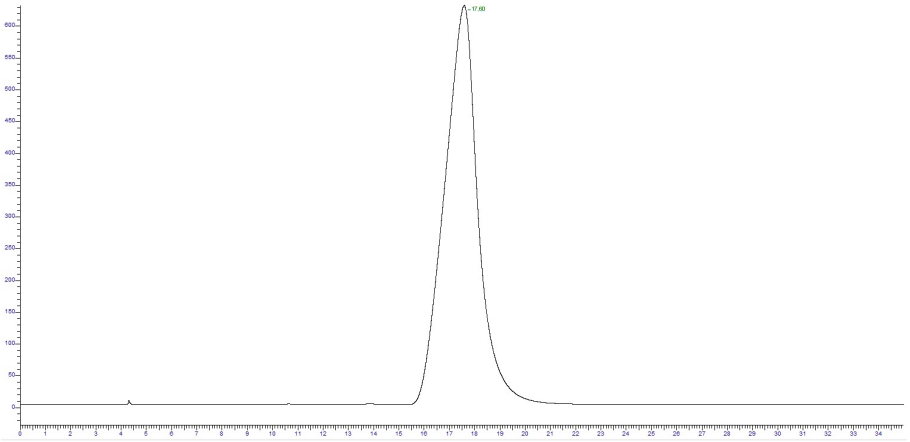

Figure 4.3: GC analysis of pure safrole sample.

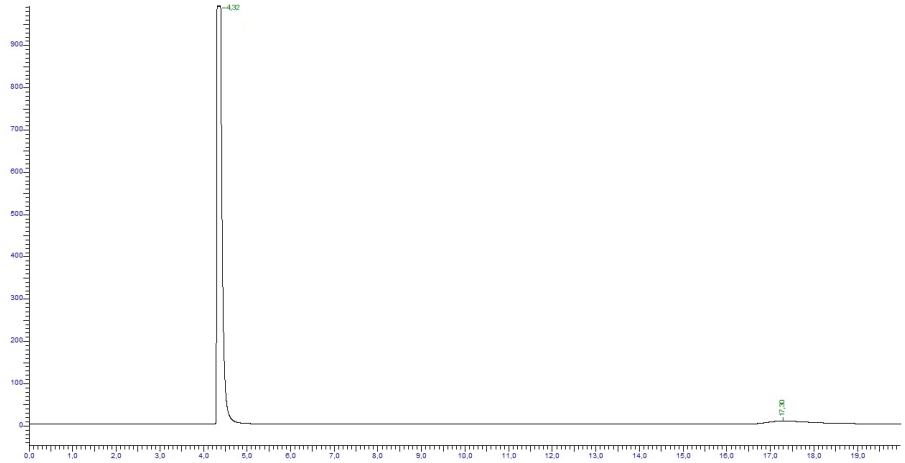

Figure 4.4: GC analysis of safrole diluted in acetone (C = 1.604E-02 g.cm^3)

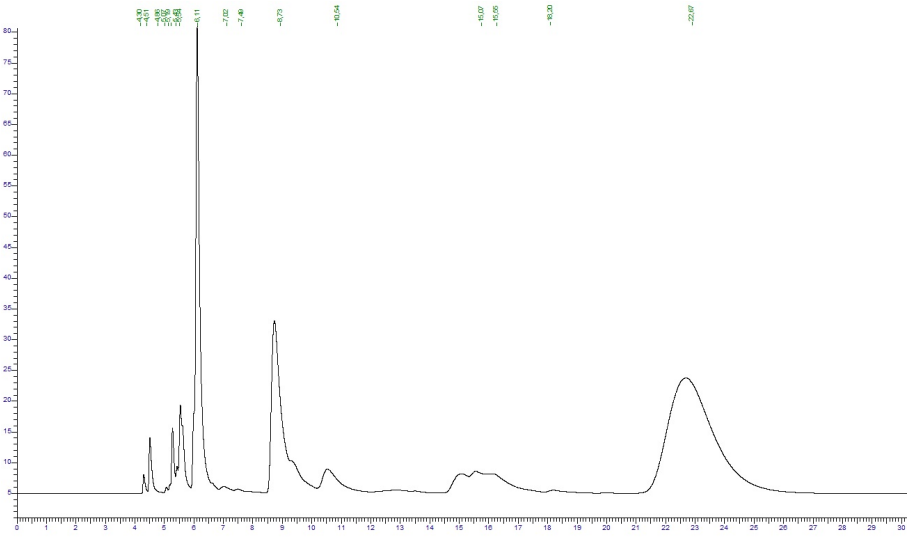

Figure 4.5: GC analysis of sassafras oil.

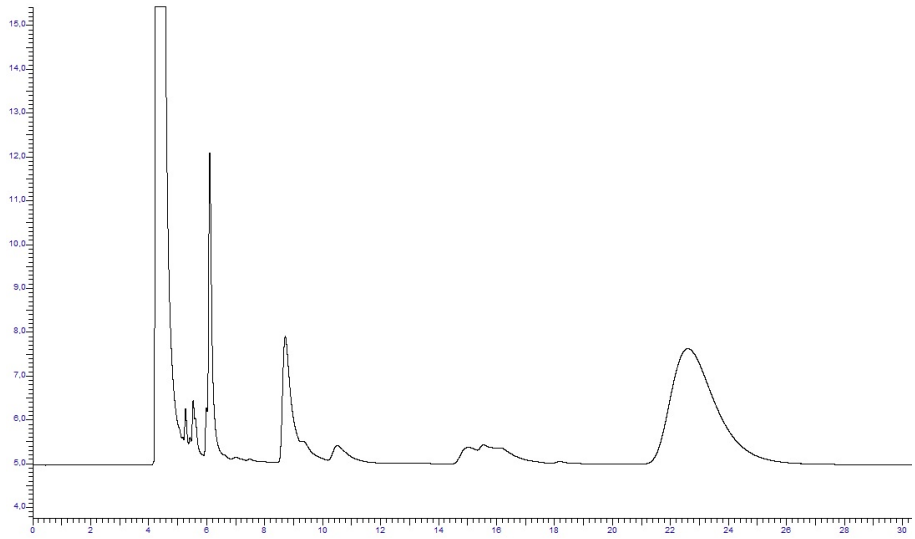

Figure 4.6: GC analysis of sassafras oil diluted in acetone. (C = 1.80E-01 g.cm^3)

The results were unexpected. There is no corresponding peak of safrole at about 17.60 minutes in the oil analysis as obtained in the safrole samples. Apart from the solvent peak at 4.32 minutes, the most relevant peaks for oil compounds were observed at about 6.11, 8.73 and 22.67 minutes.

4.4 GC-MS

The samples of safrole and sassafras oil were prepared and the analysis were performed under the conditions described in table 3.4. The samples were diluted in chloroform. Firstly, the safrole sample was analysed.

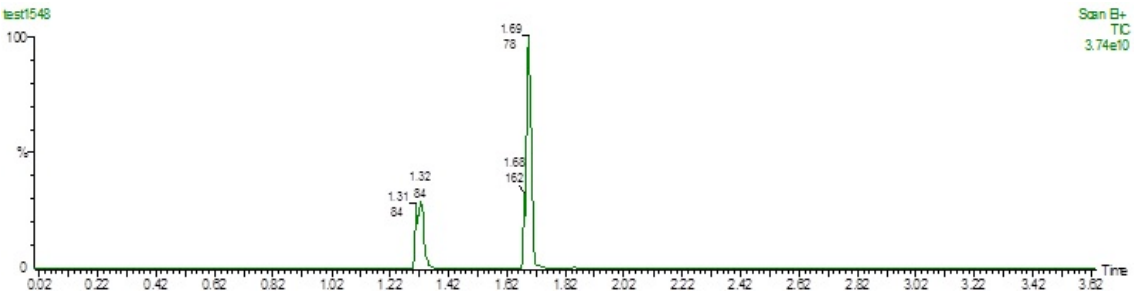

Figure 4.7: GC analysis of diluted safrole sample.

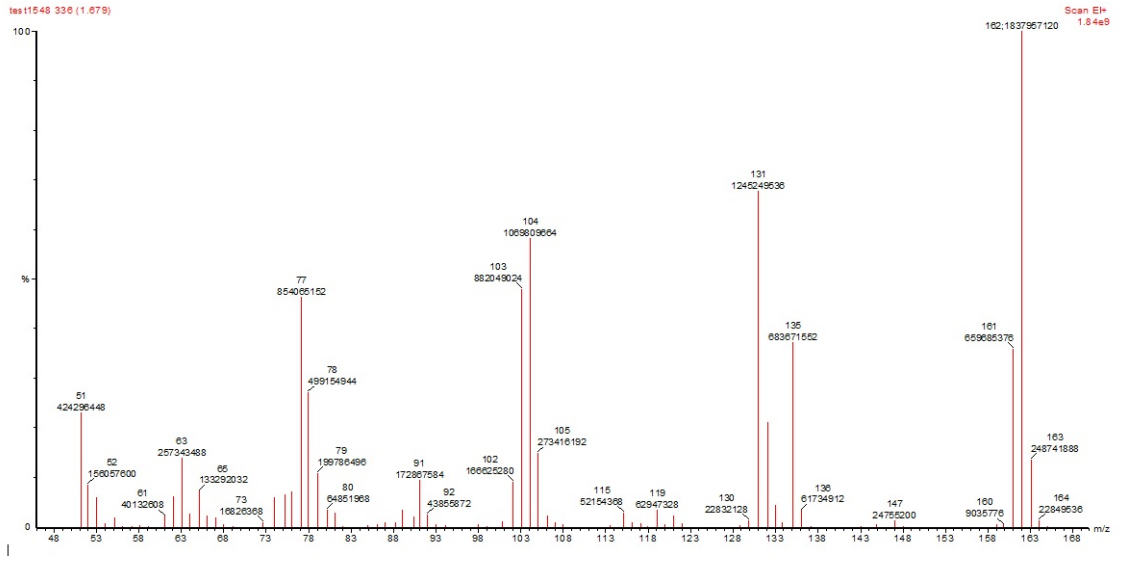

Figure 4.8: MS analysis of diluted safrole sample.

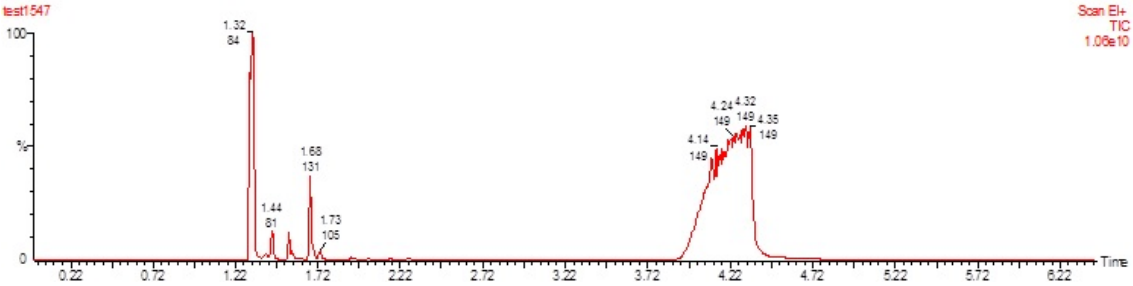

Figure 4.9: GC analysis of diluted sassafras oil sample.

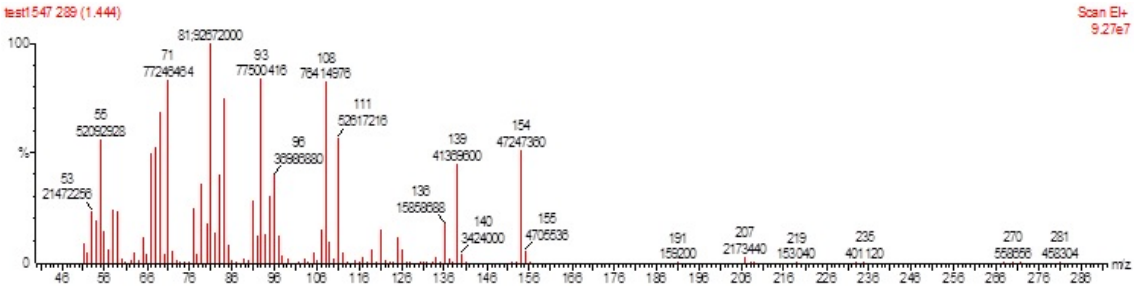

Figure 4.10: MS analysis of diluted sassafras oil sample at 1.44 minutes.

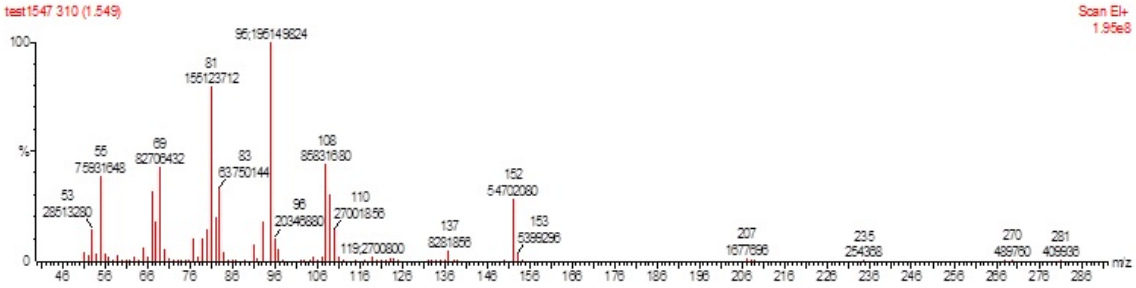

Figure 4.11: MS analysis of diluted sassafras oil sample at 1.55 minutes.

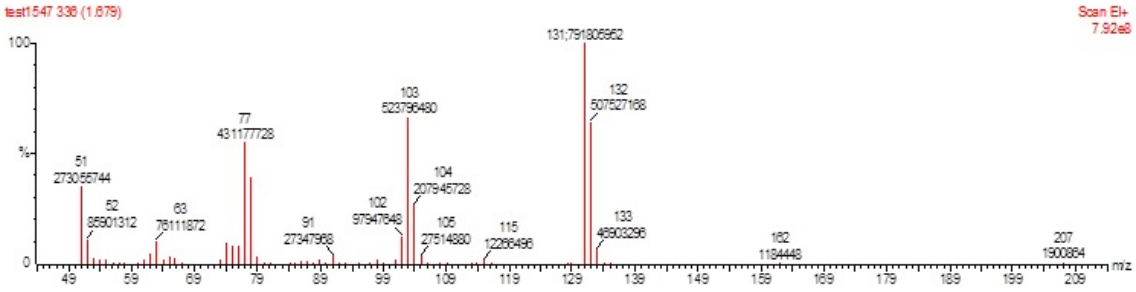

Figure 4.12: MS analysis of diluted sassafras oil sample at 1.68 minutes.

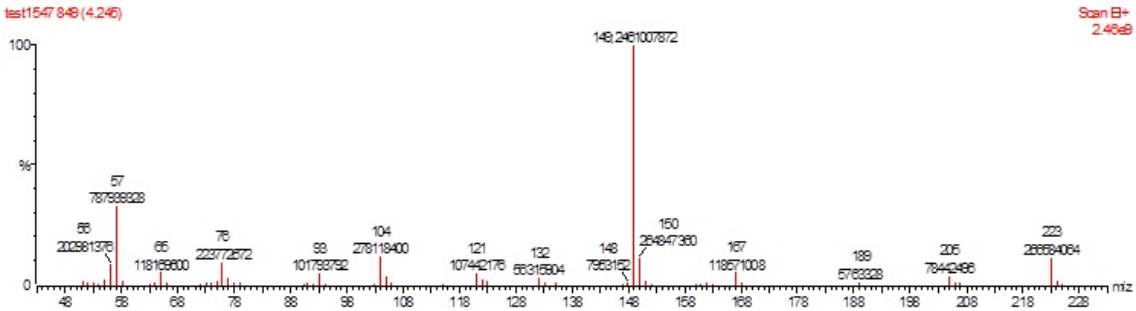

Figure 4.13: MS analysis of diluted sassafras oil sample at 4.25 minutes.

Although the conditions used for this procedure (see table 3.4) were different than those used for the GC analysis (see table 3.3), safrole should be detected in the oil at the same retention time as the safrole sample (1.68 minutes). However, the fragmentation pattern obtained in the MS at 1.68 minutes for the oil sample did not show a significative signal at 162 m/z, the highest peak obtained for safrole as in literature [41]. Other compounds were detected in the oil at 1.44, 1.55, 1.68, 1.73 and 4.25 minutes.

4.5 CNMR and HNMR analysis

The results of the nuclear magnetic resonance analysis of the safrole sample are compatible with spectrums found in literature [42] [43].

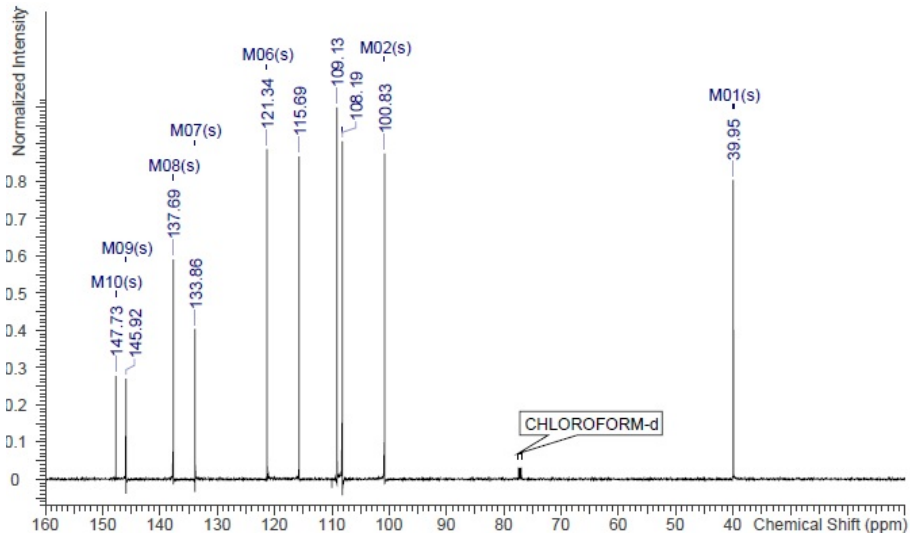

Figure 4.14: CNMR results of safrole diluted in deuterated chloroform (ratio 1:3 (v/v)).

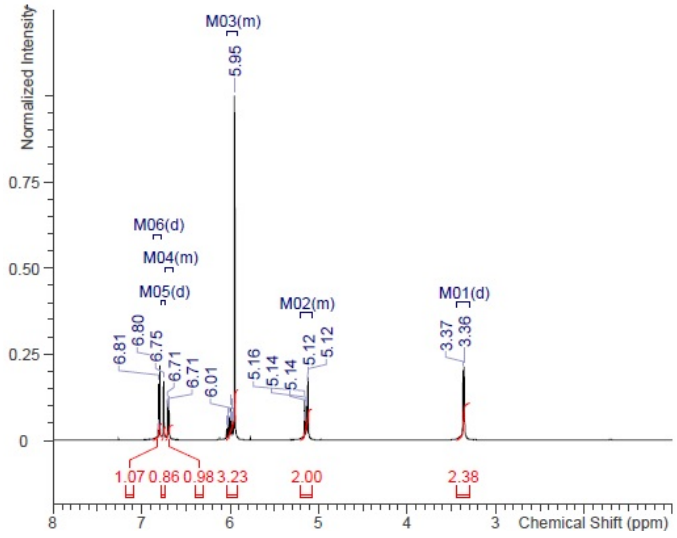

Figure 4.15: HNMR results of safrole diluted in deuterated chloroform (ratio 1:3 (v/v)).

However, when the safrole CNMR and HNMR spectrums were compared to those obtained for the oil, the results were unexpected. There were no compatible spectrum signals of safrole detected in the oil sample.

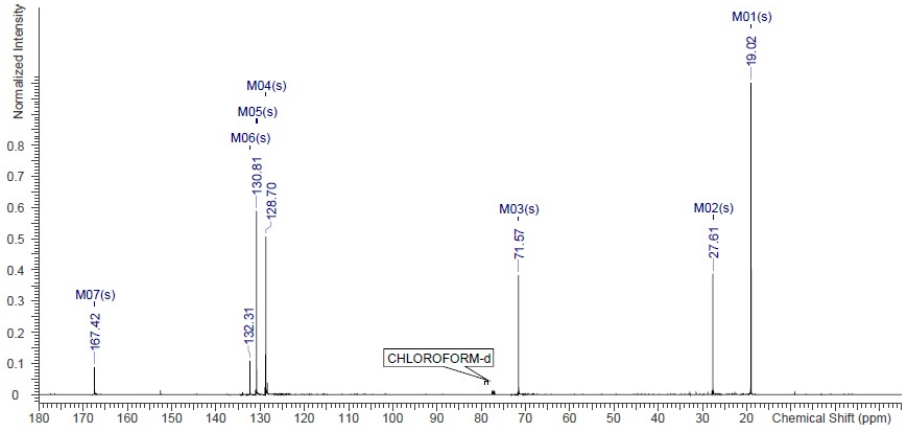

Figure 4.16: CNMR results of sassafras oil diluted in deuterated chloroform (ratio 1:3 (v/v)).

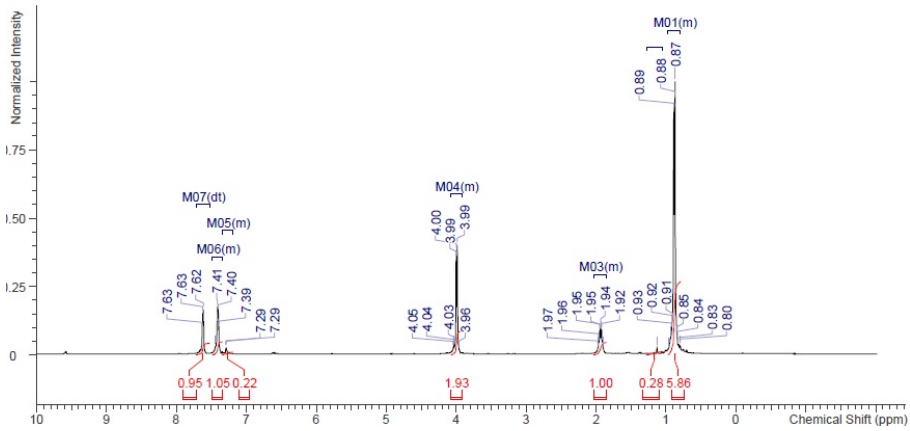

Figure 4.17: HNMR results of sassafras oil diluted in deuterated chloroform (ratio 1:3 (v/v)).

4.6 Extraction

Firstly, small samples of mixtures of sassafras oil with each one of the following ionic liquids: $[P_{6.6.6.14}][NTf_2]$, $[P_{6.6.6.14}][TCM]$ and $[DoMIM]][NTf_2]$ were prepared. However, these ionic liquids did not reveal any sign of forming two phases with the oil at room temperature, thus extraction could not be performed by this manner. Attempts to obtain two phases were also performed by means of different organic solvents. The organic solvents used in this work were: acetone, chloroform, methanol, ethanol, butanol, nonanol, dodecanol, monoethanolamine, n-methyldiethanolamine, triethanolamine, trimethylamine, 1-methylimidazole, 3-propanone, diethyl ether, acetonitrile, n-hexane, hexadecane. Two phases were obtained by mixing oil with the following solvents: monoethanolamine, n-methyldiethanolamine and triethanolamine.

Attempts with other ionic liquids were made and these were selected according to the following criteria: they must be miscible with water, short chain on alkyl group and preferably with an aromatic ring so that it interacts with safrole. Then water can be added to the ionic liquid extract and, since safrole is insoluble in water, safrole would be in the organic phase and the ionic liquid in the water phase. Therefore, miscibility tests with the the oil were made using the following ionic liquids: 1-ethyl-3-methylimidazolium dicyanamide [EMIM][DCA], 1-ethyl-3-methylimidazolium thiocyanate [EMIM][SCN], 1-ethyl-3-methylimidazolium tosylate [EMIM][TOS], 1-ethyl-3-methylimidazolium trifluoroacetate [EMIM][TFA], 1-ethyl-3-methylimidazolium ethylsulfate $[EMIM][EtSO_4]$, 1-butyl-3-methylimidazolium tetrafluoroborate $[BMIM][BF_4]$, 1-butyl-3-methylimidazolium methylsulfate $[BMIM][CH_3SO_4]$, 1-butyl-3-methylimidazolium acetate [BMIM][AcO] and 1-ethyl-3-methylmorpholinium acetate [EMMo][AcO]. All these ionic liquids have formed two liquid phases with the oil.

Chapter 5

Conclusions

The binary liquid-liquid phase equilibria data were measured in this study to investigate the miscibility of safrole with different ionic liquids. Five binary system phase diagrams were determined by a dynamic method. It has been demonstrated that the phosphonium based ionic liquids presented the most narrow miscibility gaps. Diferent methods were used to determine if safrole was present in the sassafras oil supplied by BOC Sciences, which should be 71% of safrole in weight. The NMR results have shown no presence of safrole and GC analysis did not reveal a peak compatible with the results of the safrole analysis. In conclusion, safrole was not detected in the sassafras oil supplied for the experiment and, therefore, its presence was not confirmed.

Bibliography

[1] H.-J. Bart and S. Pilz. *Industrial Scale Natural Products Extraction*. John Wiley & Sons, 2011.

[2] K. Baser and G. Buchbauer. *Handbook of Essential Oils: Science, Technology, and Applications*. 2nd edition. CRC Press, 2015.

[3] M. Martins, U. Domańska, et al. "Selection of Ionic Liquids to be Used as Separation Agents for Terpenes and Terpenoids". In: *ACS Sustainable Chem. Eng.* 4 (2016), pp. 548–556.

[4] J. Raut and S. Karuppayil. "A status review on the medicinal properties of essential oils". In: *Industrial Crops and Products* 62 (2014), pp. 250–264.

[5] A. Asbahani, K. Miladi, et al. "Essential oils: from extraction to encapsulation". In: *International Journal of Pharmaceutics* 483 (2015), pp. 220–243.

[6] *Terpenoids*. URL: http://www.cyberlipid.org/simple/simp0004.htm#1.

[7] F. Bakkali, S. Averbeck, et al. "Biological effects of essential oils - A review". In: *Food and Chemical Toxicology* 46 (2008), pp. 446–475.

[8] B. Ali, N. Al-Wabel, et al. "Essential oils used in aromatherapy: a systematic review". In: *Asian Pacific Journal of Tropical Biomedicine* 5(8) (2015), pp. 601–611.

[9] S. Burt. "Essential oils: their antibacterial properties and potential applications in foods — a review". In: *International Journal of Food Microbiology* 94 (2004), pp. 223–253.

[10] M. R. Tellez, I. A. Khan, et al. "Steam distillation–solid-phase microextraction for the detection of Ephedra sinica in herbal preparations". In: *Journal of Chromatography A* 1025.1 (2004), pp. 51–56.

[11] F Chemat, M. Lucchesi, et al. "Microwave accelerated steam distillation of essential oil from lavender: A rapid, clean and environmentally friendly approach". In: *Analytica Chimica Acta* 555.1 (2006), pp. 157–160.

[12] M. Khajeh, Y. Yamini, et al. "Comparison of essential oils compositions of Nepeta persica obtained by supercritical carbon dioxide extraction and steam distillation methods". In: *Food and bioproducts processing* 88.2 (2010), pp. 227–232.

[13] M. Z. Ozel and H. Kaymaz. "Superheated water extraction, steam distillation and Soxhlet extraction of essential oils of Origanum onites". In: *Analytical and bioanalytical chemistry* 379.7-8 (2004), pp. 1127–1133.

[14] A Donelian, L. Carlson, et al. "Comparison of extraction of patchouli (Pogostemon cablin) essential oil with supercritical CO 2 and by steam distillation". In: *Journal of Supercritical Fluids* 48.1 (2009), pp. 15–20.

[15] C Boutekedjiret, F Bentahar, et al. "Extraction of rosemary essential oil by steam distillation and hydrodistillation". In: *Flavour and Fragrance Journal* 18.6 (2003), pp. 481–484.

[16] A. Ammann, D. C. Hinz, et al. "Superheated water extraction, steam distillation and SFE of peppermint oil". In: *Fresenius' journal of analytical chemistry* 364.7 (1999), pp. 650–653.

[17] S. A. Heleno, P. Diz, et al. "Optimization of ultrasound-assisted extraction to obtain mycosterols from Agaricus bisporus L. by response surface methodology and comparison with conventional Soxhlet extraction". In: *Food chemistry* 197 (2016), pp. 1054–1063.

[18] S. Zhao and D. Zhang. "Supercritical CO 2 extraction of Eucalyptus leaves oil and comparison with Soxhlet extraction and hydro-distillation methods". In: *Separation and Purification Technology* 133 (2014), pp. 443–451.

[19] M. Faisal et al. "Extraction of essential oils from jasmine flower using solvent extraction method". PhD thesis. Universiti Malaysia Pahang, 2006.

[20] C. Da Porto, D. Decorti, et al. "Microwave pretreatment of Moringa oleifera seed: Effect on oil obtained by pilot-scale supercritical carbon dioxide extraction and Soxhlet apparatus". In: *Journal of Supercritical Fluids* 107 (2016), pp. 38–43.

[21] J. M. Danlami, A. Arsad, et al. "Characterization and process optimization of castor oil (Ricinus communis L.) extracted by the soxhlet method using polar and non-polar solvents". In: *Journal of the Taiwan Institute of Chemical Engineers* 47 (2015), pp. 99–104.

[22] *PubChem, database of the National Center for biotechnology Information, U.S. National Library of Medicine, National Institutes of Health*. URL: http://pubchem.ncbi.nlm.nih.gov/compound/safrole#section=Top.

[23] *United Nations Office on Drugs and Crime*. URL: https://www.unodc.org/unodc/en/frontpage/cambodia-tackles-safrole-oil-production.html.

[24] G. Burdock. *Encyclopedia of Food and Color Additives*. Vol. 3. CRC Press, 1997.

[25] *14th Report on Carcinogens, National Toxicology Program, U.S Department of Health and Human Services*. 2016. URL: hhttps://ntp.niehs.nih.gov/ntp/roc/content/introduction_508.pdf.

[26] Z.-L. Nie, J. Wen, et al. "Phylogeny and biogeography of Sassafras (Lauraceae) disjunct between eastern Asia and eastern North America". In: *Plant Systematics and Evolution* 267 (2007), pp. 191–203.

[27] J. Zwaving and R. Bos. "Composition of the Essential Oil from the Root of *Sassafras albidum* (Nutt.) Nees". In: *Journal of Essential Oil Research* 8 (1996), pp. 193–195.

[28] D. Kamdem and D. Gage. "Chemical Composition of Essential Oil from the Root Bark of *Sassafras albidum*". In: *Planta Medica* 61 (1995), pp. 574–575.

[29] Muchtaridi, A. Subarnas, et al. "Identification of Compounds in the Essential Oil of Nutmeg Seeds (*Myristica fragrans* Houtt.) That Inhibit Locomotor Activity in Mice". In: *International Journal of Molecular Sciences* 11 (2010), pp. 4771–4781.

[30] S. Farag and M. Abo-Zeid. "Degradation of the natural mutagenic compound safrole in spices by cooking and irradiation". In: *Nahrung* 41 (1997), pp. 359–361.

[31] *Erowid, non-profit educational & harm-reduction organization*. URL: https://www.erowid.org/archive/rhodium/chemistry/3base/safrole.plants/fafopo/sassafras_oil.html.

[32] *Farnoush Faridbod, Mohammad Reza Ganjali, Parviz Norouzi, Siavash Riahi, and Hamid Rashedi (2011). Application of Room Temperature Ionic Liquids in Electrochemical Sensors and Biosensors, Ionic Liquids: Applications and Perspectives, Prof. Alexander Kokorin (Ed.), InTech, DOI: 10.5772/14702*. URL: http://www.intechopen.com/books/ionic-liquids-applications-and-perspectives/application-of-room-temperature-ionic-liquids-in-electrochemical-sensors-and-biosensors.

[33] A. Berthod, M. Ruiz-Ángel, et al. "Ionic liquids in separation techniques". In: *Journal of Chromatography A* 1184 (2008), pp. 6–18.

[34] D. Santos, M. Góes, et al. "Phase equilibria for binary systems containing ionic liquid with water or hydrocarbon". In: *Brazilian Journal of Chemical Engineering* 32 (2015), pp. 967–974.

[35] M. Freemantle. *An Introduction to Ionic Liquids*. Royal Society of Chemistry, 2010.

[36] R. Canales and F. Brennecke. "Comparison of Ionic Liquids to Conventional Organic Solvents for Extraction of Aromatics from Aliphatics". In: *Journal of Chemical & Engineering Data* 61 (2016), pp. 1685–1699.

[37] K. Tumba et al. "Infinite dilution activity coefficient measurements of organic solutes in fluorinated ionic liquids by gas-liquid chromatography and the inert gas stripping method". mscthesis. University of KwaZulu-Natal, 2010.

[38] U. Domańska and A. Marciniak. "Activity Coefficients at Infinite Dilution Measurements for Organic Solutes and Water in the Ionic Liquid 1-Ethyl-3-methylimidazolium Trifluoroacetate". In: *Journal of Physical Chemistry B* 111 (2007), pp. 11984–11988.

[39] M. Wlazło, A. Marciniak, et al. "Activity Coefficients at Infinite Dilution and Physicochemical Properties for Organic Solutes and Water in the Ionic Liquid 1-Ethyl-3-methylimidazolium trifluorotris(perfluoroethyl)phosphate". In: *Journal of Solution Chemistry* 44 (2015), pp. 413–430.

[40] *Erowid, non-profit educational & harm-reduction organization*. URL: https://www.erowid.org/archive/rhodium/chemistry/safrolefaq.html#sources.

[41] F. Jr., C. Clark, et al. "Gas Chromatographic and Mass Spectrometric Analysis of Samples from a Clandestine Laboratory Involved in the Synthesis of Ecstacy from Sassafras Oil". In: *Journal of Chromatographic Science* 29 (1991), pp. 168–173.

[42] *National Institute of Standards and Technology (USA)*. URL: http://webbook.nist.gov/cgi/cbook.cgi?ID=94-59-7&Units=SI.

[43] *Spectral Database for Organic Compounds of the National Institute of Advanced Industrial Science and Technology*. URL: http://sdbs.db.aist.go.jp/sdbs/cgi-bin/cre_index.cgi.

[44] R. Kato and J. Gmehling. "Activity coefficients at infinite dilution of various solutes in the ionic liquids $[MMIM]^+[CH_3SO_4]^-$, $[MMIM]^+[CH_3OC_2H_4SO_4]^-$, $[MMIM]^+[(CH_3)_2PO_4]^-$, $[C_5H_5NC_2H_5]^+[(CF_3SO_2)_2N]^-$ and $[C_5H_5NH]^+[C_2H_5OC_2H_4OSO_3]^-$". In: *Fluid Phase Equilibria* 226 (2004), pp. 37–44.

[45] M. Krummen, P. Wasserscheid, et al. "Measurement of Activity Coefficients at Infinite Dilution in Ionic Liquids Using the Dilutor Technique". In: *Journal of Chemical & Engineering Data* 47 (2002), pp. 1411–1417.

[46] U. Domańska, M. Królikowska, et al. "Activity coefficients at infinite dilution measurements for organic solutes and water in the ionic liquid 1-ethyl-3-methylimidazolium tetracyanoborate". In: *Journal of Chemical Thermodynamics* 43 (2011), pp. 1050–1057.

[47] M.-L. Ge, L.-S. Wang, et al. "Activity Coefficients at Infinite Dilution of Organic Solutes in 1-Ethyl-3-methylimidazolium Tetrafluoroborate Using Gas-Liquid Chromatography". In: *Journal of Chemical & Engineering Data* 53 (2008), pp. 1970–1974.

[48] G. Foco, S. Bottini, et al. "Activity Coefficients at Infinite Dilution in 1-Alkyl-3-methylimidazolium Tetrafluoroborate Ionic Liquids". In: *Journal of Chemical & Engineering Data* 51 (2006), pp. 1088–1091.

[49] E. Olivier, T. Letcher, et al. "Activity coefficients at infinite dilution of organic solutes in the ionic liquid 1-ethyl-3-methylimidazolium trifluoromethanesulfonate using gas–liquid chromatography at T = (313.15, 323.15, and 333.15) K". In: *Journal of Chemical Thermodynamics* 42 (2010), pp. 78–83.

[50] I. Sumartschenkowa, S. Verevkin, et al. "Experimental Study of Thermodynamic Properties of Mixtures Containing Ionic Liquid 1-Ethyl-3-methylimidazolium Ethyl Sulfate Using Gas-Liquid Chromatography and Transpiration Method". In: *Journal of Chemical & Engineering Data* 51 (2006), pp. 2138–2144.

[51] N. Deenadayalu, T. Letcher, et al. "Determination of Activity Coefficients at Infinite Dilution of Polar and Nonpolar Solutes in the Ionic Liquid 1-Ethyl-3-methylimidazolium Bis(trifluoromethylsulfonyl) Imidate Using Gas-Liquid Chromatography at the Temperature 303.15 K or 318.15 K". In: *Journal of Chemical & Engineering Data* 50 (2005), pp. 105–108.

[52] U. Domańska and A. Marciniak. "Measurements of activity coefficients at infinite dilution of aromatic and aliphatic hydrocarbons, alcohols, and water in the new ionic liquid [EMIM][SCN] using GLC". In: *Journal of Chemical Thermodynamics* 40 (2008), pp. 860–866.

[53] A. Blahut, V. Dohnal, et al. "Interactions of volatile organic compounds with the ionic liquid 1-ethyl-3-methylimidazolium tetracyanoborate". In: *Journal of Chemical Thermodynamics* 47 (2012), pp. 100–108.

[54] A. Blahut, V. Dohnal, et al. "Activity coefficients at infinite dilution of organic solutes in the ionic liquid 1-ethyl-3-methylimidazolium methanesulfonate". In: *Fluid Phase Equilibria* 299 (2010), pp. 198–206.

[55] A. Heintz, D. Kulikov, et al. "Thermodynamic Properties of Mixtures Containing Ionic Liquids. 2. Activity Coefficients at Infinite Dilution of Hydrocarbons and Polar Solutes in 1-Methyl-3-ethyl-imidazolium Bis(trifluoromethyl-sulfonyl) Amide and in 1,2-Dimethyl-3-ethyl-imidazolium Bis(trifluoromethyl-sulfonyl) Amide Using Gas-Liquid Chromatography". In: *Journal of Chemical & Engineering Data* 47 (2002), pp. 894–899.

[56] I. Bahadur, B. Govender, et al. "Measurement of activity coefficients at infinite dilution of organic solutes in the ionic liquid 1-ethyl-3-methylimidazolium 2-(2-methoxyethoxy) ethylsulfate at T = (308.15, 313.15, 323.15 and 333.15) K using gas + liquid chromatography". In: *Journal of Chemical Thermodynamics* 70 (2014), pp. 245–252.

[57] J.-C. Moïse, F. Mutelet, et al. "Activity Coefficients at Infinite Dilution of Organic Compounds in Four New Imidazolium-Based Ionic Liquids". In: *Journal of Chemical & Engineering Data* 56 (2011), pp. 3106–3114.

[58] I. Bahadur, M. Naidoo, et al. "Screening of environmental friendly ionic liquid as a solvent for the different types of separations problem: Insight from activity coefficients at infinite dilution measurement using (gas + liquid) chromatography technique". In: *Journal of Chemical Thermodynamics* 92 (2016), pp. 35–42.

[59] F. Mutelet and J.-N. Jaubert. "Accurate measurements of thermodynamic properties of solutes in ionic liquids using inverse gas chromatography". In: *Journal of Chromatography A* 1102 (2006), pp. 256–267.

[60] M. Sobota, V. Dohnal, et al. "Activity Coefficients at Infinite Dilution of Organic Solutes in the Ionic Liquid 1-Ethyl-3-methyl-imidazolium Nitrate". In: *Journal of Physical Chemistry B* 113 (2009), pp. 4323–4332.

[61] M. Yan, M. Yang, et al. "Activity coefficients at infinite dilution of organic solutes in the ionic liquid 1-ethyl-3-methylimidazolium tetracyanoborate [EMIM][TCB] using gas–liquid chromatography". In: *Journal of Chemical Thermodynamics* 42 (2010), pp. 817–822.

[62] M. Karpińska, M. Wlazło, et al. "Separation of binary mixtures based on gamma infinity data using [EMIM][TCM] ionic liquid and modelling of thermodynamic functions". In: *Journal of Molecular Liquids* 225 (2017), pp. 382–390.

[63] M.-H. Wang, J.-S. Wu, et al. "Activity Coefficients at Infinite Dilution of Alkanes, Alkenes, and Alkyl Benzenes in 1-Propyl-2,3-dimethylimidazolium Tetrafluoroborate Using Gas-Liquid Chromatography". In: *Journal of Chemical & Engineering Data* 52 (2007), pp. 1488–1491.

[64] U. Domańska, M. Wlazło, et al. "Activity coefficients at infinite dilution of organic solvents and water in 1-butyl-3-methylimidazolium dicyanamide. A literature review of hexane/hex-1-ene separation". In: *Fluid Phase Equilibria* 417 (2016), pp. 50–61.

[65] E. Lukoshko, F. Mutelet, et al. "Experimental and theoretically study of interaction between organic compounds and tricyanomethanide based ionic liquids". In: *Journal of Chemical Thermodynamics* 85 (2015), pp. 49–56.

[66] M. Zawadzki, L. Nidzicki, et al. "Estimation of extraction properties of new imidazolide anion based ionic liquids on the basis of activity coefficient at infinite dilution measurements". In: *Separation and Purification Technology* 118 (2013), pp. 242–254.

[67] J. Zhang, Q. Zhang, et al. "Solubilities of the Gaseous and Liquid Solutes and Their Thermodynamics of Solubilization in the Novel Room-Temperature Ionic Liquids at Infinite Dilution by Gas Chromatography". In: *Journal of Chemical & Engineering Data* 52 (2013), pp. 2277–2283.

[68] Q. Zhou and L.-S. Wang. "Activity Coefficients at Infinite Dilution of Alkanes, Alkenes, and Alkyl Benzenes in 1-Butyl-3-methylimidazolium Tetrafluoroborate Using Gas-Liquid Chromatography". In: *Journal of Chemical & Engineering Data* 51 (2006), pp. 1698–1701.

[69] A.-L. Revelli, F. Mutelet, et al. "Activity Coefficients at Infinite Dilution of Organic Compounds in 1-Butyl-3-methylimidazolium Tetrafluoroborate Using Inverse Gas Chromatography". In: *Journal of Chemical & Engineering Data* 54 (2009), pp. 90–101.

[70] U. Domańska and A. Marciniak. "Activity Coefficients at Infinite Dilution Measurements for Organic Solutes and Water in the Ionic Liquid 1-Butyl-3-methylimidazolium Trifluoromethanesulfonate". In: *Journal of Physical Chemistry B* 112 (2008), pp. 11100–11105.

[71] M.-L. Ge, L.-S. Wang, et al. "Activity Coefficients at Infinite Dilution of Alkanes, Alkenes, and Alkyl Benzenes in 1-Butyl-3-methylimidazolium Trifluoromethanesulfonate Using Gas-Liquid Chromatography". In: *Journal of Chemical & Engineering Data* 52 (2007), pp. 2257–2260.

[72] S. Kozlova, S. Verevkin, et al. "Paramagnetic Ionic Liquid 1-Butyl-3-methylimidazolium Tetrabromidocobaltate(II): Activity Coefficients at Infinite Dilution of Organic Solutes and Crystal Structure". In: *Journal of Chemical & Engineering Data* 54 (2009), pp. 1524–1528.

[73] S. Kozlova, S. Verevkin, et al. "Activity coefficients at infinite dilution of hydrocarbons, alkylbenzenes, and alcohols in the paramagnetic ionic liquid 1-butyl-3-methyl-imidazolium tetrachloridoferrate(III) using gas–liquid chromatography". In: *Journal of Chemical Thermodynamics* 41 (2009), pp. 330–333.

[74] T. Letcher, U. Domańska, et al. "Activity coefficients at infinite dilution measurements for organic solutes in the ionic liquid 1-butyl-3-methyl-imidazolium 2-(2-methoxyethoxy) ethyl sulfate using g.l.c. at T = (298.15, 303.15, and 308.15) K". In: *Journal of Chemical Thermodynamics* 37 (2005), pp. 587–593.

[75] A. Heintz, L. Casás, et al. "Thermodynamic Properties of Mixtures Containing Ionic Liquids. 5. Activity Coefficients at Infinite Dilution of Hydrocarbons, Alcohols, Esters, and Aldehydes in 1-Methyl-3-butyl-imidazolium Bis(trifluoromethylsulfonyl) Imide Using Gas-Liquid Chromatography". In: *Journal of Chemical & Engineering Data* 50 (2005), pp. 1510–1514.

[76] T. Letcher, A. Marciniak, et al. "Determination of Activity Coefficients at Infinite Dilution of Solutes in the Ionic Liquid 1-Butyl-3-methylimidazolium Octyl Sulfate Using Gas-Liquid Chromatography at a Temperature of 298.15 K, 313.15 K, or 328.15 K". In: *Journal of Chemical & Engineering Data* 50 (2005), pp. 1294–1298.

[77] F. Mutelet, V. Butet, et al. "Application of Inverse Gas Chromatography and Regular Solution Theory for Characterization of Ionic Liquids". In: *Industrial & Engineering Chemistry Research* 44 (2005), pp. 4120–4127.

[78] U. Domańska and M. Laskowska. "Measurements of activity coefficients at infinite dilution of aliphatic and aromatic hydrocarbons, alcohols, thiophene, tetrahydrofuran, MTBE, and water in ionic liquid [BMIM][SCN] using GLC". In: *Journal of Chemical Thermodynamics* 41 (2009), pp. 645–650.

[79] E. Olivier, T. Letcher, et al. "Activity coefficients at infinite dilution of organic solutes in the ionic liquid 1-butyl-3-methylimidazolium hexafluoroantimonate using gas–liquid chromatography at T = (313.15, 323.15, and 333.15) K". In: *Journal of Chemical Thermodynamics* 43 (2011), pp. 829–833.

[80] F. Nami and F. Deyhimi. "Prediction of activity coefficients at infinite dilution for organic solutes in ionic liquids by artificial neural network". In: *Journal of Chemical Thermodynamics* 43 (2011), pp. 22–27.

[81] Q. Zhou, L.-S. Wang, et al. "Activity Coefficients at Infinite Dilution of Polar Solutes in 1-Butyl-3-methylimidazolium Tetrafluoroborate Using Gas-Liquid Chromatography". In: *Journal of Chemical & Engineering Data* 52 (2007), pp. 131–134.

[82] U. Domańska, A. Marciniak, et al. "Activity Coefficients at Infinite Dilution Measurements for Organic Solutes and Water in the Ionic Liquid 1-Hexyl-3-methylimidazolium Thiocyanate". In: *Journal of Chemical & Engineering Data* 55 (2010), pp. 2532–2536.

[83] T. Letcher, A. Marciniak, et al. "Activity coefficients at infinite dilution measurements for organic solutes in the ionic liquid 1-hexyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)-imide using g.l.c. at T = (298.15, 313.15, and 333.15) K". In: *Journal of Chemical Thermodynamics* 37 (2005), pp. 1327–1331.

[84] T. Letcher, B. Soko, et al. "Determination of Activity Coefficients at Infinite Dilution of Solutes in the Ionic Liquid 1-Hexyl-3-methylimidazolium Tetrafluoroborate Using Gas-Liquid Chromatography at the Temperatures 298.15 K and 323.15 K". In: *Journal of Chemical & Engineering Data* 48 (2003), pp. 1587–1590.

[85] X.-J. Yang, J.-S. Wu, et al. "Activity Coefficients at Infinite Dilution of Alkanes, Alkenes, and Alkyl Benzenes in 1-Hexyl-3-methylimidazolium Trifluoromethanesulfonate Using Gas-Liquid Chromatography". In: *Journal of Chemical & Engineering Data* 53 (2008), pp. 1220–1222.

[86] A. Heintz, S. Verevkin, et al. "Activity Coefficients at Infinite Dilution of Alkanes, Alkenes, and Alkyl Benzenes in 1-Hexyl-3-methylimidazolium Trifluoromethanesulfonate Using Gas-Liquid Chromatography". In: *Journal of Chemical & Engineering Data* 53 (2008), pp. 1220–1222.

[87] R. Kato and J. Gmehling. "Systems with ionic liquids: Measurement of VLE and c1 data and prediction of their thermodynamic behavior using original UNIFAC, mod. UNIFAC(Do) and COSMO-RS(Ol)". In: *Journal of Chemical Thermodynamics* 37 (2005), pp. 603–619.

[88] T. Letcher, B. Soko, et al. "Activity Coefficients at Infinite Dilution of Organic Solutes in 1-Hexyl-3-methylimidazolium Hexafluorophosphate from Gas-Liquid Chromatography". In: *Journal of Chemical & Engineering Data* 48 (2003), pp. 708–711.

[89] A. Heintz and S. Verevkin. "Thermodynamic Properties of Mixtures Containing Ionic Liquids. 6. Activity Coefficients at Infinite Dilution of Hydrocarbons, Alcohols, Esters, and Aldehydes in 1-Methyl-3-octyl-imidazolium Tetrafluoroborate Using Gas-Liquid Chromatography". In: *Journal of Chemical & Engineering Data* 50 (2005), pp. 1515–1519.

[90] W. David, T. Letcher, et al. "Activity coefficients of hydrocarbon solutes at infinite dilution in the ionic liquid, 1-methyl-3-octyl-imidazolium chloride from gas–liquid chromatography". In: *Journal of Chemical Thermodynamics* 35 (2003), pp. 1335–1341.

[91] N. Deenadayalu, S. Thango, et al. "Measurement of activity coefficients at infinite dilution using polar and non-polar solutes in the ionic liquid 1-methyl-3-octylimidazolium diethyleneglycolmonomethylethersulfate at T = (288.15, 298.15, and 313.15) K". In: *Journal of Chemical Thermodynamics* 38 (2006), pp. 542–546.

[92] E. Olivier, T. Letcher, et al. "Activity coefficients at infinite dilution of organic solutes in the ionic liquid 1-octyl-3-methylimidazolium hexafluorophosphate using gas–liquid chromatography at T = (313.15, 323.15, and 333.15) K". In: *Journal of Chemical Thermodynamics* 42 (2010), pp. 646–650.

[93] U. Domańska and A. Marciniak. "Physicochemical Properties and Activity Coefficients at Infinite Dilution for Organic Solutes and Water in the Ionic Liquid 1-Decyl-3-methylimidazolium Tetracyanoborate". In: *Journal of Physical Chemistry B* 114 (2010), pp. 16542–16547.

[94] U. Domańska and M. Wlazło. "Thermodynamics and limiting activity coefficients measurements for organic solutes and water in the ionic liquid 1-dodecyl-3-methylimidzolium bis(trifluoromethylsulfonyl)imide". In: *Journal of Chemical Thermodynamics* 103 (2016), pp. 76–85.

[95] M. Karpińska, M. Wlazło, et al. "Assessment of certain ionic liquids for separation of binary mixtures based on gamma infinity data measurements". In: (2016), pp. –.

[96] M. Wlazło, M. Karpińska, et al. "Thermodynamics and selectivity of separation based on activity coefficients at infinite dilution of various solutes in 1-allyl-3-methylimidazolium bis(trifluoromethyl)sulfonylimide ionic liquid". In: *Journal of Chemical Thermodynamics* 102 (2016), pp. 39–47.

[97] M. Wlazło, J. Gawkowska, et al. "Separation Based on Limiting Activity Coefficients of Various Solutes in 1-Allyl-3-methylimidazolium Dicyanamide Ionic Liquid". In: *Industrial & Engineering Chemistry Research* 55 (2016), pp. 5054–5062.

[98] Y. Zhang, L.-S. Wang, et al. "Activity Coefficients at Infinite Dilution of Alkanes, Alkenes, and Alkyl Benzenes in 1-(2-Hydroxyethyl)-3-methylimidazolium Tetrafluoroborate Using Gas-Liquid Chromatography". In: *Journal of Chemical & Engineering Data* 54 (2009), pp. 2887–2890.

[99] U. Domańska and A. Marciniak. "Activity coefficients at infinite dilution measurements for organic solutes and water in the 1-hexyloxymethyl-3-methyl-imidazolium and 1,3-dihexyloxymethyl-imidazolium bis(trifluoromethylsulfonyl)-imide ionic liquids—The cation influence". In: *Fluid Phase Equilibria* 286 (2009), pp. 154–161.

[100] A.-L. Revelli, F. Mutelet, et al. "Study of Ether-, Alcohol-, or Cyano-Functionalized Ionic Liquids Using Inverse Gas Chromatography". In: *Journal of Chemical & Engineering Data* 55 (2010), pp. 2434–2443.

[101] F. Mutelet and J.-N. Jaubert. "Measurement of activity coefficients at infinite dilution in 1-hexadecyl-3-methylimidazolium tetrafluoroborate ionic liquid". In: *Journal of Chemical Thermodynamics* 39 (2007), pp. 1144–1150.

[102] F. Mutelet, J.-N. Jaubert, et al. "Thermodynamic Properties of Mixtures Containing Ionic Liquids: Activity Coefficients at Infinite Dilution of Organic Compounds in 1-Propyl Boronic Acid-3-Alkylimidazolium Bromide and 1-Propenyl-3-alkylimidazolium Bromide Using Inverse Gas Chromatography". In: *Journal of Chemical & Engineering Data* 51 (2006), pp. 1274–1279.

[103] F. Mutelet, J.-N. Jaubert, et al. "Activity Coefficients at Infinite Dilution of Organic Compounds in 1-(Meth)acryloyloxyalkyl-3-methylimidazolium Bromide Using Inverse Gas Chromatography". In: *Journal of Physical Chemistry B* 112 (2008), pp. 3773–3785.

[104] P.-F. Yan, Q.-S. Liu, et al. "Activity coefficients at infinite dilution of organic solutes in N-alkylpyridinium bis(trifluoromethylsulfonyl)imide ([CnPY][NTf2], n = 2, 4, 5) using gas–liquid chromatography". In: *Journal of Chemical Thermodynamics* 42 (2010), pp. 1415–1422.

[105] U. Domańska and M. Królikowska. "Measurements of Activity Coefficients at Infinite Dilution in Solvent Mixtures with Thiocyanate-Based Ionic Liquids Using GLC Technique". In: *Journal of Physical Chemistry B* 114 (2010), pp. 8460–8466.

[106] U. Domańska and A. Marciniak. "Activity coefficients at infinite dilution measurements for organic solutes and water in the ionic liquid 4-methyl-N-butylpyridinium bis(trifluoromethylsulfonyl)-imide". In: *Journal of Chemical Thermodynamics* 41 (2009), pp. 1350–1355.

[107] T. Letcher, D. Ramjugernath, et al. "Activity coefficients at infinite dilution measurements for organic solutes in the ionic liquid N-butyl-4-methylpyridinium tosylate using GLC at T = (328.15, 333.15, 338.15, and 343.15)K". In: *Fluid Phase Equilibria* 276 (2009), pp. 31–36.

[108] A. Heintz, D. Kulikov, et al. "Thermodynamic Properties of Mixtures Containing Ionic Liquids. 1. Activity Coefficients at Infinite Dilution of Alkanes, Alkenes, and Alkylbenzenes in 4-Methyl-n-butylpyridinium Tetrafluoroborate Using Gas-Liquid Chromatography". In: *Journal of Chemical & Engineering Data* 46 (2001), pp. 1526–1529.

[109] A. Marciniak and M. Wlazło. "Activity Coefficients at Infinite Dilution Measurements for Organic Solutes and Water in the Ionic Liquid 1-Butyl-3-methylpyridinium Trifluoromethanesulfonate". In: *Journal of Chemical & Engineering Data* 55 (2010), pp. 3208–3211.

[110] A. Marciniak and M. Wlazło. "Activity Coefficients at Infinite Dilution Measurements for Organic Solutes and Water in the Ionic Liquid 1-(3-Hydroxypropyl)pyridinium Trifluorotris(perfluoroethyl)phosphate". In: *Journal of Physical Chemistry B* 114 (2010), pp. 3208–3211.

[111] A. Marciniak. "Activity coefficients at infinite dilution and physicochemical properties for organic solutes and water in the ionic liquid 1-(3-hydroxypropyl)pyridinium bis(trifluoromethylsulfonyl)-amide". In: *Journal of Chemical Thermodynamics* 43 (2011), pp. 1446–1452.

[112] M. Wlazło, M. Karpińska, et al. "A 1-alkylcyanopyridinium-based ionic liquid in the separation processes". In: *Journal of Chemical Thermodynamics* 97 (2016), pp. 253–260.

[113] U. Domańska, M. Karpińska, et al. "Activity coefficients at infinite dilution for organic solutes and water in 1-ethyl-1-methylpyrrolidinium lactate". In: *Journal of Chemical Thermodynamics* 89 (2015), pp. 127–133.

[114] U. Domańska and E. Lukoshko. "Measurements of activity coefficients at infinite dilution for organic solutes and water in the ionic liquid 1-butyl-1-methylpyrrolidinium tricyanomethanide". In: *Journal of Chemical Thermodynamics* 66 (2013), pp. 144–150.

[115] U. Domańska, M. Królikowski, et al. "Thermodynamics and activity coefficients at infinite dilution measurements for organic solutes and water in the ionic liquid 1-butyl-1-methylpyrrolidinium tetracyanoborate". In: *Journal of Chemical Thermodynamics* 43 (2011), pp. 1810–1817.

[116] U. Domańska, G. Redhi, et al. "Activity coefficients at infinite dilution measurements for organic solutes and water in the ionic liquid 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate using GLC". In: *Fluid Phase Equilibria* 278 (2009), pp. 97–102.

[117] A. Blahut and V. Dohnal. "Interactions of Volatile Organic Compounds with the Ionic Liquid 1-Butyl-1-methylpyrrolidinium Dicyanamide". In: *Journal of Chemical & Engineering Data* 56 (2011), pp. 4909–4918.

[118] A. Blahut and V. Dohnal. "Interactions of volatile organic compounds with the ionic liquids 1-butyl-1-methylpyrrolidinium tetracyanoborate and 1-butyl-1-methylpyrrolidinium bis(oxalato)borate". In: *Journal of Chemical Thermodynamics* 57 (2013), pp. 344–354.

[119] A. Marciniak and M. Wlasło. "Activity coefficients at infinite dilution and physicochemical properties for organic solutes and water in the ionic liquid 1-(2-methoxyethyl)-1-methylpyrrolidinium trifluorotris(perfluoroethyl)phosphate". In: *Journal of Chemical Thermodynamics* 60 (2013), pp. 57–62.

[120] A. Marciniak and M. Wlasło. "Activity coefficients at infinite dilution and physicochemical properties for organic solutes and water in the ionic liquid 1-(2-methoxyethyl)-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)-amide". In: *Journal of Chemical Thermodynamics* 54 (2012), pp. 90–96.

[121] A. Marciniak and M. Wlasło. "Activity coefficients at infinite dilution and physicochemical properties for organic solutes and water in the ionic liquid 1-(2-methoxyethyl)-1-methylpiperidinium trifluorotris(perfluoroethyl)phosphate". In: *Journal of Chemical Thermodynamics* 57 (2013), pp. 197–202.

[122] A. Marciniak and M. Wlasło. "Activity coefficients at infinite dilution and physicochemical properties for organic solutes and water in the ionic liquid 1-(2-methoxyethyl)-1-methylpiperidinium bis(trifluoromethylsulfonyl)-amide". In: *Journal of Chemical Thermodynamics* 49 (2012), pp. 137–145.

[123] K. Paduszyński and U. Domańska. "Limiting Activity Coefficients and Gas-Liquid Partition Coefficients of Various Solutes in Piperidinium Ionic Liquids: Measurements and LSER Calculations". In: *Journal of Physical Chemistry B* 115 (2011), pp. 8207–8215.

[124] U. Domańska and M. Królikowska. "Measurements of Activity Coefficients at Infinite Dilution for Organic Solutes and Water in the Ionic Liquid 1-Butyl-1-methylpiperidinium Thiocyanate". In: *Journal of Chemical & Engineering Data* 56 (2011), pp. 124–129.

[125] U. Domańska and K. Paduszyński. "Measurements of activity coefficients at infinite dilution of organic solutes and water in 1-propyl-1-methylpiperidinium bis(trifluoromethyl)sulfonylimide ionic liquid using g.l.c." In: *Journal of Chemical Thermodynamics* 42 (2010), pp. 1361–1366.

[126] U. Domańska and E. Lukoshko. "Thermodynamics and activity coefficients at infinite dilution for organic solutes and water in the ionic liquid 1-butyl-1-methylmorpholinium tricyanomethanide". In: *Journal of Chemical Thermodynamics* 68 (2014), pp. 53–59.

[127] M. Wlasło and A. Marciniak. "Activity coefficients at infinite dilution and physicochemical properties for organic solutes and water in the ionic liquid 4-(2-methoxyethyl)-4-methylmorpholinium trifluorotris(perfluoroethyl)phosphate". In: *Journal of Chemical Thermodynamics* 54 (2012), pp. 366–372.

[128] A. Marciniak and M. Wlasło. "Activity coefficients at infinite dilution and physicochemical properties for organic solutes and water in the ionic liquid 4-(2-methoxyethyl)-4-methylmorpholinium bis(trifluoromethylsulfonyl)-amide". In: *Journal of Chemical Thermodynamics* 47 (2012), pp. 382–388.

[129] M. Królikowska, M. Karpińska, et al. "Measurements of activity coefficientsatinfinitedilution for organic solutes and water in N-hexylisoquinolinium thiocyanate, [HiQuin][SCN] using GLC". In: *Journal of Chemical Thermodynamics* 62 (2013), pp. 1–7.

[130] U. Domańska, M. Zawadzki, et al. "Measurements of activity coefficients at infinite dilution of organic compounds and water in isoquinolinium-based ionic liquid [C8iQuin][NTf2] using GLC". In: *Journal of Chemical Thermodynamics* 43 (2011), pp. 499–504.

[131] U. Domańska, P. Papis, et al. "Thermodynamics and activity coefficients at infinite dilution for organic solutes, water and diols in the ionic liquid choline bis(trifluoromethylsulfonyl)imide". In: *Journal of Chemical Thermodynamics* 77 (2014), pp. 63–70.

[132] A. Heintz, T. Vasiltsova, et al. "Thermodynamic Properties of Mixtures Containing Ionic Liquids. 9. Activity Coefficients at Infinite Dilution of Hydrocarbons, Alcohols, Esters, and Aldehydes in Trimethyl-butylammonium Bis(trifluoromethylsulfonyl) Imide Using Gas-Liquid Chromatography and Static Method". In: *Journal of Chemical & Engineering Data* 51 (2006), pp. 648–655.

[133] Z. Jiao, Y. Sun, et al. "Activity coefficients at infinite dilution of organic solutes in the ionic liquid ethyl(2-hydroxyethyl)dimethyl-ammonium diethylphosphate using gas–liquid chromatography". In: *Fluid Phase Equilibria* 325 (2012), pp. 15–19.

[134] M. Wlazło and U. Domańska. "Gamma infinity data for the separation of water-butan-1-ol mixtures using ionic liquids". In: *Separation and Purification Technology* 162 (2016), pp. 162–170.

[135] W. Jr., G. Baker, et al. "Partition Coefficients of Organic Compounds in Four New Tetraalkylammonium Bis(trifluoromethylsulfonyl)imide Ionic Liquids Using Inverse Gas Chromatography". In: *Journal of Chemical & Engineering Data* 56 (2011), pp. 3688–3697.

[136] N. Gwala, N. Deenadayalu, et al. "Activity coefficients at infinite dilution for solutes in the trioctylmethylammonium bis(trifluoromethylsulfonyl)imide ionic liquid using gas–liquid chromatography". In: *Journal of Chemical Thermodynamics* 42 (2010), pp. 256–261.

[137] U. Domańska and K. Paduszyński. "Gas–liquid chromatography measurements of activity coefficients at infinite dilution of various organic solutes and water in tri-iso-butylmethylphosphonium tosylate ionic liquid". In: *Journal of Chemical Thermodynamics* 42 (2010), pp. 707–711.

[138] T. Letcher and P. Reddy. "Determination of activity coefficients at infinite dilution of organic solutes in the ionic liquid, tributylmethylphosphonium methylsulphate by gas–liquid chromatography". In: *Fluid Phase Equilibria* 260 (2007), pp. 23–28.

[139] T. Letcher and P. Reddy. "Determination of activity coefficients at infinite dilution of organic solutes in the ionic liquid, trihexyl(tetradecyl)-phosphonium tris(pentafluoroethyl) trifluorophosphate, by gas–liquid chromatography". In: *Fluid Phase Equilibria* 235 (2005), pp. 11–17.

[140] T. Letcher, D. Ramjugernath, et al. "Activity coefficients at infinite dilution measurements for organic solutes in the ionic liquid trihexyltetradecylphosphonium-bis-(2,4,4-trimethylpentyl)-phosphinate using g.l.c. at T = (303.15, 308.15, 313.15, and 318.15) K". In: *Journal of Chemical Thermodynamics* 40 (2008), pp. 1243–1247.

[141] T. Banerjee and A. Khanna. "Infinite Dilution Activity Coefficients for Trihexyltetradecyl Phosphonium Ionic Liquids: Measurements and COSMO-RS Prediction". In: *Journal of Chemical & Engineering Data* 51 (2006), pp. 2170–2177.

[142] A.-L. Revelli, L. Sprunger, et al. "Activity Coefficients at Infinite Dilution of Organic Compounds in Trihexyl(tetradecyl)phosphonium Bis(trifluoromethylsulfonyl)imide Using Inverse Gas Chromatography". In: *Journal of Chemical & Engineering Data* 54 (2009), pp. 977–985.

[143] T. Letcher, D. Ramjugernath, et al. "Determination of Activity Coefficients at Infinite Dilution of Solutes in the Ionic Liquid, Trihexyltetradecylphosphonium Bis(trifluoromethylsulfonyl) Imide, Using Gas-Liquid Chromatography at T) (303.15, 308.15, 313.15, and 318.15) K". In: *Journal of Chemical & Engineering Data* 53 (2008), pp. 2044–2049.

[144] A. Marciniak and M. Wlazło. "In preparation". In: *Journal of Chemical Thermodynamics* (2017), pp. –.

[145] F. Mutelet, D. Alonso, et al. "Infinite Dilution Activity Coefficients of Solutes Dissolved in Two Trihexyl(tetradecyl)phosphonium Ionic Liquids". In: *Journal of Chemical & Engineering Data* 59 (2014), pp. 1877–1885.

[146] U. Domańska, M. Królikowski, et al. "Physicochemical properties and activity coefficients at infinite dilution for organic solutes and water in a novel bicyclic guanidinium superbase-derived protic ionic liquid". In: *Journal of Chemical Thermodynamics* 58 (2013), pp. 62–69.

[147] P. Reddy, M. Siddiqi, et al. "Activity coefficients at infinite dilution of organic solutes in the ionic liquid PEG-5 cocomonium methylsulfate at T = (313.15, 323.15, 333.15, and 343.15) K: Experimental results and COSMO-RS predictions". In: *Journal of Chemical Thermodynamics* 58 (2013), pp. 322–329.

[148] U. Domańska and A. Marciniak. "Activity coefficients at infinite dilution measurements for organic solutes and water in the ionic liquid triethylsulphonium bis(trifluoromethylsulfonyl)imide". In: *Journal of Chemical Thermodynamics* 41 (2009), pp. 754–758.

Appendix

Experimental liquid-liquid equilibria table results

Table A.1: Experimental LLE data for binary systems safrole(1) + IL(2) at P = 0.1 MPa (x1 is the mole fraction of safrole)

$[P_{6.6.6.14}][NTf_2]$		$[P_{6.6.6.14}][TCM]$		$[DoMIM]][NTf_2]$	
x1	T/K	x1	T/K	x1	T/K
0.9952	284.8	0.9935	301.0	0.9974	284.2
0.9928	288.3	0.9877	308.1	0.9949	302.3
0.9902	290.6	0.9837	309.3	0.9920	319.9
0.9853	292.8	0.9788	309.6	0.9860	332.5
0.9826	293.4	0.9762	309.6	0.9783	337.4
0.9804	293.7	0.9725	309.5	0.9743	339.1
0.9778	293.8	0.9688	309.1	0.9688	339.9
0.9748	293.9	0.9657	309.0	0.9631	340.3
0.9734	294.0	0.9620	308.8	0.9595	340.5
0.9709	293.9	0.9443	305.9	0.9545	340.6
0.9684	293.8	0.9417	305.3	0.9496	340.5
0.9653	293.7	0.9400	304.6	0.9286	339.2
0.9615	293.5	0.9235	299.0	0.9244	338.4
0.9586	293.3	0.9210	297.9	0.9187	337.2
0.9551	292.8	0.9165	296.1	0.9149	336.2
0.9506	292.3	0.9142	295.2	0.9085	334.2
0.9470	291.7	0.8906	284.4	0.9022	331.5
0.9437	290.9	0.8889	283.7	0.8946	328.9
0.9398	289.9			0.8703	317.1
0.9315	287.9			0.8667	314.9
0.9282	287.0			0.8457	302.1
0.9266	286.4			0.8274	290.1
0.9247	285.7			0.8237	288.5

Table A.2: Experimental LLE data for binary systems safrole(1) + IL(2) at P = 0.1 MPa (x1 is the mole fraction of safrole)

$[N_{2.2.2.8}][NTf_2]$		$[COC_2mPIP][FAP]$		$[COC_2mPYR][FAP]$	
x1	T/K	x1	T/K	x1	T/K
0.7440	362.0	0.5871	362.8	0.5479	359.2
0.7420	359.5	0.5862	361.9	0.5472	357.6
0.7409	358.1	0.5823	358.7	0.5464	354.7
0.7393	355.9	0.5784	355.1	0.5446	351.8
0.7370	353.3	0.5749	351.0	0.5438	349.2
0.7339	349.4	0.5711	346.1	0.5408	345.6
0.7321	346.9	0.5680	343.1	0.5381	343.2
0.7278	341.5	0.5638	338.2	0.5408	345.6
0.7222	334.3	0.5606	335.2	0.5381	343.2
0.7187	328.1	0.5572	331.3	0.5346	340.5
0.7170	325.6	0.5535	326.9	0.5309	336.1
0.7121	319.4	0.5504	322.8	0.5276	330.9
0.7108	317.5	0.5468	319.7	0.5239	325.5
0.7078	313.8	0.5431	315.5	0.5205	322.5
0.7054	310.1	0.5391	311.4	0.5171	319.0
0.7025	306.5	0.5358	307.7	0.5135	314.4
0.6991	302.4	0.5322	304.3	0.5106	312.4
0.6943	297.1	0.5292	301.0	0.5072	308.5
0.6918	293.6	0.5260	297.6	0.5040	305.1
0.6894	290.4	0.5230	294.7	0.5007	302.3
0.6886	288.9	0.5200	292.2	0.4976	300.0
0.6872	286.6	0.5164	288.6	0.4912	294.7
0.6857	284.7	0.5152	287.3	0.4853	290.3
				0.4793	284.9

Table A.3: Maximum of binodal curves and corresponding composition

Ionic liquid	Maximum of binodal curve	Mole fraction of safrole	Mole fraction of ionic liquid
$[P_{6.6.6.14}][NTf_2]$	294.0	0.9734	0.0266
$[P_{6.6.6.14}][TCM]$	309.6	0.9775	0.0225
$[DoMIM][NTf_2]$	340.6	0.9545	0.0455

APPENDIX B

CALIBRATION CURVE

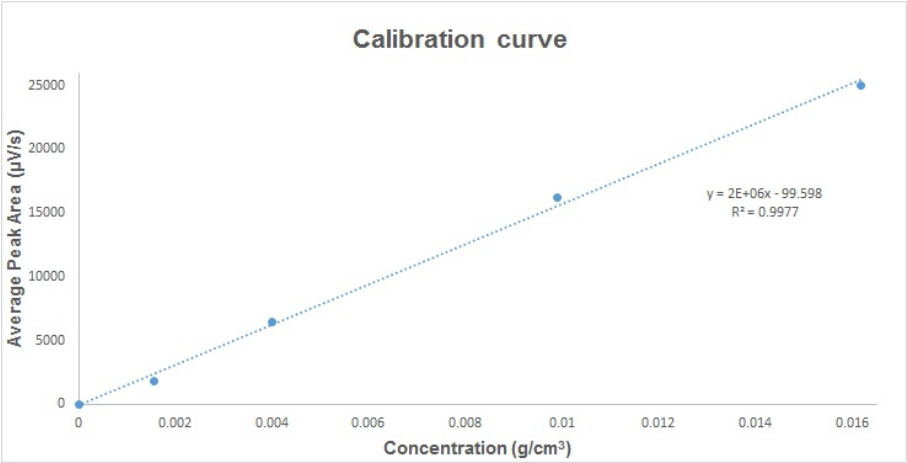

Figure B.1: Calibration curve: safrole diluted in acetone.

Table B.1: Calibration curve for safrole.

Mass concentration ($g.cm^{-3}$)	Average safrole peak area ($\mu V.s$)
0	0
1.559E-03	1.783E+03
4.000E-03	6.432E+03
9.891E-03	1.618E+04
1.617E-02	2.502E+04

Appendix C

Activity coefficients at infinite dilution literature table

Table C.1: γ_{13}^{∞} for solutes Benzene and 1,4-Dioxane in several ionic liquids at T = 328.15 K (a:323.15 K; b:333.15 K)

Abbreviation	Designation	γ Benzene	γ 1,4-Dioxane	Ref.
$[MMIM][(CH_3)_2PO_4]$	1,3-dimethylimidazolium dimethylphosphate	3.61^a 3.66^b	-	[44]
$[MMIM][CH_3OC_2H_4SO_4]$	1,3-dimethylimidazolium 2-methoxyethylsulfate	4.30^a 4.17^b	-	[44]
$[MMIM][CH_3SO_4]$	1,3-dimethylimidazolium methylsulfate	6.31^a 5.93^b	-	[44]
$[MMIM][NTf_2]$	1-methyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	1.36^a 1.37^b	-	[45]
$[EMIM][FAP]$	1-ethyl-3-methylimidazolium trifluorotris(perfluoroethyl)phosphate	0.833	0.391	[39]
$[EMIM][TCB]$	1-ethyl-3-methylimidazolium tetracyanoborate	1.18	-	[46]
$[EMIM][TFA]$	1-ethyl-3-methylimidazolium trifluoroacetate	2.767	-	[38]
$[EMIM][NTf_2]$	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	1.21^a	-	[45]
$[EMIM][BF_4]$	1-ethyl-3-methylimidazolium tetrafluoroborate	2.087^a 2.052^b	1.423^a 1.436^b	[47]
$[EMIM][BF_4]$	1-ethyl-3-methylimidazolium tetrafluoroborate	2.51^a	-	[48]

$[EMIM][CF_3SO_3]$	1-ethyl-3-methylimidazolium trifluoromethanesulfonate	2.24^a 2.27^b	-	[49]
$[EMIM][EtSO_4]$	1-ethyl-3-methylimidazolium ethylsulfate	2.84^a	-	[50]
$[EMIM][NTf_2]$	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	0.702^a	-	[51]
$[EMIM][SCN]$	1-ethyl-3-methylimidazolium thiocyanate	3.49	-	[52]
$[EMIM][B(CN)_4]$	1-ethyl-3-methylimidazolium tetracyanoborate	1.15^a 1.17^b	-	[53]
$[EMIM][MeSO_3]$	1-ethyl-3-methylimidazolium methanesulfonate	4.50^a 4.48^b	-	[54]
$[EMIM][C_2H_5OSO_3]$	1-ethyl-3-methylimidazolium ethylsulfate ethylsulfate	2.80^a 2.83^b	-	[45]
$[EMIM][NTf_2]$	1-methyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide	1.179^a 1.179^b	-	[55]
$[EMIM][MDEGSO_4]$	1-ethyl-3-methylimidazolium 2-(2-methoxyethoxy)ethylsulfate	2.41^a 2.48^b	-	[56]
$[EMIM][MeSO_3]$	1-ethyl-3-methylimidazolium methanesulfonate	4.271^a 4.235^b	2.666^a 2.660^b	[57]
$[EMIM][OcOSO_3]$	1-ethyl-3-methylimidazolium octylsulfate	0.89^b	-	[58]
$[EMIM][TOS]$	1-ethyl-3-methylimidazolium tosylate	2.61^a	1.71^a	[59]
$[EMIM][NO_3]$	1-ethyl-3-methylimidazolium nitrate	4.88^a 4.91^b	-	[60]
$[EMIM][TCB]$	1-ethyl-3-methylimidazolium tetracyanoborate	1.34^a 1.31^b	-	[61]
$[EMIM][TCM]$	1-ethyl-3-methylimidazolium tricyanomethanide	1.76	0.799	[62]
$[EMMIM][NTf_2]$	1,2-dimethyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide	1.100^a 1.101^b	-	[55]
$[PMMIM][BF_4]$	2,3-Dimethyl-1-propylimidazolium tetrafluoroborate	3.123^a 2.745^b	-	[63]
$[BMIM][DCA]$	1-butyl-3-methylimidazolium dicyanamide	1.95	1.13	[64]
$[BMIM][TCM]$	1-butyl-3-methylimidazolium tricyanomethanide	1.29	0.673	[65]
$[BMIM][TDI]$	1-butyl-3-methylimidazolium	0.849^a	-	[66]

	4,5-dicyano-2-(trifluoromethyl)imidazolide			
$[BMIM][BF_4]$	1-butyl-3-methylimidazolium tetrafluoroborate	1.45[a]	-	[67]
$[BMIM][BF_4]$	1-butyl-3-methylimidazolium tetrafluoroborate	1.770[a] 1.798[b]	-	[68]
$[BMIM][BF_4]$	1-butyl-3-methylimidazolium tetrafluoroborate	2.43[a]	-	[48]
$[BMIM][BF_4]$	1-butyl-3-methylimidazolium tetrafluoroborate	2.25[a] 2.16[b]	-	[69]
$[BMIM][CF_3SO_3]$	1-butyl-3-methylimidazolium trifluoromethanesulfonate	1.59	-	[70]
$[BMIM][CF_3SO_3]$	1-butyl-3-methylimidazolium trifluoromethanesulfonate	1.831[a] 1.841[b]	-	[71]
$[BMIM][CoBr_4]$	1-butyl-3-methylimidazolium tetrabromocobaltate(II)	1.8[a]	-	[72]
$[BMIM][EtSO_4]$	1-butyl-3-methylimidazolium ethylsulfate	2.80[a] 2.83[b]	-	[45]
$[BMIM][FeCl_4]$	1-butyl-3-methylimidazolium tetrachloroferrate(III)	0.812[a]	-	[73]
$[BMIM][MDEGSO_4]$	1-butyl-3-methylimidazolium 2-(2-methoxyethoxy)ethylsulfate	2.01[a]	-	[74]
$[BMIM][NTf_2]$	1-methyl-3-butylimidazolium bis(trifluoromethylsulfonyl)imide	0.903[a]	-	[45]
$[BMIM][NTf_2]$	1-methyl-3-butylimidazolium bis(trifluoromethylsulfonyl)imide	0.8[a]	-	[67]
$[BMIM][NTf_2]$	1-methyl-3-butylimidazolium bis(trifluoromethylsulfonyl)imide	0.850[a]	-	[75]
$[BMIM][OcOSO_3]$	1-butyl-3-methylimidazolium octylsulfate	1.45	-	[76]
$[BMIM][PF_6]$	1-butyl-3-methylimidazolium hexafluorophosphate	1.96[a] 2.13[b]	1.01[a] 1.14[b]	[77]
$[BMIM][SCN]$	1-butyl-3-methylimidazolium thiocyanate	2.18	-	[78]
$[BMIM][SbF_6]$	1-butyl-3-methylimidazolium hexafluoroantimonate	1.33[a] 1.34[b]	-	[79]
$[BMIM][BETI]$	1-butyl-3-methylimidazolium bis(pentafluoroethylsulfonyl)imide	1.012[a]	0.429[a]	[57]
$[BMIM][n-C_{16}H_{31}OO]$	1-butyl-3-methylimidazolium palmitate	0.7[b]	-	[67]
$[BMIM][n-C_{18}H_{35}OO]$	1-butyl-3-methylimidazolium	0.7[a]	-	[67]

	stearate	0.7^b		
$[BMIM][C_8SO_4]$	1-butyl-3-methylimidazolium octylsulfate	0.95^a 1.19^b	1.09^a 1.17^b	[59]
$[BMIM][BF_4]$	1-butyl-3-methylimidazolium tetrafluoroborate	1.77^a	-	[80]
$[BMIM][BF_4]$	1-butyl-3-methylimidazolium tetrafluoroborate	-	1.549^a 1.559^b	[81]
$[HMIM][SCN]$	1-hexyl-3-methylimidazolium thiocyanate	2.02	-	[82]
$[HMIM][NTf_2]$	1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	0.700^b	-	[83]
$[HMIM][BF_4]$	1-hexyl-3-methylimidazolium tetrafluoroborate	0.95^a	-	[84]
$[HMIM][BF_4]$	1-hexyl-3-methylimidazolium tetrafluoroborate	1.65^a	-	[48]
$[HMIM][CF_3SO_3]$	1-hexyl-3-methylimidazolium trifluoromethane-sulfonate trifluoromethanesulfonate	1.501^a 1.550^b	-	[85]
$[HMIM][NTf_2]$	1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	0.777^a	-	[86]
$[HMIM][NTf_2]$	1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	0.78^a 0.79^b	-	[87]
$[HMIM][PF_6]$	1-hexyl-3-methylimidazolium hexafluorophosphate	1.07^a	-	[88]
$[HMIM][FAP]$	1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate	0.552^b	0.327^b	[57]
$[HMIM][NTf_2]$	1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	0.774^b	-	[80]
$[OMIM][BF_4]$	3-methyl-1-octylimidazolium tetrafluoroborate	0.6^a	-	[67]
$[OMIM][BF_4]$	3-methyl-1-octylimidazolium tetrafluoroborate	1.16^a	-	[89]
$[OMIM][BF_4]$	3-methyl-1-octylimidazolium tetrafluoroborate	1.29^a	-	[48]
$[OMIM][Cl]$	3-methyl-1-octylimidazolium chloride	1.45^a	-	[90]
$[OMIM][MDEGSO_4]$	3-methyl-1-octylimidazolium 2-(2-methoxyethoxy)ethylsulfate	1.38^a	-	[91]
$[OMIM][NTf_2]$	3-methyl-1-octylimidazolium bis(trifluoromethylsulfonyl)imide	0.65^a 0.66^b	-	[87]

$[OMIM][PF_6]$	1-methyl-3-octylimidazolium hexafluorophosphate	0.99^a 1.02^b	-	[92]
$[DMIM][TCB]$	1-decyl-3-methylimidazolium tetracyanoborate	0.581	-	[93]
$[D_2MIM][NTf_2]$	1,3-didecyl-2-methylimidazolium bis(trifluoromethylsulfonyl)imide	0.429^a 0.431^b	0.463^a 0.460^b	[57]
$[DoMIM][NTf_2]$	1-Dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	0.594	0.499	[94]
$[BzMIM][NTf_2]$	1-benzyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	1.05	0.523	[95]
$[BzMIM][DCA]$	1-benzyl-3-methylimidazolium dicyanamide	2.44	1.23	[95]
$[AMIM][NTf_2]$	1-allyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	1.22	0.616	[96]
$[AMIM][DCA]$	1-allyl-3-methylimidazolium dicyanamide	3.12	1.44	[97]
$[OH-C_2C_1Im][BF_4]$	1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate	9.097^a 9.076^b	-	[98]
$[C_6H_{13}OCH_2-C_1Im][NTf_2]$	1-hexyloxymethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	0.816	-	[99]
$[C_6H_{13}OCH_2)_2Im][NTf_2]$	1,3-dihexyloxymethylimidazolium bis(trifluoromethylsulfonyl)imide	0.607	-	[99]
$[CpMIm][NTf_2]$	1-butyronitrile-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	1.7^a	-	[67]
$[CpMIm][N(CN)_2]$	1-butyronitrile-3-methylimidazolium dicyanamide	2.2^a	-	[67]
$[CpMMIm][NTf_2]$	1-butyronitrile-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide	1.71^a	-	[67]
$[CpMMIm][N(CN)_2]$	1-butyronitrile-2,3-dimethylimidazolium dicyanamide	2.8^a	-	[67]
$[(OC_1)_2im][NTf_2]$	1,3-dimethoxyimidazolium bis(trifluoromethylsulfonyl)imide	2.09^a 2.03^b	0.51^a 0.54^b	[100]
$[C_2OC_1mim][NTf_2]$	1-(methylethylether)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	1.18^b	0.60^b	[100]
$[C_2OHmim][NTf_2]$	1-ethanol-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	2.12^a 2.08^b	0.59^a 0.62^b	[100]
$[C_3CNmim]$[DCA]	1-(3-cyanopropyl)-3-methylimidazolium dicyanamide	4.48^a 4.42^b	1.59^a 1.62^b	[100]

$[C_{16}mim][BF_4]$	1-hexadecyl-3-methylimidazolium tetrafluoroborate	0.780^a 0.780^b	-	[101]
$[CH_2 = C_2mim]$[Br]	1-propenyl-3-methylimidazolium bromide	3.60^a	1.59^a	[102]
$[CH_2 = C_2oim]$[Br]	1-propenyl-3-octylimidazolium bromide	1.40^a	1.52^a	[102]
$[CH_2 = C_2dim]$[Br]	1-propenyl-3-decylimidazolium bromide	1.39^a	1.39^a	[102]
$[CH_2 = C_2dodim]$[Br]	1-propenyl-3-dodecylimidazolium bromide	1.08^a	1.30^a	[102]
$[B(OH)_2C_3mim]$[Br]	1-propyl boronic acid-3-methylimidazolium bromide	18.07^a	11.21^a	[102]
$[B(OH)_2C_3oim]$[Br]	1-propyl boronic acid-3-octylimidazolium bromide	1.84^a	1.78^a	[102]
$[B(OH)_2C_3dim]$[Br]	1-propyl boronic acid-3-decylimidazolium bromide	1.33^a	1.38^a	[102]
$[B(OH)_2C_3dodim]$[Br]	1-propyl boronic acid-3-dodecylimidazolium bromide	1.21^a	1.32^a	[102]
$[n-AcOxC_3mim]$[Br]	3-(3-(acryloyloxy)propyl)-1-methylimidazolium bromide	5.51^a	2.98^a	[103]
$[EPY][NTf_2]$	n-ethylpyridinium bis(trifluoromethylsulfonyl)imide	1.47^a 1.43^b	-	[104]
$[EPY][NTf_2]$	N-ethylpyridinium bis(trifluoromethylsulfonyl)imide	1.35^a 1.4^b	-	[44]
$[BPY][NTf_2]$	n-butylpyridinium bis(trifluoromethylsulfonyl)imide	1.35^a 1.35^b	-	[104]
$[BMPY][TCM]$	1-butyl-4-methylpyridinium tricyanomethanide	0.916	0.601	[65]
$[BMPY][SCN]$	1-butyl-4-methylpyridinium thiocyanate	1.71	-	[105]
$[BMPY][NTf_2]$	4-methyl-N-butylpyridinium bis(trifluoromethylsulfonyl)imide	0.735	-	[106]
$[BMPY][TOS]$	1-butyl-4-methylpyridinium tosylate	4.01	-	[107]
$[BMPY][BF_4]$	4-methyl-n-butylpyridinium tetrafluoroborate	1.645^a 1.648^b	-	[108]
$[BM_3PY][TDI]$	1-butyl-3-methylpyridinium 4,5-dicyano-2-(trifluoromethyl)imidazolide	0.687^a	-	[66]
$[1,3BMPY][CF_3SO_3]$	1-butyl-3-methylpyridinium	1.25	-	[109]

	trifluoromethanesulfonate			
$[PePY][NTf_2]$	n-pentylpyridinium bis(trifluoromethylsulfonyl)imide	1.01[a] 1.02[b]	-	[104]
$[N-C_3OHPY][FAP]$	1-(3-hydroxypropyl)pyridinium trifluorotris(perfluoroethyl)phosphate	0.933	-	[110]
$[N-C_3OHPY][NTf_2]$	1-(3-hydroxypropyl)pyridinium bis(trifluoromethylsulfonyl)imide	1.58	0.541	[111]
$[PY][C_2H_5OC_2H_4SO_4]$	Pyridinium ethoxyethylsulfate	3.78[a] 3.76[b]	-	[44]
$[BCN_4PY][NTf_2]$	1-butyl-4-cyanopyridinium bis(trifluoromethylsulfonyl)imide	1.17	0.502	[112]
$[EMPYR][Lac]$	1-ethyl-1-methylpyrrolidinium lactate	2.94	2.33	[113]
$[BMPYR][TCM]$	1-butyl-1-methylpyrrolidinium tricyanomethanide	1.04	0.669	[114]
$[BMPYR][TCB]$	1-butyl-1-methylpyrrolidinium tetracyanoborate	0.816	-	[115]
$[BMPYR][SCN]$	1-butyl-1-methylpyrrolidinium thiocyanate	1.91	-	[105]
$[BMPYR][CF_3SO_3]$	1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate	1.48	-	[116]
$[BMPYR][NTf_2]$	1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide	0.88[a] 0.89[b]	-	[87]
$[BMPYR][DCA]$	1-butyl-1-methylpyrrolidinium dicyanamide	1.42[a] 1.46[b]	-	[117]
$[BMPYR][B(CN)_4]$	1-butyl-1-methylpyrrolidinium tetracyanoborate	0.841[a] 0.858[b]	-	[118]
$[BMPYR][BOB]$	1-butyl-1-methylpyrrolidinium bis(oxalato)borate	1.65[b]	-	[118]
$[COC_2mPYR]$[FAP]	1-(2-methoxyethyl)-1-methylpyrrolidinium trifluorotris(perfluoroethyl)phosphate	0.663	0.422	[119]
$[COC_2mPYR][NTf_2]$	1-(2-methoxyethyl)-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide	1.04	0.679	[120]
$[COC_2mPIP]$[FAP]	1-(2-methoxyethyl)-1-methylmethylpiperidinium trifluorotris(perfluoroethyl)phosphate	0.582	0.388	[121]
$[COC_2mPIP][NTf_2]$	1-(2-methoxyethyl)-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide	0.922	0.636	[122]
$[BMPIP][NTf_2]$	1-butyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide	0.805	-	[123]

$[BMPIP][SCN]$	1-butyl-1-methylpiperidinium thiocyanate	1.93	-	[124]
$[PMPIP][NTf_2]$	1-propyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide	0.94	-	[125]
$[BMMOR][TCM]$	1-butyl-1-methylmorpholinium tricyanomethanide	1.55	0.740	[126]
$[COC_2mMOR][FAP]$	4-(2-methoxyethyl)-4-methylmorpholinium trifluorotris(perfluoroethyl)phosphate	0.810	0.323	[127]
$[COC_2mMOR][NTf_2]$	4-(2-methoxyethyl)-4-methylmorpholinium bis(trifluoromethylsulfonyl)imide	1.32	0.596	[128]
$[C_6iQuin][SCN]$	N-hexylisoquinolinium thiocyanate	1.47	1.23	[129]
$[C_8iQuin][NTf_2]$	N-octylisoquinolinium bis(trifluoromethylsulfonyl)imide	0.605	-	[130]
$[N_{1.1.1.2}OH][NTf_2]$	choline bis(trifluoromethylsulfonyl)imide	2.52	0.585	[131]
$[N_{1.1.1.4}][NTf_2]$	Butyl-trimethylammonium bis(trifluoromethylsulfonyl)imide	1.30^a	-	[132]
$[N_{1.1.2.2}OH][DEP]$	ethyl(2-hydroxyethyl)dimethylammonium diethylphosphate	2.84^a 2.79^b	-	[133]
$[N_{8.2.2.2}][NTf_2]$	Octyltriethylammonium bis(trifluoromethylsulfonyl)imide	0.666	0.616	[134]
$[MB_3AM][NTf_2]$	Methyl(tributyl)ammonium bis(trifluoromethylsulfonyl)imide	0.9^a 0.93^b	0.61^a 0.67^b	[135]
$[OMA][NTf_2]$	Trioctylmethylammonium bis(trifluoromethylsulfonyl)imide	0.315^a	-	[136]
$[O_4AM][NTf_2]$	Tetraoctylammonium bis(trifluoromethylsulfonyl)imide	0.40^a 0.41^b	0.47^a 0.47^b	[135]
$[OM_3AM][NTf_2]$	Octyl(trimethyl)ammonium bis(trifluoromethylsulfonyl)imide	0.73^a 0.74^b	0.62^a 0.62^b	[135]
$[DM_3AM][NTf_2]$	Decyl(trimethyl)ammonium bis(trifluoromethylsulfonyl)imide	0.71^a 0.73^b	0.56^a 0.57^b	[135]
$[P1,4,4,4][TOS]$	tri-iso-butylmethylphosphonium tosylate	1.28	-	[137]
$[P_{1,4,4,4}][MeSO_4]$	Tributylmethylphosphonium methylsulfate	0.9	-	[138]
$[P_{6.6.6.14}][FAP]$	trihexyltetradecylphosphonium tris(pentafluoroethyl)trifluorophosphate	0.19	-	[139]
$[P_{6,6,6,14}][Phos]$	Trihexyltetradecylphosphonium	0.508^a	-	[140]

	bis-(2,4,4-trimethylpentyl)phosphinate			
$[P_{6.6.6.14}][BF_4]$	trihexyltetradecylphosphonium tetrafluoroborate	0.366	-	[141]
$[P_{6.6.6.14}][Cl]$	trihexyltetradecylphosphonium chloride	0.400	-	[141]
$[P_{6.6.6.14}][NTf_2]$	trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide	0.402	-	[141]
$[P_{6.6.6.14}][NTf_2]$	Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide	0.39[a]	0.49[a]	[142]
$[P_{6.6.6.14}][NTf_2]$	Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide	0.430[a]	-	[143]
$[P_{6.6.6.14}]$[TCM]	Trihexyltetradecylphosphonium tricyanomethanide	0.472	0.594	[144]
$[P_{6.6.6.14}]$[+CS]	Trihexyltetradecylphosphonium (1S)-(+)-10-Camphorsulfonate	0.36[a]	0.52[a]	[145]
$[P_{6.6.6.14}]$[L-Lact]	Trihexyltetradecylphosphonium L-Lactate	0.38[a]	-	[145]
$[MTBDH][BETI]$	1,3,4,6,7,8-hexahydro-1-methyl-2H-pyrimido[1,2-a]pyrimidine bis(pentafluoroethyl)sulfonylimide	0.854	0.624	[146]
$PEG5$	PEG-5 cocomonium methylsulfate	0.817[a] 0.822[b]	-	[147]
$[Et_3S][NTf_2]$	Triethylsulphonium bis(trifluoromethylsulfonyl)imide	1.12	-	[148]