INSTITUTO POLITÉCNICO DE BRAGANÇA
Escola Superior de Tecnologia e Gestão

Methylimidazolium-based Ionic Liquids as Separation Agents in Terpenes and Fuel Processes

Aline Zambom Coelho

Dissertation presented to

Escola Superior de Tecnologia e Gestão

Instituto Politécnico de Bragança

In order to obtain the master's degree in

Chemical Engineering

This work was supervised by

Maria Olga Amorim de Sá Ferreira

Simão Pedro de Almeida Pinho

Bragança
July 2022

"Never regard study as a duty but as an enviable opportunity to learn to know the liberating influence of beauty in the realm of the spirit for your own personal joy and to the profit of the community to which your later works belong".

Albert Einstein

Acknowledgments

First of all, I would like to thank my mother immensely, because since I can remember, she gave me all the opportunities to study, to follow my dreams, and fly as high as I could. I cannot thank you enough. Everything will always be for you, Mom.

A special gratefulness to Sergio Vilas-Boas, a friend and a co-worker who extremely assisted my research, for all his patience, learning and trust.

I wish to express my heartfelt appreciation to my IPB supervisors, Olga Ferreira and Simão Pinho, for the opportunity to be part of this excellent research team, for all the supporting, assistance, and guidance during this work.

This acknowledgment extends to my sister, father, and friends who encouraged, supported, and believed in me when I needed it the most. Furthermore, I would like to wish my thankfulness to everyone who collaborated in this dissertation, directly or indirectly, my eternal gratitude, besides that, without you I could not achieve this dream.

Abstract

This work is focused on the study of two methylimidazolium-based ionic liquids (IL) as more sustainable solvents not only in deterpenation processes, but also in petrochemical processes, including separating aromatic from aliphatic hydrocarbons and the removal of impurities in fossil fuels. In fact, IL can act as alternative separation agents to traditional organic solvents in different liquid-liquid extraction processes.

For this purpose, the activity coefficients at infinite dilution, γ^{∞}, of 52 solutes (water, alkanes, cycloalkanes, ketones, ethers, cyclic ethers, aromatic hydrocarbons, esters, alcohols, terpenes and terpenoids) in 1-butyl-3-methylimidazolium hexafluorophosphate [C_4mim][PF_6] and in the equimolar IL mixture of [C_4mim][PF_6] and 1-butyl-3-methylimidazolium chloride [C_4mim][Cl] were measured by inverse gas chromatography technique over the temperature range of (333.2-453.2) K. Similar data in pure [C_4mim][Cl] was already available in the literature. From the γ^{∞} values, some thermodynamic parameters (such as excess partial molar properties, selectivities, capacities, gas-liquid partition coefficients, and solvent performance indexes) can be estimated in order to evaluate the ionic liquid performance.

The majority of the studied solutes showed higher γ^{∞} values in the equimolar IL mixture than in pure [C_4mim][PF_6]. Poor interaction ($\gamma^{\infty} >> 1$) was observed between both IL studied and the less polar solutes (alkanes and cycloalkanes). On the other hand, alcohols and water showed high interaction with the equimolar IL mixture ($\gamma^{\infty} < 1$). Hydrocarbon terpenes, ether, and ketone terpenoids have higher interaction with pure [C_4mim][PF_6], and alcohol terpenoids have more favorable interactions with the equimolar IL mixture. With regard to separation factors, the IL studied showed, in general, poor selectivities and capacities for terpenes/terpenoids mixtures being the best result obtained for the carvacrol/γ-terpinene mixture. On the other hand, promising results were obtained for the separation of several model mixtures (octane/benzene, cyclohexane/benzene, octane/thiophene, and octane/pyridine) of the fuel industries. The studied solvents were among the IL having the best performance indexes which provided important insights on the use of alternative solvents for the removal of aromatics from aliphatic hydrocarbons and the removal of contaminants from fuels.

Keywords: Ionic Liquid, Deterpenation, Activity Coefficients, Fuels, Inverse Gas Chromatography.

Resumo

Este trabalho está focado no estudo de dois líquidos iónicos (LI) à base de metilimidazólio como solventes mais sustentáveis não só em processos de desterpenação, mas também em processos petroquímicos, incluindo a separação de hidrocarbonetos aromáticos e alifáticos e a remoção de impurezas em combustíveis fósseis. De facto, os IL podem atuar como agentes de separação alternativos aos solventes orgânicos tradicionais em diferentes processos de extração líquido-líquido. Para este efeito, os coeficientes de atividade a diluição infinita, γ^{∞}, de 52 solutos (água, alcanos, cicloalcanos, cetonas, éteres, éteres cíclicos, hidrocarbonetos aromáticos, ésteres, álcoois, terpenos e terpenóides) em 1-butil-3-metilimidazólio hexafluorofosfato [C_4mim][PF_6] e na mistura equimolar dos LI [C_4mim][PF_6] e cloreto de 1-butil-3-metilimidazólio [C_4mim][Cl] foram medidos pela técnica de cromatografia gasosa inversa na gama de temperaturas de (333.2-453.2) K. Dados semelhantes em [C_4mim][Cl] puro já se encontravam disponíveis na literatura. A partir dos valores de γ^{∞}, alguns parâmetros termodinâmicos (tais como propriedades molares parciais em excesso, seletividades, capacidades, coeficientes de partição gás-líquido, e índices de desempenho do solvente) podem ser estimados a fim de avaliar o desempenho do líquido iónico.

A maioria dos solutos estudados mostrou valores mais elevados γ^{∞} na mistura de LI equimolar do que no [C_4mim][PF_6] puro. Observou-se uma fraca interação ($\gamma^{\infty} >> 1$) entre os LI estudados e os solutos menos polares (alcanos e cicloalcanos). Todavia, álcoois e água mostraram uma interação elevada com a mistura de LI equimolar ($\gamma^{\infty} < 1$). Os terpenos hidrocarbonetos, e alguns terpenóides (éteres e cetonas) têm uma maior interação com o [C_4mim][PF_6] puro, e os terpenóides alcoólicos têm interações mais favoráveis com a mistura de LI equimolar. No que diz respeito aos fatores de separação, os LI estudados mostraram, em geral, baixas seletividades e capacidades para misturas de terpenos/terpenóides sendo o melhor resultado obtido para a mistura carvacrol/γ-terpineno. Por outro lado, foram obtidos resultados promissores para a separação de várias misturas modelo (octano/benzeno, ciclohexano/benzeno, octano/tiofeno e octano/piridina) comuns em indústrias de combustíveis. Os solventes estudados estavam entre os que apresentavam melhores índices de desempenho, proporcionando informações importantes sobre a utilização deste tipo de solventes alternativos para a remoção de hidrocarbonetos alifáticos e para a remoção de contaminantes dos combustíveis.

Palavras-Chave: Líquido Iónico, Desterpenação, Coeficientes de Atividade, Combustíveis, Cromatografia Gasosa Inversa.

Table of Contents

List of Symbols and Acronyms

List of Symbols

B_{ab}	Crossed Second Virial Coefficient [m^3/mol]
B_{aa}	Second Virial Coefficient of Pure Compound *a* [m^3/mol]
$G_m^{E,\infty}$	Excess Gibbs Free Energy at Infinite Dilution [kJ/mol]
$\bar{H}_m^{E,\infty}$	Excess Enthalpy at Infinite Dilution [kJ/mol]
J_2^3	Pressure Correction Term
k_j^∞	Capacity of the Solute *j*
K_L	Gas-Liquid Partition Coefficient
n_a	Number of Moles of Compound *a* [mol]
p_a^*	Vapor Pressure of Pure Compound *a* [Pa]
p_i	Column Inlet Pressure [Pa]
p_0	Column Outlet Pressure [Pa]
p_f	Pressure Measured by the Flowmeter [Pa]
R	Ideal Gas Constant [kJ/(mol·K)]
$\mathrm{T_{ref}}\bar{S}_m^{E,\infty}$	Excess Entropy at Infinite Dilution [kJ.K/mol]
S_{ij}^∞	Selectivity between the Solutes *i* and *j*
t_a	Retention Time of Compound *a* [s]
T	Temperature Inside the Oven of the Gas-Chromatograph [K]
T_f	Temperature Measured by the Flowmeter [K]
U	Volumetric Flow Measured by the Flowmeter [m^3/s]
U_0	Column Outlet Volumetric Flow Rate [m^3/s]

V_a^*	Molar Volume of Pure Compound *a* [m^3/mol]
V_N	Net Retention Volume [m^3]
V_a^∞	Partial Molar Volume of Pure Compound *a* at Infinite Dilution [m^3/mol]

Greek Letters

γ_{ab}^∞	Activity Coefficient at Infinite Dilution of Compound *b* in the IL
ρ_a	Density of Compound *a* [kg/m^3]

List of Figures

List of Tables

Appendix A: Calculation of the Pressure Drop at Outlet Column Conditions

Appendix B: List of Solutes

Appendix C: Thermodynamics Properties

Chapter 1. Introduction

1.1. Scope and Objectives

The industrial field growth demands the sustainable and environment-friendly manufacture of products without affecting their quality and efficiency. Green Chemistry has as one of its principles the reduction of the environmental toxicity of chemical compounds used in industrial processes. One of the innovations that has emerged over time is the use of a new class of solvents, ionic liquids, that may be designed to provide both environmental and technological benefits. In such a view, the studies in this work aim to contribute to the selection of IL as potential separation agents of several relevant mixtures in two fields: terpenes fractionation and fuel mixtures processing.

Essential oils (EO) are an important source of terpenes that find diverse applications in the cosmetics, food, and pharmaceutical industries.[1] These compounds are widely used as flavor enhancers, in products like disinfectants and detergents, as well as fragrance ingredients in cosmetic industries to produce shampoos and soaps, for example.[2] Carotenoids and a few other terpenes are also added value ingredients in skincare and cosmetic industries.[3,4]

In the pharmaceutical area, the worldwide sales of terpene-based products were estimated in US$12 billion in 2002. Among these pharmaceuticals, the anticancer (paclitaxel) and antimalarial (artemisinin) drugs are two of most renowned terpene-based drugs.[5] In general, the compounds responsible for the therapeutic properties in EO are denominated terpenes and/or terpenoids. Terpenoids are mainly responsible for the aroma and antioxidant properties, whereas terpenes have a low contribution to the aroma, being easily oxidized and producing off-flavors that deteriorate the quality of EO. Therefore, deterpenation (removal of the terpene from the oxygenated part) is of utmost importance since this procedure improves the stability and solubility of commercial EO.[6]

Other separation problems relevant in fuel processing such as desulfurization and denitrification of fuels, removal of aromatic from aliphatic hydrocarbons will be also addressed.

Thus, the main objectives of this thesis are:

1. Measurement by inverse gas chromatography of the activity coefficient at infinite dilution of water and a set of organic solutes including terpenes and terpenoids, using two stationary phases: 1) the ionic liquid ([C_4mim][PF_6]; 2) the equimolar IL mixture of [C_4mim][PF_6] and [C_4mim][Cl]).

2. Determination of the selectivity, capacity, solvent performance index, excess partial molar properties at infinite dilution, and gas-liquid partition coefficient to analyse if the IL studied are suitable entrainers for terpenes fractionation and other relevant separation problems in fuel processing.

1.2. Structure of the Report

Chapter 2 provides an introduction about essential oils, terpenes/terpenoids, their separation processes, and their industrial importance. Additionally, the use of "*green*" solvents, such as deep eutectic solvents (DES) and ionic liquids (IL), as an alternative to traditional organic solutes will be also briefly discussed.

Chapter 3 describes the experimental methodology that was performed to obtain the thermodynamic parameters related to the efficiency of the ionic liquid ([C_4mim][PF_6] and the equimolar mixture of [C_4mim][PF_6] and [C_4mim][Cl]) as separation agents of several mixtures. In addition, the equations necessary to calculate these important thermodynamic parameters are also presented in this chapter.

Chapter 4 presents the discussion of all the experimental results obtained in this work – activity coefficient at infinite dilution, gas-partition coefficients, molar properties in excess at infinite dilution, selectivities, capacities, and solvent performance indexes. In addition, the results are critically compared with data available in the literature, including the previous works from our research group. Finally, in Chapter 5, the main conclusions about the IL investigated as separation agents are summarized and some suggestions for future work pointed out.

Chapter 2. State of the Art

2.1. Introduction

For some separation processes to be carried out, organic solvents are necessary and commonly used in the chemical industry. These solvents are often toxic, volatile, flammable, and environmentally ubiquitous which suggests their replacement by greener alternatives. To address this problem, IL have been studied as alternative separation agents. The main purpose of this chapter is to discuss the use of IL in the separation of terpene/terpenoid mixtures and other separation problems, by taking advantage of its "*designer solvent*" characteristics. This chapter first introduces EO and their applications, followed by a brief discussion of the importance of terpenes and terpenoids and their separation processes, such as liquid-liquid extraction, vacuum distillation, and supercritical fluid extraction, and membrane separation. In addition, the use of DES and IL in the separation of different mixtures is also reviewed. Finally, the importance of desulfurization and denitrification processes in fuels it is addressed.

2.2. Essential Oils

Plants produce a high diversity of secondary metabolites, and due to their biocidal properties, these metabolites have the relevant function of protecting plants against predators and microbial pathogens.[14] Among these secondary metabolites, 3000 EO are estimated to be known, of which about 300 are commercially important – destined mainly for the flavors and fragrances market.[15] EO are also known as volatile or ethereal oils.[16] In addition, they are aromatic oily liquids that can be obtained by fermentation, enfleurage, or extraction, being steam distillation the most used process for their commercial production.[15] EO are also defined as mixtures of fragrant and odorless substances. They are composed mainly of lipophilic and highly volatile secondary metabolites (*e.g.*, *mono*- and *sesqui*terpene) of plant origin.[17]

The EO are widely used in cosmetics and have medicinal applications due to their therapeutic properties as well as agro-alimentary uses, because of their antimicrobial and antioxidant effects. EO can also be defined as mixtures of volatile compounds that are most often present at low concentrations in plants. Several different extraction techniques are widely used for EO extraction, such as steam distillation and solvent extraction. However, these methods are characterized by some disadvantages, such as low extraction efficiency, and selectivity, use of large amounts of solvents, and long extraction times that negatively influence the quality of the EO due to hydrolysis or oxidation of some components and the high amount of spent water.[17,18]

Given these limitations, innovative methods for EO extraction have been developed, such as supercritical fluid extraction and microwave-assisted extraction. These alternative methods aim to significantly reduce extraction times, increase yields, and improve EO quality. These methods are predominantly exploited at laboratory scale though some industrial applications can be found.[17]

2.3. Terpenes and Terpenoids

Terpenes are predominantly found as constituents of EO, being mainly hydrocarbons. Besides that, they can be defined as linear or cyclic compounds composed of N isoprene units that are saturated or unsaturated and modified in several ways.[19] Terpenes are divided into groups and sub-groups, due to some factors such as the pathway by which they are synthesized by nature or according to their structures.[20] Terpene hydrocarbons can be classified according to the number of isoprene units as follows:[19]

- *Monoterpenes*: 2 isoprene units, 10 carbon atoms; components of anticancer and antimicrobial drugs.[19]
- *Sesquiterpenes*: 3 isoprene units, 15 carbon atoms; most common in fungi and marine organisms; exhibit antibiotic activity.[19]
- *Diterpenes*: 4 isoprene units, 20 carbon atoms; taxol is an example of diterpene used in drugs to treat cancer.[19]

- *Triterpenes*: 6 isoprene units, 30 carbon atoms; mainly found in nature, mostly in resins, and are indispensable structural components of plant cell membranes.[19]

- *Tetraterpenes*: 8 isoprene units, 40 carbon atoms; as important tetraterpenes, the yellow or orange-red carotenoid pigments can be cited.[19]

- *Polyterpenes*: composed of many isoprene units, and there is no recent research proving the existence of any biological function associated with these compounds.[19]

Terpenoids are terpene oxygenated derivatives, which include functional groups such as aldehydes, alcohols, carboxylic acids, ethers, and ketones.[6,21–24] The term terpene usually refers to a hydrocarbon molecule while terpenoid refers to a terpene that has been modified by the addition of oxygen.[24] Although terpenes have significant properties such as antifungal, anticancer, antimicrobial, etc., they contribute very little to the aroma and flavor of EO. Terpenoids, on the other hand, contribute immensely to the organoleptic properties of EO.[6]

Given this, terpenes (mostly *mono*terpenes) act as "impurities" for some EO, due to their low solubility in aqueous and alcoholic solution, and their oxidation processes, producing off-flavors that ultimately deteriorate the quality of the marketed EO.[22,24,25] Thus, it becomes indispensable to remove these compounds to increase the value of EO in the marketplace. The deterpenation of EO or the concentration/purification of the EO, as detailed in the next section, remove the odorless and flavorless hydrocarbons from the oxygenated compounds, which are highly odoriferous and flavored.[23] Specific terpenes and terpenoids also find application in the pharmaceutical industry as summarized in **Table 1**.

Table 1: Pharmaceutical application of terpenes and terpenoids naturally found in plants.

Compound	Pharmaceutical properties	Category of terpene	Source
Citral	Antibacterial and antifungal activity.	acyclic monoterpene aldehyde	26
Myrcene	Antifungal and antibacterial activity.	acyclic monoterpene	27
Eugenol	Anaesthetic properties and antibacterial and antifungal activity.	monoterpenoid	28
Geraniol	Antifungal, antitumoral and antibacterial activity.	monoterpenoid	29
D-Limonene	Chemopreventive and therapeutic antitumoral properties.	cyclic monoterpene	2
Artemisinin and its derivatives	Antileukemia, and other antitumoral properties; antimalaria drug.	monocyclic sesquiterpene lactone peroxide	30
Cucurbitacin	Antileukemia, and other antitumoral properties.	tetracyclic terpene	31
Eucalyptol	Expectorant against bronchial catarrh (asthma), anti-ulcer activity.	monocyclic monoterpene	32
(-)-Menthol	Antibacterial, antispasmodic, antiseptic, and anti-ulcer activities.	monocyclic monoterpene alcohol	33
(-)-*cis*-Carveol	Prophylaxis against breast and prostate cancer.	monocyclic monoterpene alcohol	34
(-)-Forskolin	Activity against heart failure, autoimmune disorders, psoriasis, erectile dysfunction.	bicyclic diterpene	35
(-)-Taxol	Cytostatic agent in cancer therapy.	tricyclic diterpene alkaloid	36
(-)-Merrilactone	Treatment of Alzheimer's and Parkinson's diseases.	bicyclic sesquiterpene	37
(-)-Matricin	Anti-inflammatory activity and bowel diseases.	bicyclic sesquiterpene lactone	38
(+)-β-Eudesmol	Anti-dementia drug, antiangiogenic activity, induces apoptosis.	bicyclic sesquiterpene	39

2.4. Separation Processes

The most common classical methods of deterpenation, at industrial scale, are vacuum distillation and liquid-liquid extraction.[25] These methods are good alternatives because of the low water and energy consumption and low cost since the procedures take place at moderate temperature and pressure conditions.[40]

Supercritical fluid extraction has been also an attractive alternative because of the use non-toxic and non-flammable solvents such as carbon dioxide, that is also easily separable from the final product, and operation at low temperatures. On the contrary, this process requires expensive investment in robust equipment and safety, which has hindered its use on a large scale.[25,41,42] A similar disadvantage applies to membrane separation. Despite the high separation efficiency and quality of the end- product, high equipment costs also apply.[43]

2.4.1. Liquid-Liquid Extraction

Among the several techniques applied for the fractionation of EO, liquid-liquid extraction (LLE) or solvent extraction, has advantages since the operation is usually carried out without heating (as in conventional distillation) or pressure changes (as in supercritical fluid extraction or vacuum distillation). Consequently, it results in a low energy consumption process. Additionally, milder operating conditions also tend to preserve the organoleptic properties of oils because they contain heat-sensitive components that may degrade to produce undesirable odors.[44,45]

The first step is the choice of a suitable solvent for the development of this method. This solvent should result in large distribution coefficients and high selectivity.[46] The main principle of LLE is the separation of components presents in a liquid solution by contact with another liquid; for this process to work, the two liquids that are in direct contact must have partial miscibility or immiscibility.[47]

This extraction process takes place in two stages: in the first stage, the solute dissolved in a solvent (S_1) from which it cannot be easily removed is transferred to a second solvent (S_2) from which it can be more easily separated. Finally, the solute is extracted from S_2 to regenerate it, thus allowing its reuse in a subsequent extraction.[48,49]

2.4.2. Vacuum Distillation

Distillation is a physical separation process based on the relative volatility differences of the components over a given temperature range. Vacuum distillation (VD) works at lower operating pressures, aiming to increase the relative volatility of the compounds, thus resulting in a more efficient separation.[49]

Some researchers report that the main advantage of applying vacuum to the distillation system is the reduction of the boiling temperature of the crude EO inside the column, which consequently reduces the degradation of the components of interest.[50] VD separates the hydrocarbon terpenes from the oxygenated terpenes. The hydrocarbon terpenes are removed from the top of the distillation column, while the heavier oxygenated fraction is collected at the bottom.[51]

2.4.3. Supercritical Fluid Extraction

Supercritical fluid extraction (SFE) has been used for the extraction of volatile components, *e.g.*, EO and aroma compounds from plant materials, at industrial scale.[52] This technique is established by the solvating properties of the supercritical fluid, which can be obtained by employing pressure and temperature above the critical point of a compound, mixture, or element. It depends also on some extrinsic features (*e.g.*, characteristics of the sample matrix and interaction with the targeted analytes).[49,52]

This technique allows fine adjustments of the solvent physical properties and capacity for each separation, by changing temperature and pressure conditions, so SFE is considered more flexible than conventional methods.[23]

Since SFE does not use chemical solvents with drastic environmental impacts, this separation method is regarded as a "*green process*".[53] The most common solvent used in this technique is carbon dioxide (CO_2) due to three major reasons: (i) It is non-toxic to human health and the environment; (ii) It has a moderate critical temperature, 31.2ºC, (this way, the bioactive compound preservation in the extracts is guaranteed); (iii) Once the pressure is reduced, the CO_2 returns to its gaseous state and can be easily separated from the oil and then recycled.[48,54,55]

2.4.4. Membrane Separation

Membrane separation (MS) is an interesting alternative method for the LLE of highly valuable oxygenated terpenes from EO. The mainly expected benefit of using membrane contactors is the phase separation step elimination (since mixing of phases is avoided), which can be difficult in these systems. In LLE with membrane contactors, the interface between phases is stabilized in a porous membrane.[49,56]

In MS, the pores are filled with one of two immiscible fluids (depending on the hydrophilic or hydrophobic nature of the membrane). The porous material does not normally influence the selectivity of mass transfer. Importantly, the use of membrane contactors provides a wide choice of solvents, since the density difference between the phases (essential for the settling step) is no longer relevant.[49,57,58]

MS has other advantages such as low energy consumption, facilitates product purification, and recovers valuable co-products from complex liquids. On contrary, it has a limited pressure range to ensure a stable interface between fluids, relatively short membrane life, and extra resistance to mass transfer. For industrial scale application, these disadvantages can become severe restrictions.[49,56,57]

2.5. Designer Solvents

The so-called "*designer solvents*" are solvents which can be tailored to have specific properties, such as solvation capacity, viscosity, density, thermal stability, polarity, and so on, depending on the application of the solvent. Deep eutectic solvents and ionic liquids are common examples of "*designer solvents*", as discussed below.

2.5.1. Deep Eutectic Solvents

Deep eutectic solvents (DES) are considered an emerging class of green solvents. Nowadays, they are widely acknowledged as sharing many characteristics and properties with ionic liquids[59] such as high thermal stability, low volatility, low vapor pressures, and tuned polarity, making DES promising candidates for a potential replacement of existing volatile organic compounds widely used throughout research and industry.[60]

DES can be defined as systems formed from a mixture of Lewis or Brønsted acids and bases, presenting a melting temperature well below to that assuming the ideal liquid solution model.[59] They are generally obtained by the complexation of a quaternary ammonium salt with a metal salt or hydrogen bond donor (HBD), but recently type V DES between two molecular (non-ionic) substances have been proposed.[61] The charge delocalization occurring through hydrogen bonding between, for instance, a halide ion and the hydrogen-donor moiety is responsible for the decrease in the melting point of the mixture relative to the melting points of the individual components.[60]

Moreover, DES can present some advantages over IL, such as their ease of preparation and, in some cases, depending on the components used to prepare them, relatively cheaper. On the downside, they are generally less chemically inert.[59,62]

DES can be prepared thorough the combination of materials from renewable sources with non-toxic and biodegradable compounds such as carboxylic acids, polyols, and sugars, being the majority hydrophilic. Recently, the design of hydrophobic eutectic mixtures wholly composed of non-ionic species has received a particular attention. Terpenes have been used to prepare hydrophobic eutectic mixtures, (classified as DES type V) due to their very low solubility in water, and relatively low price.[63,64]

2.5.2. Ionic Liquids

Ionic liquids (IL) are organic or inorganic salts of low-melting-point (less than 100ºC) that form liquids composed entirely of ions.[6] The inorganic IL have limited applications over organic IL due to their typically higher melting points, poor solvation properties for organic compounds, and reactivity.[65,66] Organic-based IL, in general, have significantly lower melting points combined with favorable solvation properties supporting a wider range of applications in the chemical, materials science, chemical engineering, and environmental areas.[65]

As IL are considered "*designer solvents*", it would be possible to generate the required combination of reactivity, solubility, and viscosity, among other. A simple, but viable as a zeroth-order approximation, is that the anion defines the chemistry, while the cation controls the physical properties.[67,68] A few IL have been already studied, using inverse gas chromatography, as potential separation agents in several terpenes and fuel processes.[6,69–76] A summary of those literature results will be provided in Chapter 4, where a comparison is made with the results obtained in this work.

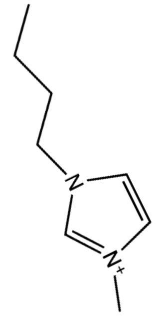
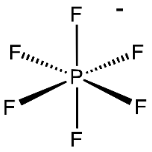
A binary mixture can be used to fine-tune the physical properties (such as viscosity, polarity, density, or miscibility), for example, by adding a second ionic liquid, with a common anion (or cation), but a different cation (or anion). In this work, the binary equimolar mixture of [C_4mim][PF_6] and [C_4mim][Cl] will be tested for some important terpenes and fuel processing mixtures.

Chapter 3. Experimental Work

3.1. Materials

Information about the ionic liquids such as chemical structure, supplier, molar mass, melting point, and purity are described in **Table 2.** Similar information about the solutes is presented in **Table B1** of **Appendix B**. Before use, the IL were dried at vacuum conditions (at 1 Pa and 298.2 K), under continuous stirring, for at least 48 h. The organic solutes were used as received from the suppliers.

Table 2: Chemical structure, name, molar mass, purity, melting point, and suppliers of IL studied.

Cation	**Anion**	**Chemical name and abbreviation**	**Molar mass ($g\cdot mol^{-1}$)**	**Purity (w/w) [a]**	**Melting temperature (K) [a]**	**Supplier**
		1-butyl-3-methylimidazolium hexafluorophosphate $[C_4mim][PF_6]$	284.19	0.990	265.2[a]	Iolitec
	Cl^-	1-butyl-3-methylimidazolium chloride $[C_4mim][Cl]$	174.68	0.990	338.2[a]	Iolitec

[a] Declared by the supplier.

3.2. Chromatographic Methodology

The experimental procedure for the measurement of the activity coefficient at infinite dilution (γ_{13}^{∞}) for all solutes (1) in the ionic liquid (3), including the column packing method and preparation, were already detailed in previous works.[69,70] The IGC technique was adopted for the measurements of retention times, using a Varian 3380 gas chromatograph (GC) equipped with a 1041 on-column injector and a thermal conductivity detector (TCD). For such type of analysis, a glass column (1 m length and 4 mm internal diameter) was filled with the ionic liquid (stationary phase (45-55%)) and subsequently placed in the oven of the chromatograph.

First, the column was pre-conditioned, *i.e.*, a stream of helium gas was passed through the column for, at least, 6 h at 393.2 K, to facilitate the removal of eventual impurities. During the analyses with traditional organic solvents and water, the injector and detector temperatures were at 503.2 K and 523.2 K respectively. For the analyses with terpenes and terpenoids, the injector and detector temperatures were set to 553.2 K and 573.2 K respectively. Before measurements, the injector must be at the setpoint temperature for at least 30 min.

In order to achieve infinite dilution conditions, the solutes were injected in the column in volume range of (0.2-0.5) μL. Together with the organic solute, air was injected, as a non-retained component. The experiments were performed, at least, at three temperatures in the range (333.2-453.2) K. Each experiment was repeated, at least, twice.

For a set of solutes (minimum 10 solutes, for each ionic liquid in the stationary phase, including compounds from different families), the γ_{13}^{∞} were measured in two independent columns, at three temperatures. As reference, absolutes values of retention times varied between 0.9 to 70 min corresponding to heptane and eugenol, respectively, in pure [C_4mim][PF_6]. Retention times were calculated by the difference of the retention times of the solute, t_R, and air, t_G.

3.3. Thermodynamic Background

3.3.1. Activity Coefficient at Infinite Dilution

The retention times obtained by IGC measurements were used to calculate the activity coefficients at infinite dilution for a solute (1) partitioning between a carrier gas (2) and a non-volatile liquid solvent (3), using the methodologies developed by Everett[79] and Cruickshank et al.[80] in 1960s, as presented in Eq. (1).

$$\ln \gamma_{13}^{\infty} = \ln \frac{n_3 RT}{V_N p_1^*} - \frac{p_1^*(B_{11} - V_1^*)}{RT} + \frac{p_0 J_2^3 (2B_{12} - V_1^{\infty})}{RT} \tag{1}$$

Where n_3 is the mole number of solvent on the column packing, R is the ideal gas constant, p_1^* is the saturated vapor pressure of the solute, p_0 is the column outlet pressure, B_{11} is the second virial coefficient of the pure solute, V_1^* is the molar volume of the solute, B_{12} is the crossed second virial coefficient of the solute and the carrier gas (helium), V_1^{∞} is the partial molar volume of the solute at infinite dilution in the solvent, V_N is the net retention volume of the solute, T is the absolute temperature of the column (regulated by the GC oven). In Eq. (1), J_2^3 is the pressure correction term, as discussed in detail by Everett[79], and is given by Eq. (2):

$$J_2^3 = \frac{2\left({}^{p_i}/_{p_0}\right)^3 - 1}{3\left({}^{p_i}/_{p_0}\right)^2 - 1} \tag{2}$$

Where p_i is the column inlet pressure. The net retention volume of the solute passing inside the column is calculated by Eq. (3):

$$V_N = (J_2^3)^{-1} U_0 (t_R - t_G) \tag{3}$$

Where U_0 is the outlet volumetric flow rate (at the column temperature), and t_r and t_g are the retention times of the solute and air (non-retained substance), respectively. The flow rate U is measured with a flowmeter placed after the carrier gas leaves the detector, so it needs to be corrected by Eq. (4):

$$U_0 = U \, \frac{p_f}{p_0} \frac{T}{T_f} \tag{4}$$

Where U_f, p_f and T_f are the volumetric flow, the pressure, and the temperature measured by the flowmeter after the carrier gas goes through the detector, respectively . The second order virial coefficients, used in Eq. (1) were estimated using the correlation proposed by Tsnonopoulos and discussed, in detail, by Poling.[81]

To estimate the column outlet pressure p_0, a linear regression between the pressure drop value (ΔP) and the volumetric flow rate was established at different temperatures, using Eq. (5). The coefficients (*A* and *B*) are presented in **Table A1** of **Appendix A**.

$$\Delta P = p_0 - p_f = A \cdot U + B \tag{5}$$

The activity coefficient at infinite dilution represents the solute-solvent affinity, where:

- $\gamma_{13}^{\infty} > 1$, the solute-solute interactions are stronger than the solute-solvent ones.
- $\gamma_{13}^{\infty} = 1$, solute-solute and solute-solvent interactions are similar.
- $\gamma_{13}^{\infty} < 1$, the solute-solvent interactions are higher than the solute-solute.

3.3.2. Excess Partial Molar Properties at Infinite Dilution

To further interpret the interactions and the measured γ_{13}^{∞} data, the excess partial molar properties at infinite dilution, namely excess enthalpy ($\overline{H}_m^E$) and entropy ($\bar{S}_m^E$), which are contributions to the excess Gibbs energy ($\bar{G}_m^E$), can be determined by using the linear dependence of γ_{13}^{∞} with temperature (van’t Hoff plot), using the following equations:

$$\ln \gamma_{13}^{\infty} = \frac{\overline{H}_m^{E,\infty}}{R}\frac{1}{T} - \frac{\bar{S}_m^{E,\infty}}{R} \tag{6}$$

$$\bar{G}_m^{E,\infty} = RT ln\, \gamma_{13}^{\infty} \tag{7}$$

And, at a reference temperature T_{ref}:

$$\bar{G}_m^{E,\infty} = \overline{H}_m^{E,\infty} - \bar{S}_m^{E,\infty}\, T_{ref} \tag{8}$$

3.3.3. Gas-Liquid Partition Coefficient

The gas-liquid partition coefficient (K_L) of the solutes can also provide important information about the solvent performance. Thus, the K_L for a solute partitioning between the carrier gas (helium) and the stationary phase (IL) can be determined from the same IGC experiments according to:[82]

$$\ln(K_L) = \frac{c_1^3}{c_1^2} = \ln\frac{V_N \rho_3}{m_3} - \frac{p_0 J_2^3 (2B_{12} - V_1^\infty)}{RT} \tag{9}$$

In which c is the molar concentration of the solute (1), m_3, and ρ_3 are the mass, and density of ionic liquid (3), respectively, in the column.

3.3.4. Fractionation Factors

In order to evaluate the performance of IL as entrainer in several chemical separation problems, the selectivity between the solutes i and j, (S_{ij}^∞), and the separation capacity, (k_j^∞), were calculated as follows:

$$S_{ij}^\infty = \frac{\gamma_{i3}^\infty}{\gamma_{j3}^\infty} \tag{10}$$

$$k_j^\infty = \frac{1}{\gamma_{j3}^\infty} \tag{11}$$

Being j the solute with the lowest activity coefficient for a given separation between two components, and 3 refers to the ionic liquid. For an ionic liquid to be a good separation agent, high selectivities and capacities are desirable. Unfortunately, often, these two parameters counteract, *i.e.*, high values for selectivity are accompanied by low capacities. Thus, it is important to have a balance between these two parameters to be able to evaluate the IL more efficiently. To this end, the solvent performance index (which fairly describes this balance) was determined. The solvent performance index, (Q_{ij}^∞), also defined at infinite dilution, can be calculated using Eq. (12).[72,83]

$$Q_{ij}^\infty = S_{ij}^\infty k_j^\infty \tag{12}$$

Chapter 4. Experimental Results

4.1. Activity Coefficients at Infinite Dilution

In this work, two IL with a common cation, but unlike anions of different polarity, were selected as stationary phases, in order to see the effect of changing the anion in the γ_{13}^{∞}, and derived properties. The γ_{13}^{∞} of 52 solutes were measured by the IGC technique in the global temperature range of (333.2-453.2) K. The lower temperature value was chosen considering the pure IL melting points. For each solute, at least three different temperatures were set, depending on the solvent/solute combination. The results are listed, in detail, in **Appendix C**, **Table C1**. To our best knowledge, all the experimental results for γ_{13}^{∞} in the mixture [C_4mim][PF_6]/[C_4mim][Cl] are reported for the first time in this work, as well as the experimental γ_{13}^{∞} values of several solutes in [C_4mim][PF_6], more precisely, for terpenes and terpenoids.

Figure 1 represents the experimental γ_{13}^{∞} values of most solutes in the two stationary phases ([C_4mim][PF_6] and in the equimolar mixture of [C_4mim][PF_6]/[C_4mim][Cl]), that were obtained at a fixed temperature of 353.2 K. For a group of less volatile terpenoids, experiments were done at higher temperatures and the corresponding results are explored in **Figure 2**, at 413.2 K. The retention times of the phenolic terpenoids (eugenol, carvacrol and thymol) in the equimolar IL mixture were too high, and it was not possible to perform the experiments.

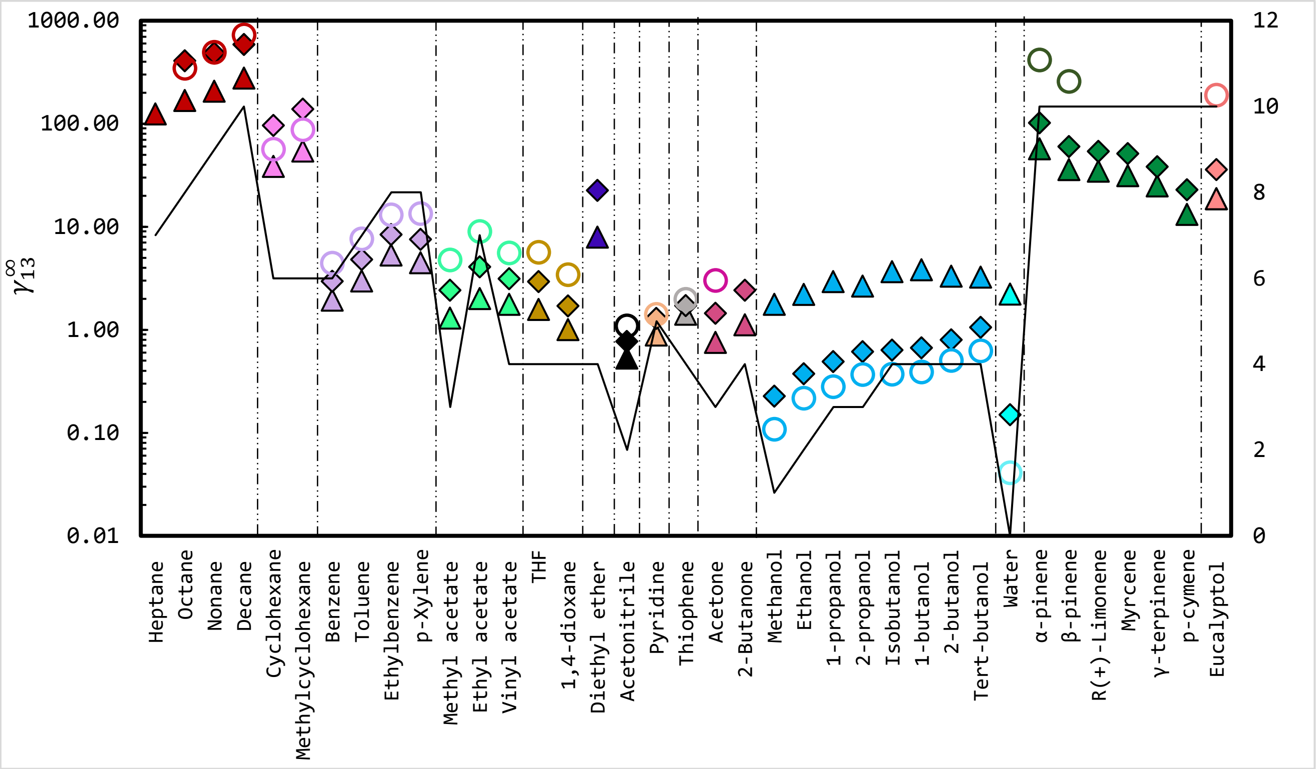


Figure 1: Infinite dilution activity coefficients (γ_{13}^{∞}) of traditional organic solutes, water, and some terpenes/terpenoids at 353.2 K: measured in this work in [C$_4$mim][PF$_6$] (Δ) and [C$_4$mim][PF$_6$]/[C$_4$mim][Cl] equimolar mixture (◊); obtained from literature in [C$_4$mim][Cl] (○)[69]. The dotted lines separate the different families of organic compounds, while the solid line indicates the number of carbons (N) present in each solute.

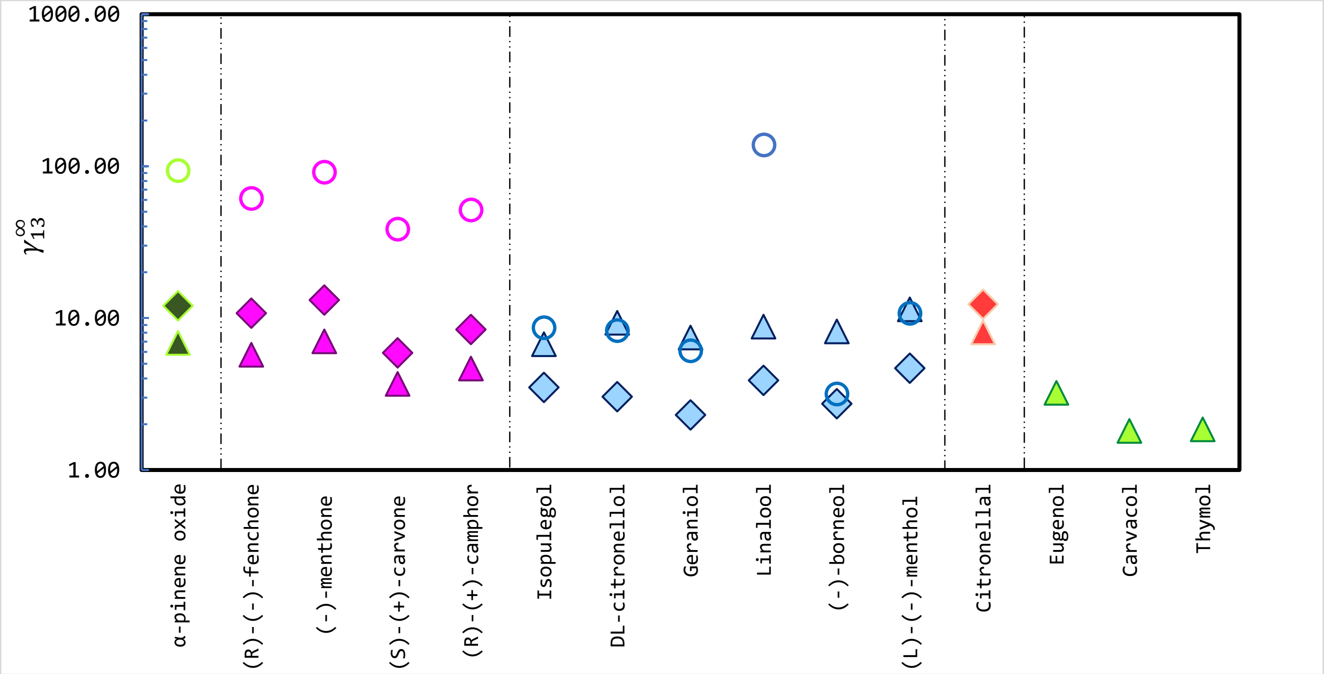


Figure 2: Infinite dilution activity coefficients (γ_{13}^{∞}) of less volatile terpenes/terpenoids at 413.2 K: measured in this work in [C$_4$mim][PF$_6$] (Δ) and [C$_4$mim][PF$_6$]/[C$_4$mim][Cl] equimolar mixture (◊); obtained from literature in [C$_4$mim][Cl] (○)(Martins et al., 2016). The dotted lines separate the different families of organic compounds. All solutes have 10 carbons.

From a global analysis of **Figure 1**, at 353.2 K, the γ_{13}^{∞} values for almost all solutes were higher in the studied equimolar mixture than in pure [C_4mim][PF_6], except for the more polar solutes such as alcohols and water. This is supported by the higher polarity of the equimolar mixture of [C_4mim][PF_6]/[C_4mim][Cl]. Alcohols and water are capable of hydrogen bonding and their interactions should be stronger with the more polar chloride anion than with the PF_6^- ion, which has a more shielded negative charge.

By comparing the results for the equimolar IL mixture with pure [C_4mim][Cl][69], is possible to notice that, for almost all solutes (apart from alkanes and cycloalkanes) in the equimolar IL mixture, the γ_{13}^{∞} assumes intermedium values between the pure IL. In the case of the less polar solutes, for alkanes the γ_{13}^{∞} values are very similar to those found in pure [C_4mim][Cl][69]. On the contrary, for cycloalkanes the γ_{13}^{∞} values are lower than for pure [C_4mim][Cl].[69]

Figure 2 represents the γ_{13}^{∞} values for some terpenes and terpenoids studied here. The data reported by Martins et al.[70] for pure [C_4mim][Cl] are majority higher than those reported in this work, being the deviations more evident in hydrocarbons terpenes, ether terpenoids, and ketones terpenoids. Regarding alcohol terpenoids, the experimental results for [C_4mim][PF_6] are close to the literature data for [C_4mim][Cl], apart from linalool (which is lower than pure [C_4mim][Cl][70]) and (-)-borneol (which the γ_{13}^{∞} for the equimolar IL mixture is similar to pure [C_4mim][Cl][70]). Overall, this brief comparison gives excellent indications about the consistency of the data found in this work.

Another important comparison should be carried out with the γ_{13}^{∞} data obtained by Martins et al.[69] for several solutes in [C_4mim][Cl]. In general, the experimental results for γ_{13}^{∞} in the equimolar mixture of [C_4mim][PF_6]/[C_4mim][Cl] are closer to those observed in the pure [C_4mim][Cl](Martins et al., 2015) than in pure [C_4mim][PF_6] indicating that the chloride anion has a significant effect on the γ_{13}^{∞} values.

Generally, γ_{13}^{∞} lower than unity, indicating a stronger solute-solvent than solute-solute interactions, were obtained only in a few systems: acetonitrile, water, and most alkanols in the [C_4mim][PF_6]/[C_4mim][Cl] equimolar mixture, and 1,4-dioxane, acetonitrile, pyridine and acetone in [C_4mim][PF_6]. Other polar solutes such as thiophene, butan-2-one, esters, and some ethers showed also low γ_{13}^{∞}, though higher than 1, in either set of IL. On the other hand, as expected, the activity coefficients of the nonpolar alkanes and cycloalkanes are the highest, all much higher than 1, which indicates the weakest interactions with the investigated IL. Regarding the influence of the chain size, normally, for a given family, the γ_{13}^{∞} increase with the number of carbons in the chemical structure, reflecting the corresponding increase in apolarity.

The γ_{13}^{∞} for acetonitrile at 353.2 K is lower than unity in all IL investigated suggesting the high potential of these IL to extract it from aliphatic hydrocarbons. Other solutes such as pyridine (0.89 for [C_4mim][PF_6] and 1.29 for [C_4mim][PF_6]/[C_4mim][Cl]), and thiophene (1.41 for [C_4mim][PF_6] and 1.71 for [C_4mim][PF_6]/[C_4mim][Cl]) showed low γ_{13}^{∞} values.

As well known, these compounds act as impurities of alkane mixtures; these results suggest a higher selectivity of these IL for the removal of nitrogen and sulfur-containing compounds from alkanes, as will be discussed later in this work.

For alcohols, the activity coefficients follow the order [C_4mim][PF_6] > [C_4mim][PF_6]/[C_4mim][Cl] > [C_4mim][Cl] and are also much lower than the γ_{13}^{∞} for aliphatic hydrocarbons. In fact, all investigated alcohols presented γ_{13}^{∞} lower than 1 for the mixture [C_4mim][PF_6]/[C_4mim][Cl], except for *tert*-butanol that is slightly higher (1.05 at 353.2 K). Regarding [C_4mim][PF_6], the γ_{13}^{∞} for alcohols are higher than 1, yet not too far from the unity. This behavior can be explained by a stronger hydrogen bond-ion interaction in the chloride containing systems.

The lower γ_{13}^{∞} (though > 1) of hydrocarbons (aliphatic and aromatic) and polar aprotic solutes (esters, an ethers) in [C_4mim][PF_6] when compared to the IL mixture shows that the interactions with this less polar IL are less unfavorable.

The effect of temperature on the activity coefficients is also very important in process design, and that will be analyzed in the next plots. In general, there is a linear increase or decrease in the natural logarithm of γ_{13}^{∞} with the inverse absolute temperature. **Figures 3** and **4** present the results for the aliphatic and aromatic hydrocarbons, respectively. As can be seen, the $\ln(\gamma_{13}^{\infty})$ values for alkanes and cycloalkanes are high and increase linearly with $1/T$. As discussed before, there is a slight difference between the values depending on the ionic liquid used, as the values for the equimolar mixture of [C_4mim][PF_6]/[C_4mim][Cl] are higher than in pure [C_4mim][PF_6]. The mixture has a higher polarity, resulting in less favorable solute-solvent interactions.

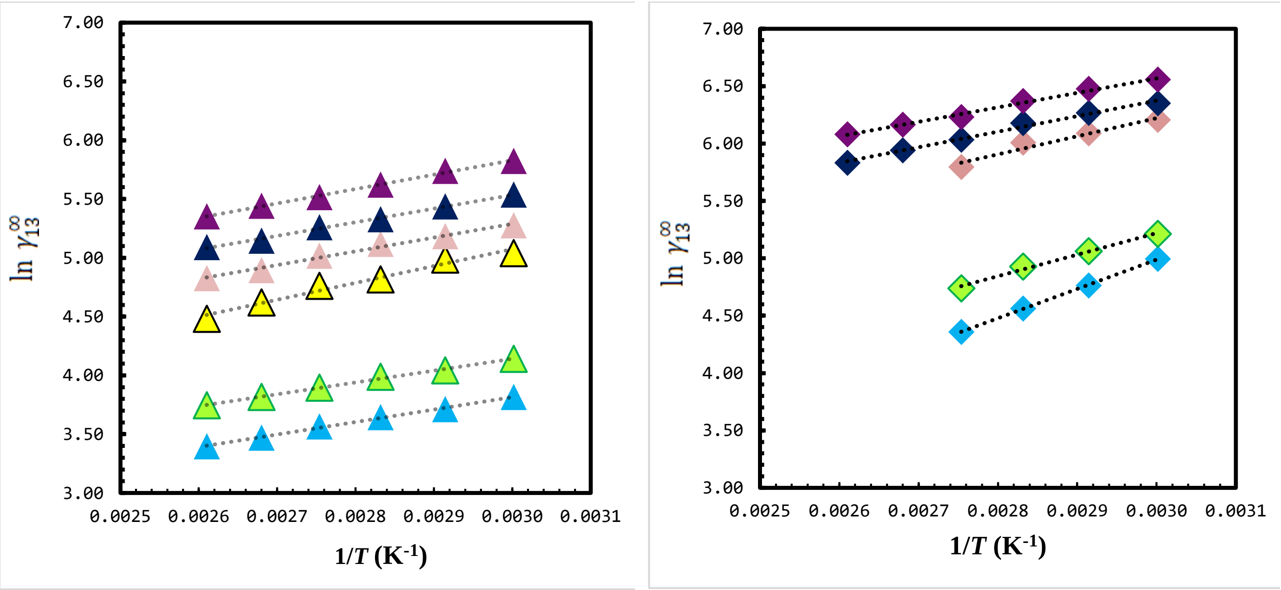


Figure 3: Experimental $ln\,\gamma_{13}^{\infty}$ of alkanes and cycloalkanes in [C$_4$mim][PF$_6$] (Δ) and [C$_4$mim][PF$_6$]/[C$_4$mim][Cl] equimolar mixture (◊) as a function of 1/T. Color code: ● heptane, ● octane, ● nonane, ● decane, ● cyclohexane, and ● methylcyclohexane.

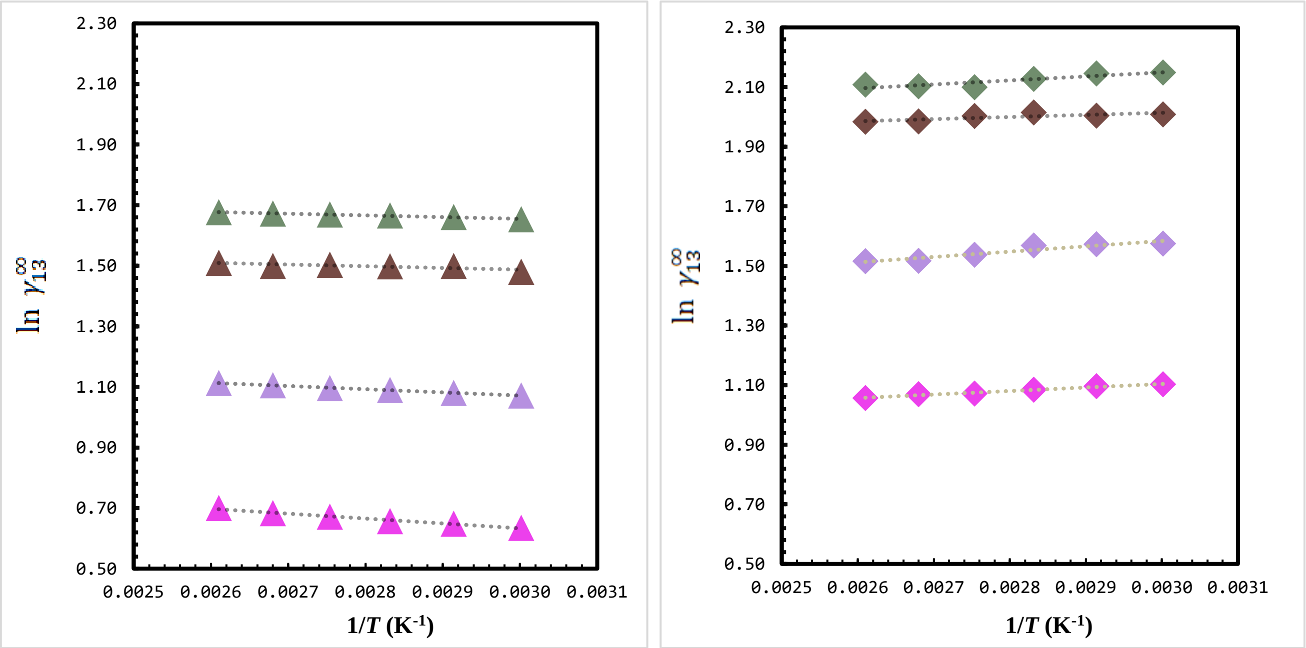


Figure 4: Experimental $ln\,\gamma_{13}^{\infty}$ of aromatic hydrocarbons in [C$_4$mim][PF$_6$] (Δ) and [C$_4$mim][PF$_6$]/[C$_4$mim][Cl] equimolar mixture (◊) and as a function of 1/T. Color code: ● benzene, ● ethylbenzene, ● toluene, ● p-xylene.

The $\ln\gamma_{13}^{\infty}$ of the aromatic hydrocarbons are lower than for alkanes and cycloalkanes, as the former are more polar (related to the π–electron) and change only very slightly with temperature, with a different slope depending on the stationary phase. The number of carbons in the alkyl groups bonded to the aromatic ring has a significant effect on the $\ln\gamma_{13}^{\infty}$ value; as the number of carbons increases, $\ln\gamma_{13}^{\infty}$ also increases, due to the increased molecule apolarity. The position and type of substituents of the benzene ring seem to have a lower effect on $\ln\gamma_{13}^{\infty}$ value.

The value of $\ln\gamma_{13}^{\infty}$ for the esters are represented in **Figure 5**. As can be seen, there is a stronger interaction between the less polar [C$_4$mim][PF$_6$] and the acetates and the slope is opposite (negative for the pure IL and positive to the mixture). The interaction between both IL and the esters studied gets weaker as the number of carbons increases. Besides that, the results showed a higher value of $\ln\gamma_{13}^{\infty}$ for ethyl acetate than vinyl acetate, resulting from the unsaturated bond in vinyl acetate.

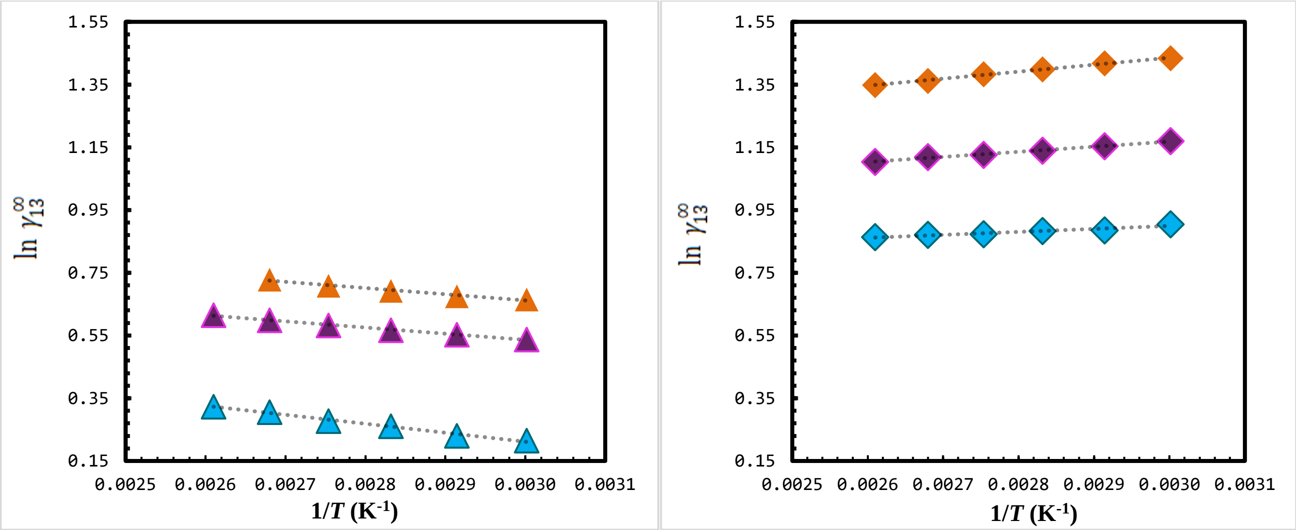


Figure 5: Experimental $ln\,\gamma_{13}^{\infty}$ of esters in [C$_4$mim][PF$_6$] (Δ) and [C$_4$mim][PF$_6$]/[C$_4$mim][Cl] equimolar mixture ($\Diamond$) as a function of $1/T$. Color code: ● methyl acetate, ● vinyl acetate, ● ethyl acetate.

Figure 6 shows the temperature dependence results for three different ethers. As can be seen, again [C$_4$mim][PF$_6$] has stronger interactions with the ethers studied, particularly with 1,4-dioxane, a cyclic ether containing two oxygen atoms. It has the highest molecular weight and boiling point of the studied ethers.

The behavior of sulfur (thiophene) and nitrogen (acetonitrile, pyridine) containing molecules and ketones (acetone and butan-2-one) can be analyzed in **Figure 7**. As demonstrated, the pure [C$_4$mim][PF$_6$] has stronger interaction with those compounds; for acetonitrile and pyridine γ_{13}^{∞} are lower than 1, in the studied temperature range, indicating that this ionic liquid might be useful to remove nitrogen-compounds from fuels oils.

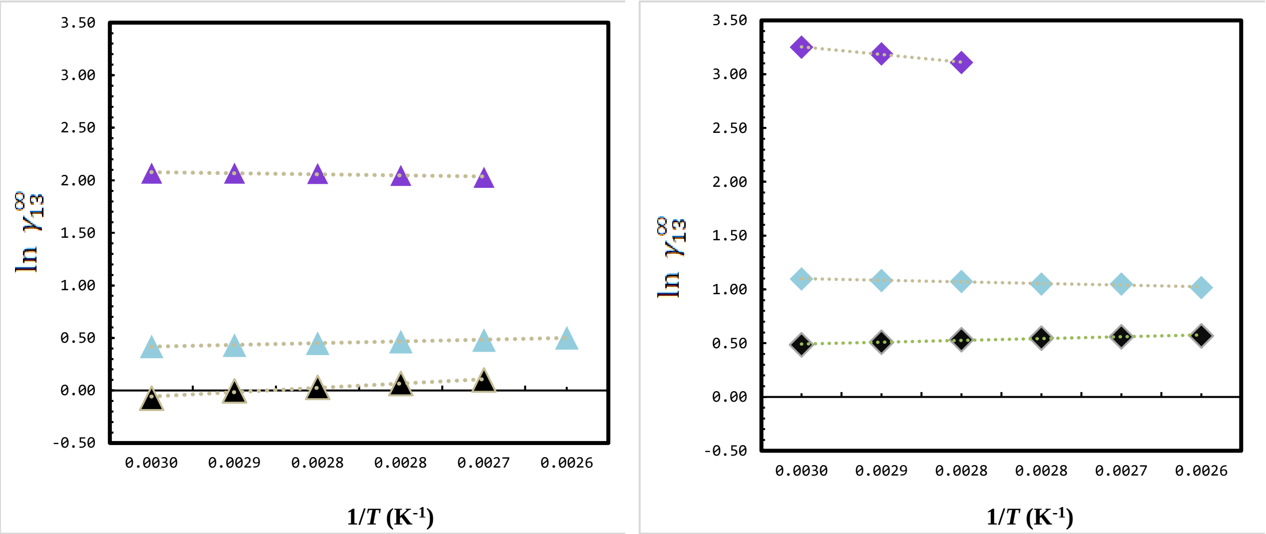


Figure 6: Experimental $ln\,\gamma_{13}^{\infty}$ of ethers in [C$_4$mim][PF$_6$] (Δ) and [C$_4$mim][PF$_6$]/[C$_4$mim][Cl] equimolar mixture (◊) as a function of 1/*T*. Color code: ● THF, ● 1,4-dioxane, ● diethyl ether.

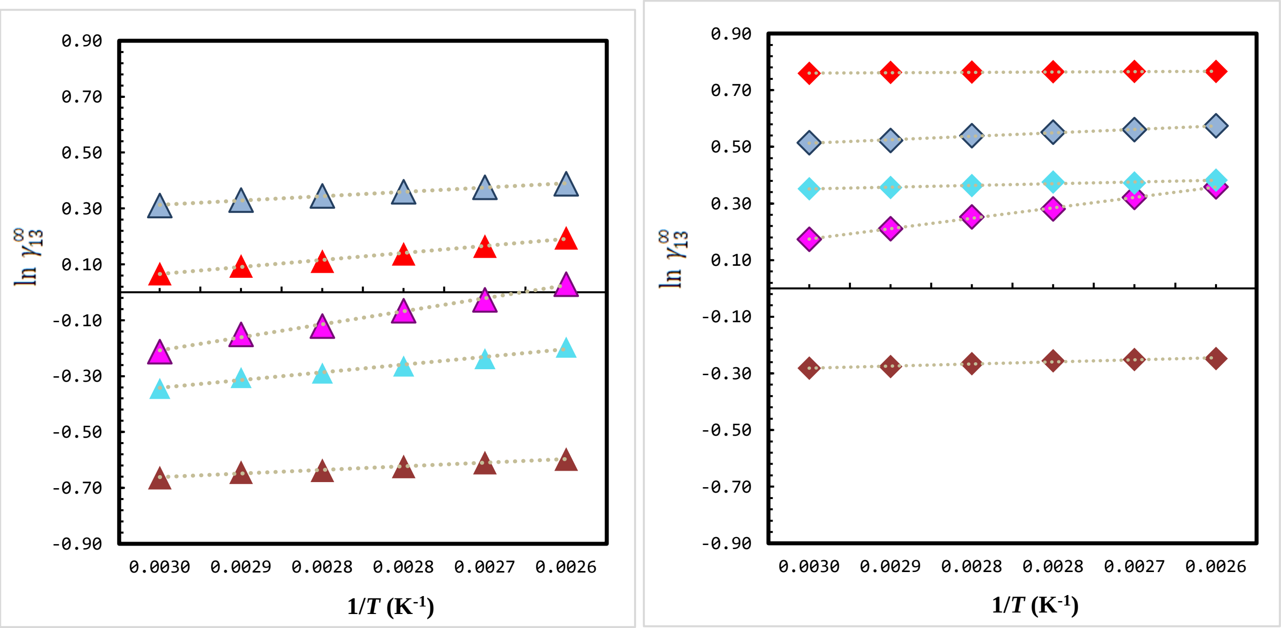


Figure 7: Experimental $ln\,\gamma_{13}^{\infty}$ of acetonitrile, pyridine, thiophene and two ketones in [C$_4$mim][PF$_6$] (Δ) and [C$_4$mim][PF$_6$]/[C$_4$mim][Cl] equimolar mixture (◊) as a function of 1/*T*. Color code: ● acetonitrile, ● pyridine, ●, thiophene, ● acetone, ● 2-butanone.

It is noticeable that alcohols and water (**Figure 8**) showed the lowest $ln\,\gamma_{13}^{\infty}$ values than any other solute in the equimolar mixture [C$_4$mim][PF$_6$]/[C$_4$mim][Cl], which was expected once the anion Cl$^-$ is able to form hydrogen bond more easily, in the studied temperature range. For this family of compounds, in general the interactions decrease with increasing number of carbons, in the ranking methanol > ethanol > 1-propanol > 2-propanol > isobutanol > 1-butanol > 2-butanol > *tert*-butanol.

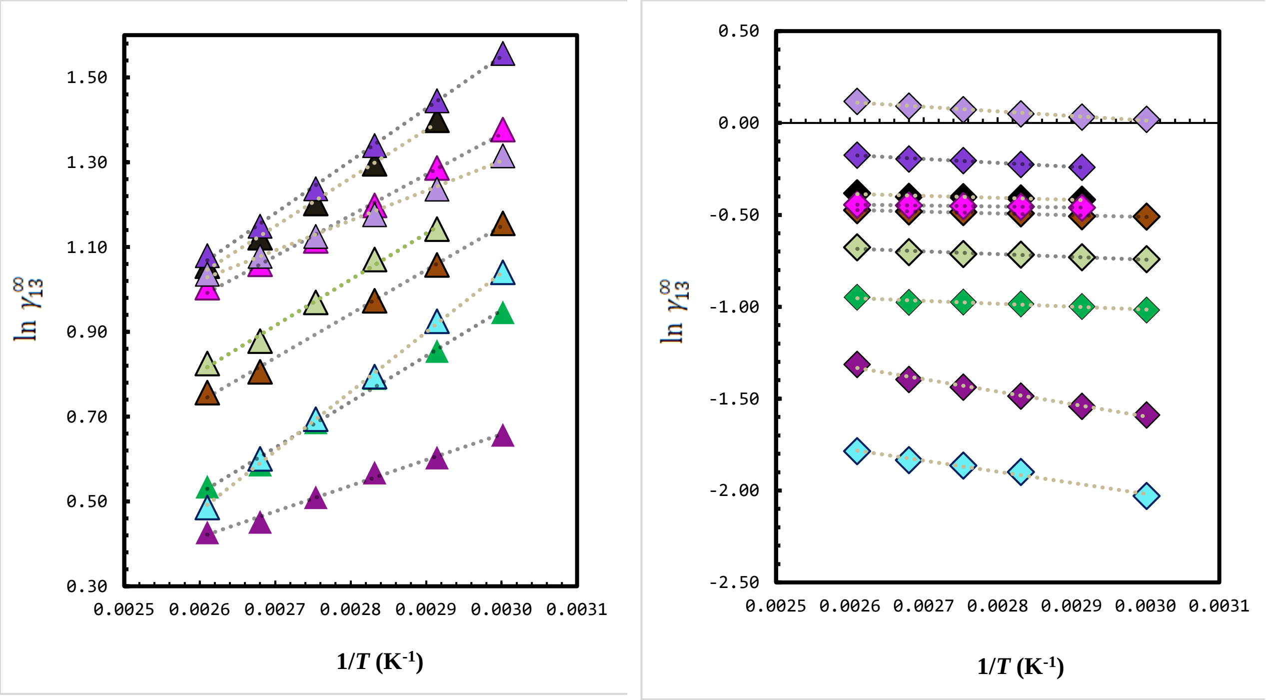


Figure 8: Experimental $ln\,\gamma_{13}^{\infty}$ of alcohols and water in [C$_4$mim][PF$_6$] (Δ) and [C$_4$mim][PF$_6$]/[C$_4$mim][Cl] equimolar mixture (◊) as a function of 1/*T*. Color code: ● methanol, ● ethanol, ● 1-propanol, ● 2-propanol, ● 1-butanol, ● 2-butanol, ● *tert*-butanol, ● isobutanol, ● water.

Taking into account the equimolar mixture of [C$_4$mim][PF$_6$]/[C$_4$mim][Cl], the type of alcohol (primary, secondary or tertiary) has more impact in the $ln\,\gamma_{13}^{\infty}$ values (considering a fixed number of carbon atoms), where the interactions between the ionic liquid and the alcohols (with four carbon atoms) decrease in the following order: *tert*-butanol (tertiary alcohol) > 2-butanol (secondary alcohol) > 1-butanol (primary alcohol) > isobutanol (primary alcohol), with the values for the last two being very close to each other. The same behavior was observed for the alcohols with three carbon atoms.

Another aim of this work is the fractionation of terpenes and terpenoids by using IL as separation agents. **Figure 9** explores the experimental data for different terpenes. The data for ether terpenoids, ketone and aldehyde terpenoids, alcohol terpenoids and phenolic terpenoid are shown in **Figures 10**, **11**, **12** and **13**, respectively.

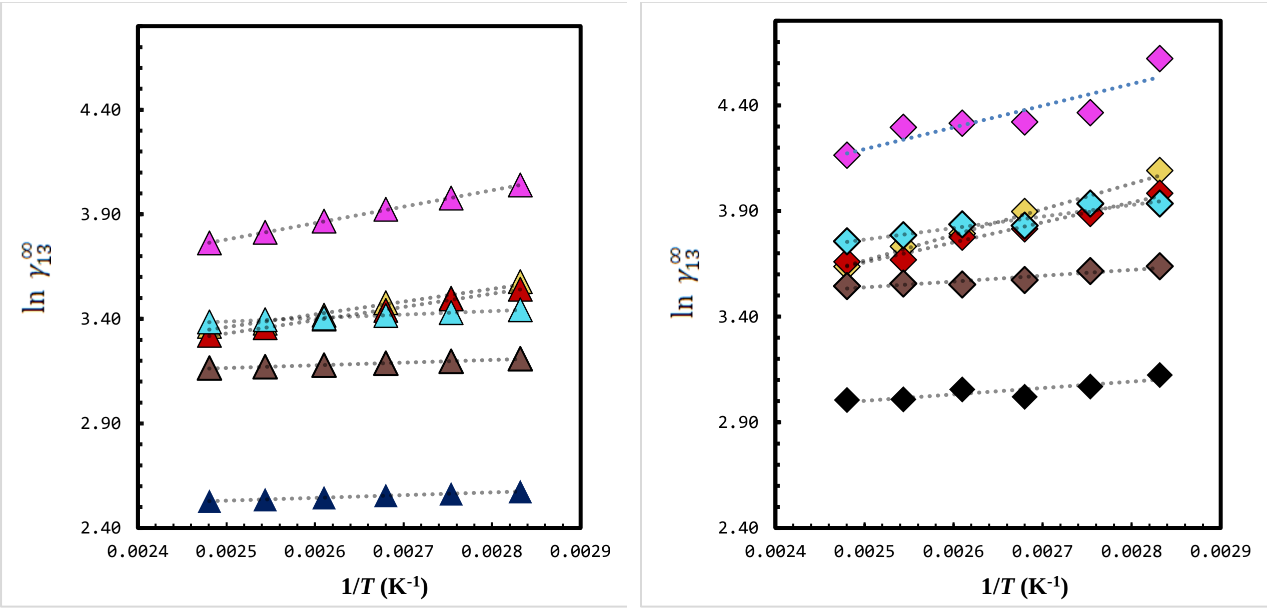


Figure 9: Experimental $ln\,\gamma_{13}^{\infty}$ of terpenes in [C$_4$mim][PF$_6$] (Δ) and [C$_4$mim][PF$_6$]/[C$_4$mim][Cl] equimolar mixture (◊) as a function of 1/*T*. Color code: ● α-pinene, ● β-pinene, ● *R*-(+)-limonene, ● myrcene, ● *p*-cymene, ● γ-terpinene.

As shown in **Figure 9**, in both IL investigated, a poor interaction with hydrocarbons terpenes was found. As expected, these solutes presented similar behavior with alkanes and cycloalkanes, with a positive slope and large positive deviations from ideality and, in addition, showing a greater interaction with [C$_4$mim][PF$_6$] when compared to the [C$_4$mim][PF$_6$]/[C$_4$mim][Cl] equimolar mixture.

Similarly, the results for the low polarity ethers (**Figure 10)** showed a higher interaction with the pure ionic liquid [C$_4$mim][PF$_6$] than in the equimolar mixture of [C$_4$mim][PF$_6$]/[C$_4$mim][Cl]. Eucalyptol has higher $ln\,\gamma_{13}^{\infty}$ values than α-pinene oxide.

Regarding ketone terpenoids (**Figure 11**), these compounds do not behave like the common ketones previously studied due to their higher molecular weight and apolarity. Besides the difference between $ln\,\gamma_{13}^{\infty}$ values, the slope also changes. Nevertheless, ketone terpenoids also showed higher interaction (lower γ_{13}^{∞}) with pure [C$_4$mim][PF$_6$] compared to the IL mixture as common ketones (acetone and 2-butanone). Citronellal, an aldehyde terpenoid, had the poorest interaction in both IL studied when compared with the ketones terpenoids.

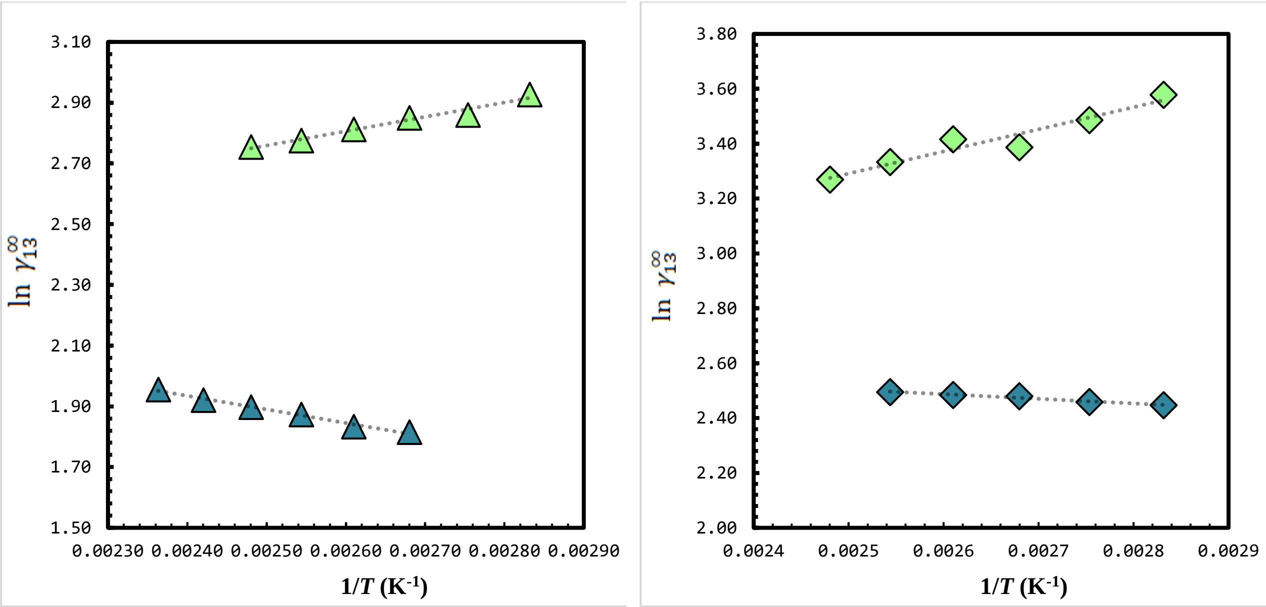


Figure 10: Experimental $ln\,\gamma_{13}^{\infty}$ of ether terpenoids in [C$_4$mim][PF$_6$] (Δ) and [C$_4$mim][PF$_6$]/[C$_4$mim][Cl] equimolar mixture (◊) as a function of 1/*T*. Color code: ● α-pinene oxide, ● eucalyptol.

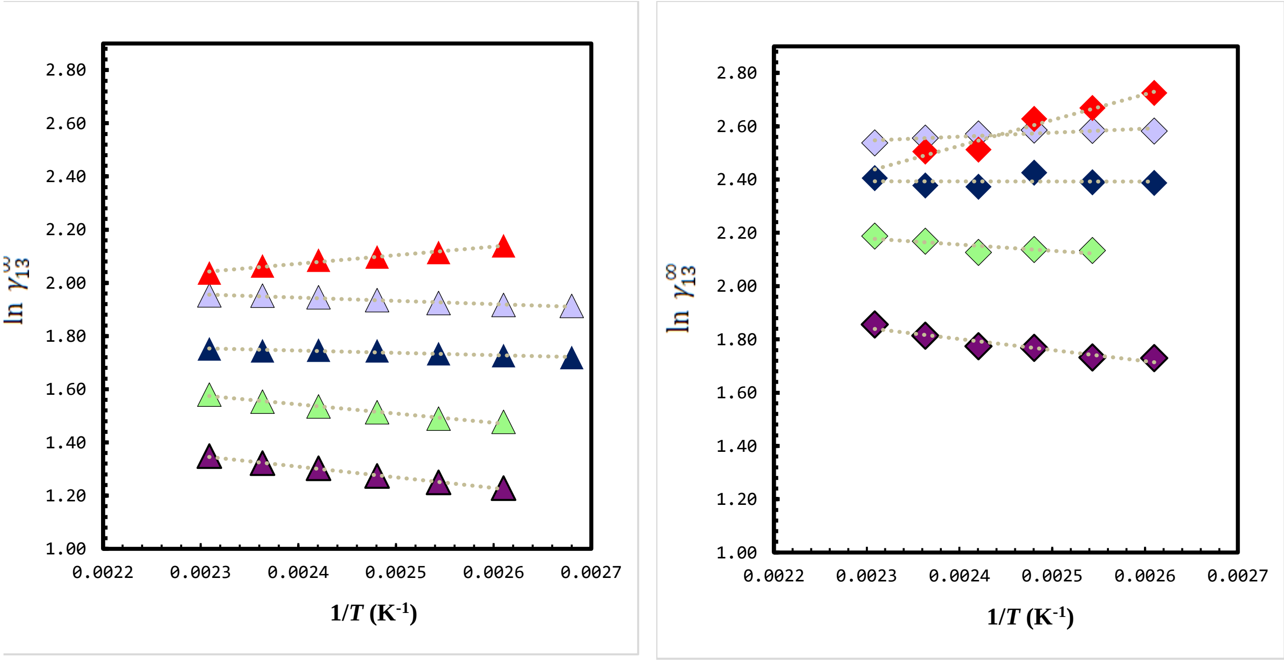


Figure 11: Experimental $ln\,\gamma_{13}^{\infty}$ values of ketone terpenoids in [C$_4$mim][PF$_6$] (Δ) and [C$_4$mim][PF$_6$]/[C$_4$mim][Cl] equimolar mixture (◊) as a function of 1/*T*. Color code: ● *S*-(+)-carvone, ● (-)-menthone, ● (1*R*)-(+)-camphor, ● citronellal, ● *R*-(-)-fenchone.

On the contrary, alcohol terpenoids (**Figure 12**) showed more favorable interactions with the equimolar mixture of [C$_4$mim][PF$_6$]/[C$_4$mim][Cl] than in pure [C$_4$mim][PF$_6$]. This behavior was also observed for traditional alcohols due to the high capacity of the anion Cl$^-$ to form hydrogen bonds.

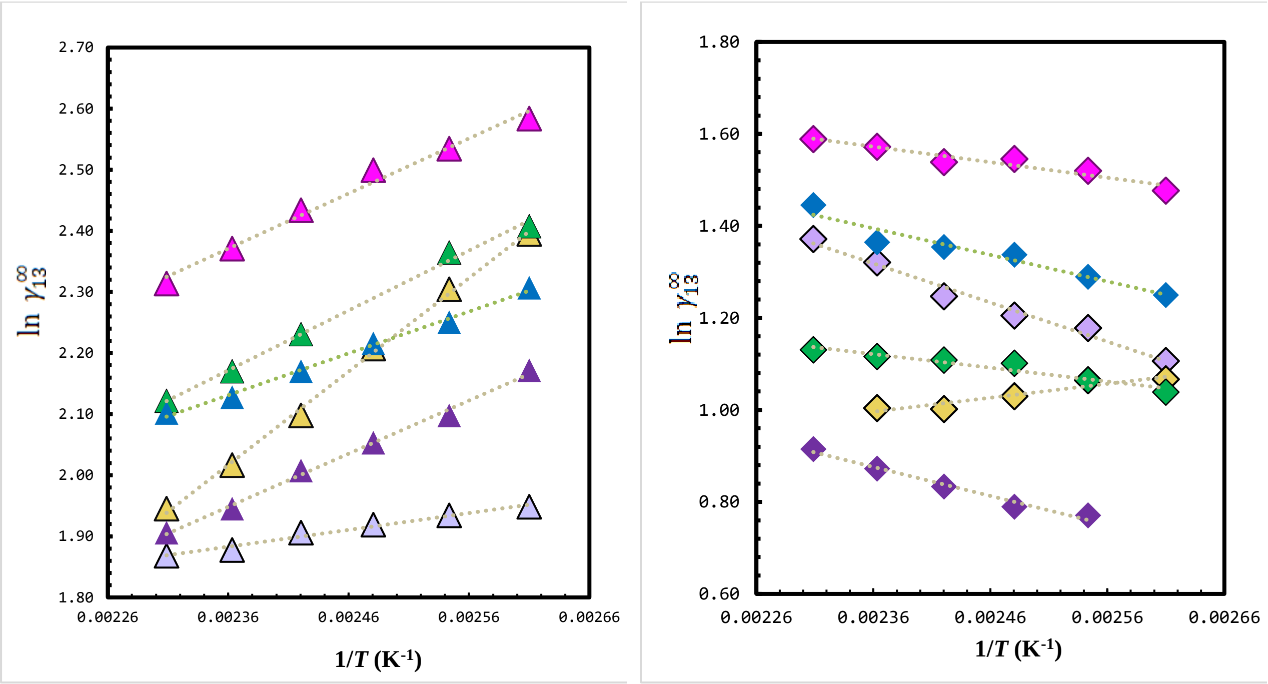


Figure 12: Experimental $ln\,\gamma_{13}^{\infty}$ values of alcohol terpenoids in [C$_4$mim][PF$_6$] (Δ) and [C$_4$mim][PF$_6$]/[C$_4$mim][Cl] equimolar mixture (◊) as a function of 1/T. Color code: ● *L*-(-)-menthol, ● (-)-isopulegol, ● (-)-borneol, ● geraniol, ● *DL*-citronellol, ● linalool.

Linalool is the only tertiary alcohol terpenoid studied, but this seems not affect too much the $ln\,\gamma_{13}^{\infty}$ values, since it is close to other solutes classified as secondary alcohols. It is perceptible that the slope changes in the two sets of IL studied – observed for the alcohols terpenoids, are similar to the change in traditional alcohols, with the exception of (-)-borneol in the equimolar IL mixture.

The phenolic terpenoids are compounds that have a hydroxyl group linked to the aromatic ring, presenting a high boiling point, and being the less volatile terpenoids studied in this work. **Figure 13** shows the results of $ln\,\gamma_{13}^{\infty}$ as a function of 1/T. It was only possible to obtain experimental data in pure [C$_4$mim][PF$_6$] due to the very high retention times of these solutes, even at the highest possible operation temperature. Carvacrol and thymol are also isomers and have close $ln\,\gamma_{13}^{\infty}$ values. Eugenol showed the lowest interaction with the ionic liquid studied, as expected since it has a higher nonpolar part.

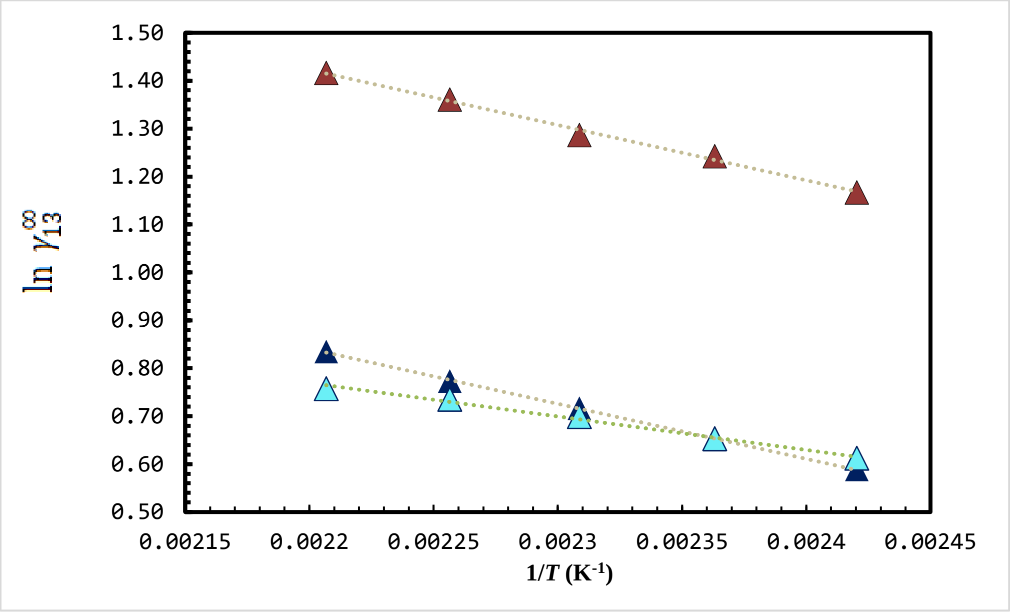


Figure 13: Experimental $ln\,\gamma_{13}^{\infty}$ values of phenolic terpenoids in [C_4mim][PF_6] (Δ) as a function of 1/*T*. Color code: ● eugenol, ● carvacrol, ● thymol.

Comparison with literature data

In **Figure 14**, the activity coefficients at infinite dilution obtained in this work in [C_4mim][PF_6] are compared to the data reported in a previous study by Mutelet et al.[71]. Data are available for several traditional organic solutes – alkanes, aromatic hydrocarbons, ketones, alcohols, nitrogen- compounds (pyridine), and sulfur- compounds (thiophene). The literature values are quite consistent with the results reported in this work, except for alkanes and cycloalkanes for which the literature values are lower than the values measured in this work.

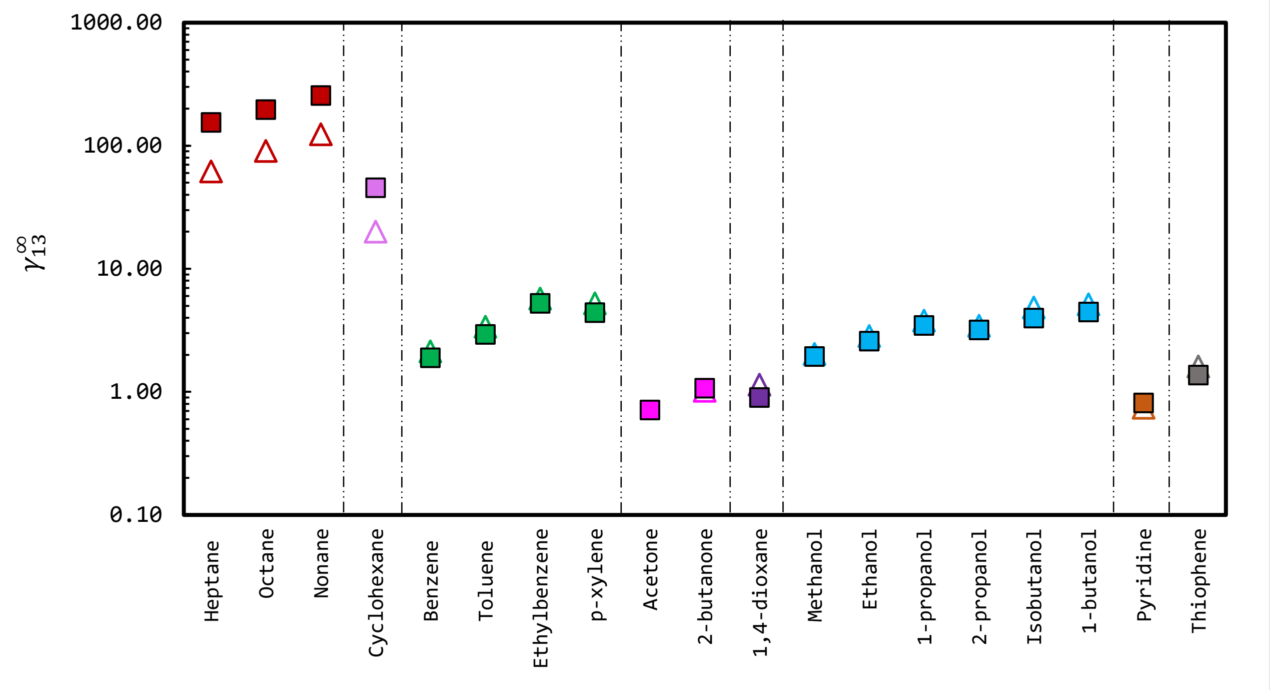


Figure 14: Comparison between the experimental activity coefficients at infinite dilution for traditional organic solutes, obtained in [C_4mim][PF_6]: this work (□) literature[71] (Δ), at 333.2 K. The dotted lines separate the different families for the organic compounds.

4.2. Infinite Dilution Thermodynamic Functions

The excess partial molar properties at infinite dilution allow to obtain additional information about the interactions between the solutes and the ionic liquid. Using the γ_{13}^{∞} values it was possible to calculate the Gibbs energy ($\bar{G}_m^{E,\infty}$), enthalpy ($\bar{H}_m^{E,\infty}$), and entropy ($T_{ref}S_m^{E,\infty}$) for all solutes.

The results are presented in detail in **Appendix C**, **Table C5**. The excess partial molar properties for traditional organic solutes, and water are presented in **Figure 15**. For terpenes and different types of terpenoids, the results are in **Figure 16**, and for phenolic terpenoids in **Figure 17**.

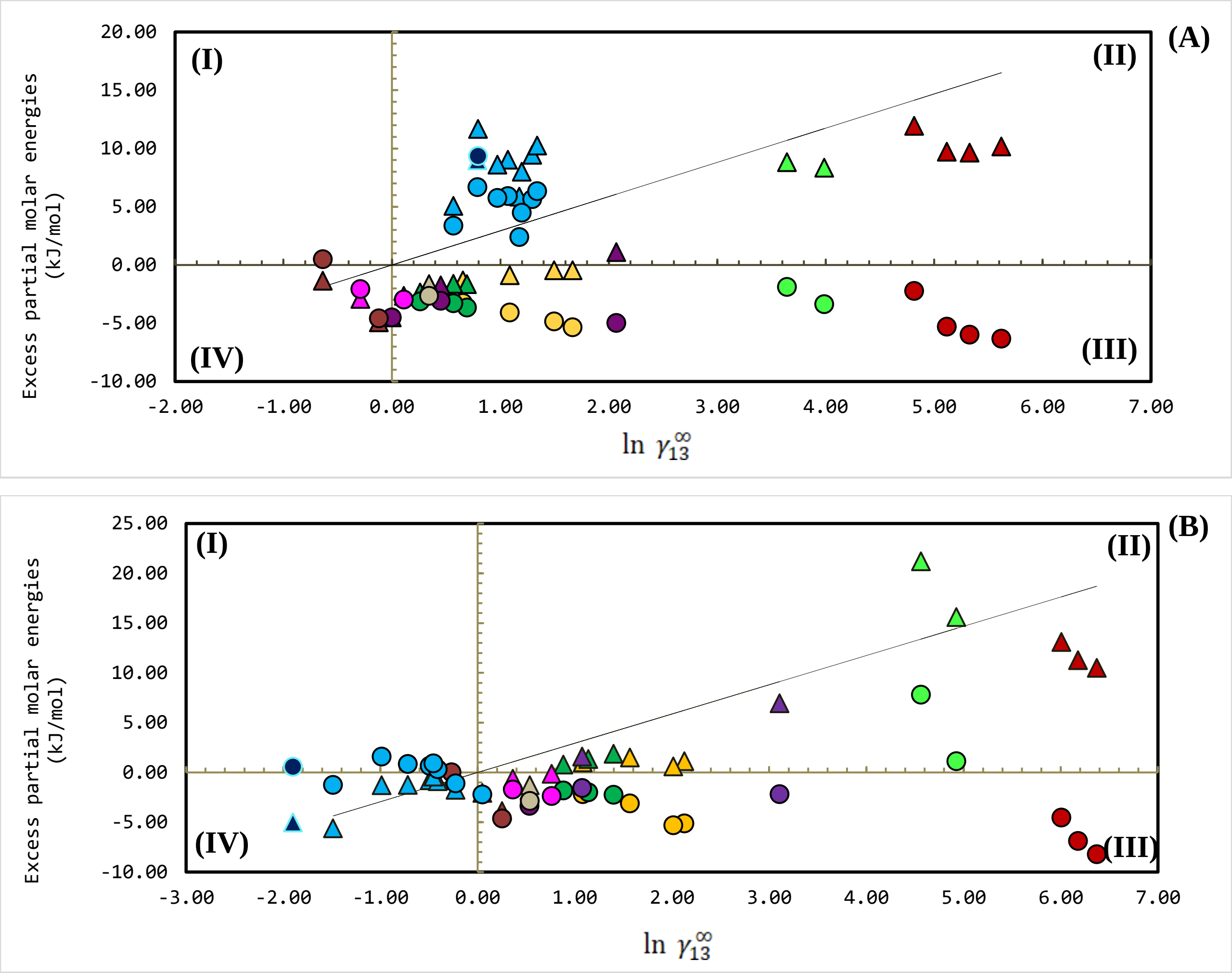


Figure 15: Excess partial molar energies at infinite dilution as function of the natural logarithm of the activity coefficients at infinite dilution of organic solutes and water in **(A)** [C$_4$mim][PF$_6$] and **(B)** the equimolar mixture [C$_4$mim][PF$_6$]/[C$_4$mim][Cl], at 353.2 K. The solid line represents $\bar{G}_m^{E,\infty}$, and the symbols correspond to $\bar{H}_m^{E,\infty}$ (Δ) and $T_{ref}S_m^{E,\infty}$ (○). Color code: ● alkanes, ● cycloalkanes, ● aromatic hydrocarbons, ● ethers, ● esters, ● ketones, ● alcohols, ● water, ● acetonitrile, and pyridine, ● thiophene.

For the less polar solutes such as alkanes and cycloalkanes, the γ_{13}^{∞} are all higher than unity, consequently, $\bar{G}_m^{E,\infty}$ showed positive values. The $\bar{H}_m^{E,\infty}$ are also positive for these solutes, indicating that solute-IL interactions increase as temperature increases.

Concerning the aromatic hydrocarbons , the $\bar{G}_m^{E,\infty}$ values are all positive, the $\bar{H}_m^{E,\infty}$ values are closer to zero, and the $T_{ref}S_m^{E,\infty}$ are negative indicating that the entropic factor predominates in both IL systems. Positive values for $\bar{G}_m^{E,\infty}$ and negative values for $T_{ref}S_m^{E,\infty}$ indicate that the solvation of these compounds in the investigated IL is highly unfavorable. The distribution of the thermodynamic energies is throughout region (II) and (III) for these solutes.

Analyzing **Figure 15 (A)**, it is worth noting that for methyl acetate, 1,4-dioxane, pyridine, thiophene, and ketones in [C4mim][PF6] have a $\bar{G}_m^{E,\infty}$ value close to zero, meaning that enthalpic and entropic effects on the solvation of this compounds are similar, *i.e.*, they cancel each other. The same effect was observed for acetonitrile, pyridine, 2-butanol, and *tert*-butanol in **Figure 15 (B)**.

In the case of the polar protic solutes such as alcohols and water, the excess partial molar properties are all positive for pure [C4mim][PF6] which results in a distribution in region (II). The $T_{ref}S_m^{E,\infty}$ values were the highest observed among all the solutes studied (being all positive), though lower than the enthalpic contribution.

On the other hand, in the equimolar mixture of [C4mim][PF6]/[C4mim][Cl], the $\bar{H}_m^{E,\infty}$and $\bar{G}_m^{E,\infty}$values are almost all negative with one exception in the $\bar{G}_m^{E,\infty}$ for *tert*-butanol (being almost zero), this way, the entropic and enthalpic effects practically cancel each other out for this alcohol. Moreover, the $T_{ref}S_m^{E,\infty}$ values for this IL mixture are, generally, positive with some exceptions such as methanol, 2-butanol and *tert*-butanol which presented negative values for entropy.

For terpenes and terpenoids (**Figure 16**), there is no $\gamma_{13}^{\infty} < 1$, so for these solutes the thermodynamics energies cannot be in regions (I) and (IV). **Figure 16 (A)** and **(B)** represents the excess partial molar properties for the pure [C4mim][PF6] and for the equimolar IL mixture, respectively. In both IL systems, for ketone terpenoids, the entropic effects seem to dominate over the enthalpic ones (higher absolute values for $T_{ref}S_m^{E,\infty}$). For alcohol terpenoids, **Figure 16 (A)** shows higher values for enthalpy (dominant effect) and entropy among all terpenes/terpenoids studied, being the (-)-borneol the highest.

Inversely , for alcohol terpenoids, the Gibbs energy values are generally lower than all other terpenes studied for the equimolar mixture of [C4mim][PF6]/[C4mim][Cl], **Figure 16 (B)**, this behavior may be happened due the higher interaction between these solutes and this IL mixture. Furthermore, all alcohol terpenoids have an entropic and enthalpy effect just slightly different. Analyzing the enthalpies, generally, for the terpenes it assumes positive values, and for terpenoids nearly all of them has negative enthalpies.

Considering the less polar solutes such as terpenes (hydrocarbons molecules), a positive deviation from Raoult's law was observed (as well as in the common hydrocarbons) with $\gamma_{13}^{\infty} > 1$, and consequently $\bar{G}_m^{E,\infty} > 1$. The $\overline{H}_m^{E,\infty}$ values are also positive, and $T_{ref}S_m^{E,\infty}$ is negative, in both IL systems.

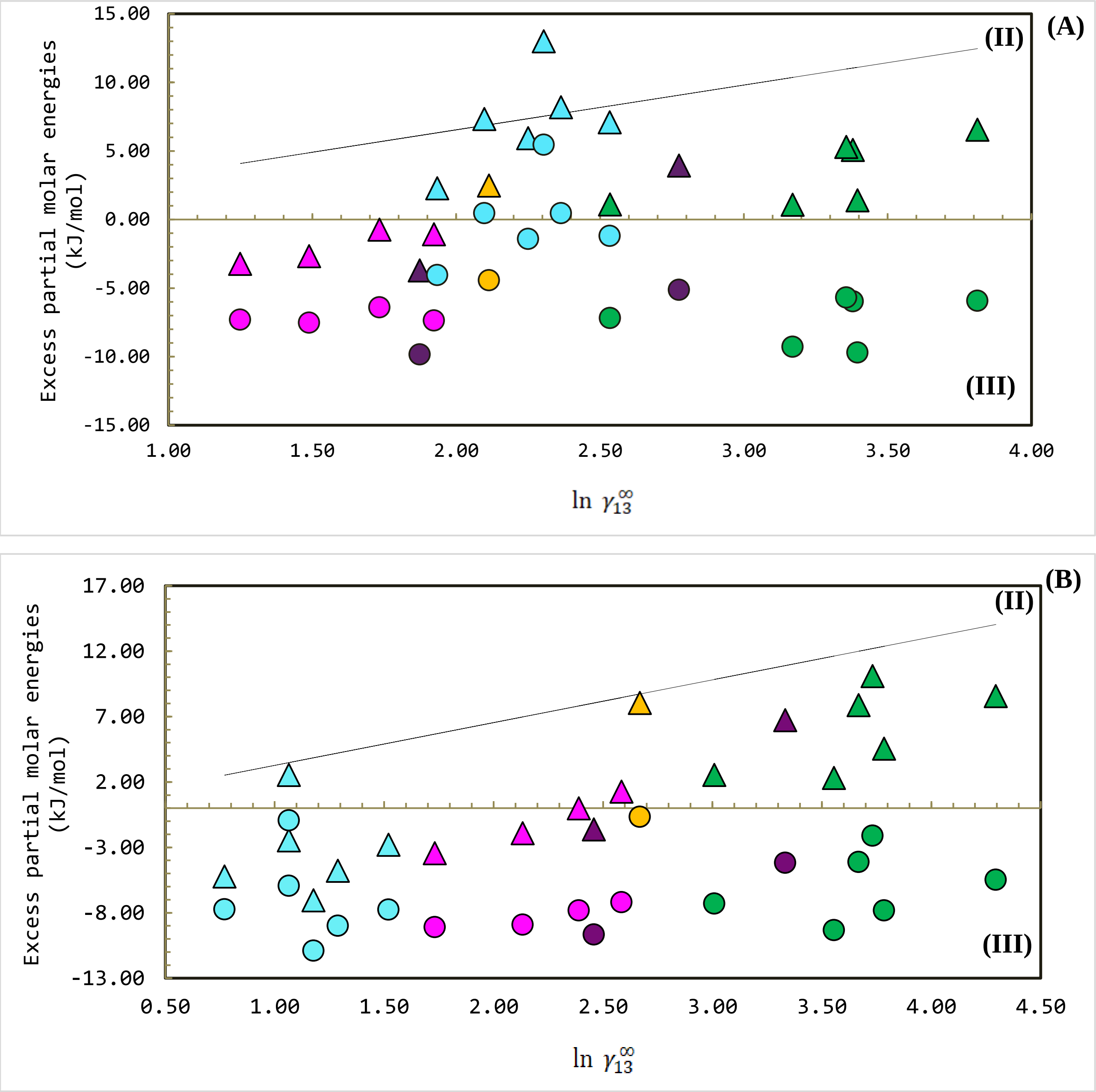


Figure 16: Excess partial molar energies at infinite dilution as a function of the natural logarithm of the activity coefficients at infinite dilution of terpenes and terpenoids in **(A)** [C$_4$mim][PF$_6$] and in **(B)** the equimolar mixture [C$_4$mim][PF$_6$]/[C$_4$mim][Cl], at 393.2 K. The solid line represents $\bar{G}_m^{E,\infty}$, and the symbols correspond to $\Delta\overline{H}_m^{E,\infty}$ (Δ) and $T_{ref}S_m^{E,\infty}$ (○). Color code: ● alcohol terpenoids, ● ketone terpenoids, ● ether terpenoids, ● citronellal, ● hydrocarbon terpenes.

For phenolic terpenoids, there is no results for the equimolar mixture of [C4mim][PF6]/[C4mim][Cl] due to the high retention times. As **Figure 17** shows, the excess partial molar properties for this type of terpenoids are negative, with the exception of the $\bar{G}_m^{E,\infty}$ values (region (II)). So, the thermodynamics energies for enthalpy and entropy are distributed in region (III). It was observed that for pure [C4mim][PF6] there is a higher interaction between ionic liquid-solute among all terpenes and terpenoids studied. The $\bar{H}_m^{E,\infty}$ and $T_{ref}S_m^{E,\infty}$ for carvacrol and thymol are close due to their similar molecule structure. Entropies effects seem to be the dominant (higher absolute values for this excess partial molar property).

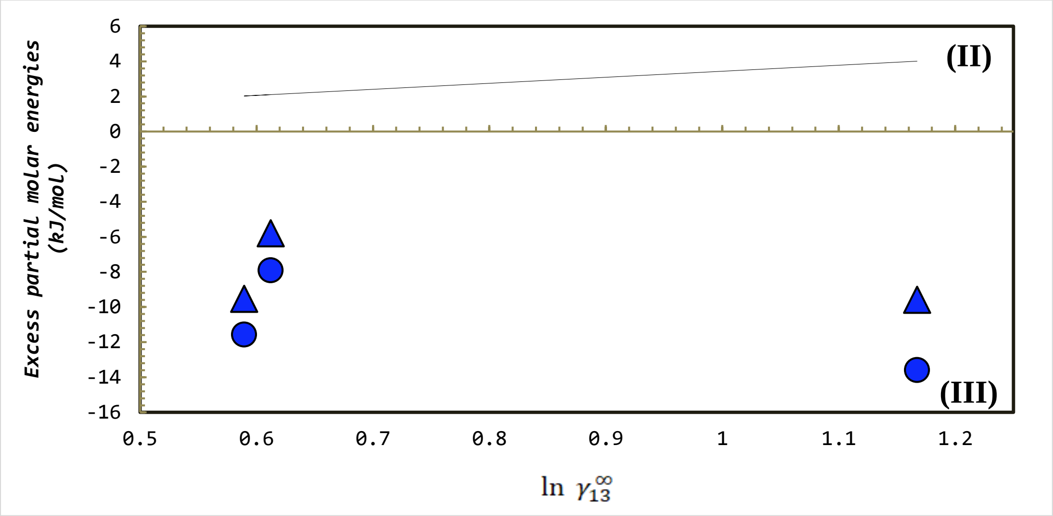


Figure 17: Excess partial molar energies at infinite dilution as a function of the natural logarithm of the activity coefficients at infinite dilution of phenolic terpenoids in [C4mim][PF6] at 413.2 K. The solid line represents $\bar{G}_m^{E,\infty}$, and the symbols correspond to $\Delta\bar{H}_m^{E,\infty}$ (Δ) and $T_{ref}S_m^{E,\infty}$ (○).

4.3. Gas-Liquid Partition Coefficient

The gas-liquid partition coefficients of the studied solutes, K_L, were calculated from retention times using the density of the ionic liquid [C4mim][PF6]. For the equimolar mixture of [C4mim][PF6]/[C4mim][Cl] no information is available yet, so it was not possible to determine the K_L for this system.

The results are reported in detail in **Appendix C**, **Table C6**. In order to better understand the relationship between this parameter and the structure and functionality of the solutes, **Figure 18** shows the K_L values measured at 353.2 K for water, a set of organic solutes, terpenes, and eucalyptol.

For the less volatile terpenoids, the results are represented in **Figure 19** at 413.2 K.

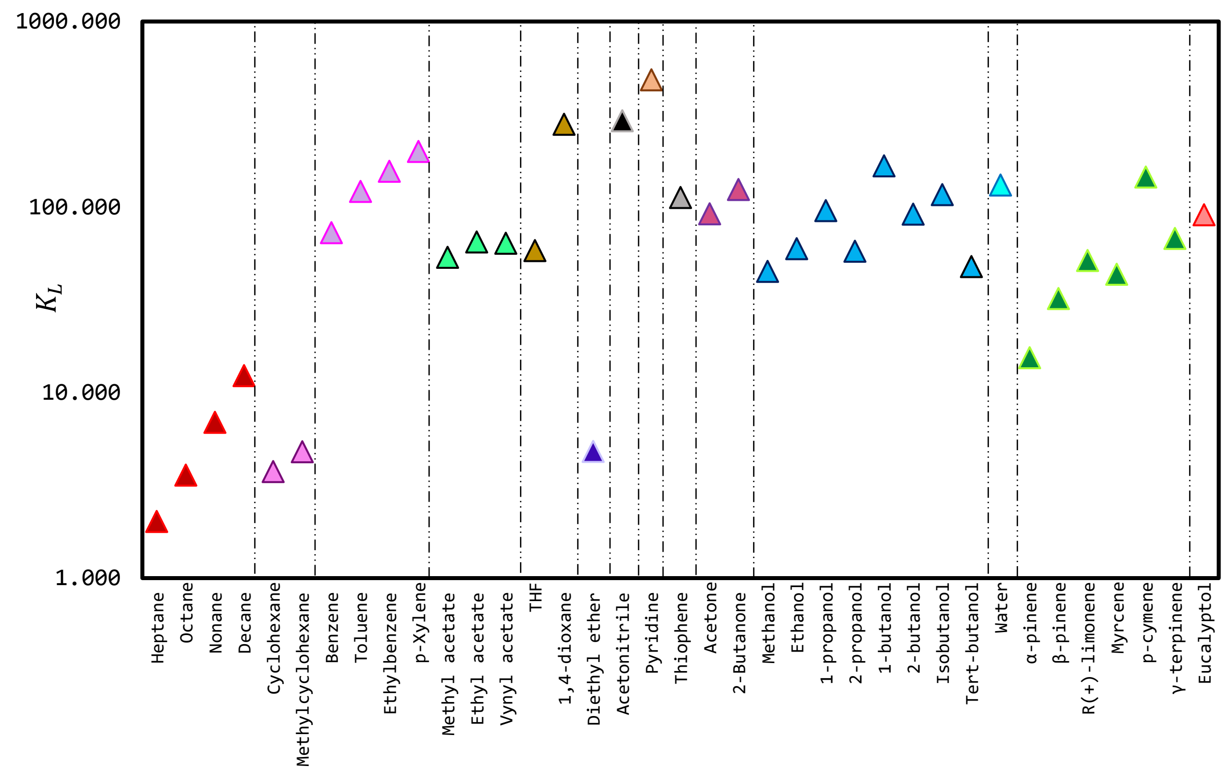


Figure 18: Gas-liquid partition coefficients (K_L) for traditional organic solutes, water, and some terpenes/terpenoids at 353.2 K in [C$_4$mim][PF$_6$]. The dotted lines separate the different families for the organic compounds.

This thermodynamic parameter allows better understanding of the distribution of solute between the ionic liquid and the gas phases, providing insight on the suitability of the ionic liquid as separation agent for a given industrial separation process, *e.g.*, a LLE, followed by the subsequently solute evaporation in order to recover the ionic liquid, at low pressures.

It is perceptive that for all solutes the number of carbons influence the K_L values. An increase is observed in the K_{L} values as the alkyl-chain increases in alkanes, cycloalkanes, aromatic hydrocarbons, acetates, ethers, ketones, and alcohols. Moreover, as expected, as temperature increases, K_L decreases, as the solute concentration in the liquid phase is lower.

Analyzing ethers, a higher number of oxygen atoms seems to contribute to enhance the solute concentration in the liquid phase. The highest value found for this family was in 1,4-dioxane (two oxygen atoms), and the lowest was in diethyl ether (higher volatility). For the nitrogen-compounds (acetonitrile and pyridine) the values are similar and the highest for all solutes present in **Figure 18.**

Concerning the alcohols, the nature of the alcohol has a greater influence on the K_L values than the number of carbons. As showed, primary alcohols such as 1-propanol and 1-butanol present high values for K_L, following by secondary (2-propanol, 2-butanol, isobutanol) alcohols. The tertiary alcohol studied (*tert*-butanol) showed the lowest K_L value (47.60) between all investigated alcohols. Finally, considering terpenes, *p*-cymene has the highest K_L value (314.04), and α-pinene the lowest one. The K_L values for α-pinene and β-pinene are 30.0 and 59.8, respectively, structurally differing only in the position of the double bond, showing a stronger interaction between this IL and β-pinene. Concerning the other terpenes, no clear pattern can be noticed.

Comparing the K_L values for the more volatile terpenes (**Figure 18**) with the less volatile (**Figure 19**), the values are higher for all terpenoids present in **Figure 19**, which indicates that the ionic liquid [C_4mim][PF_6] has more favorable interactions with the oxygenated terpenes. High K_L values were found in the phenolic terpenoids, having eugenol (2793.3) the highest K_L value, and thymol (1548.4) the lowest.

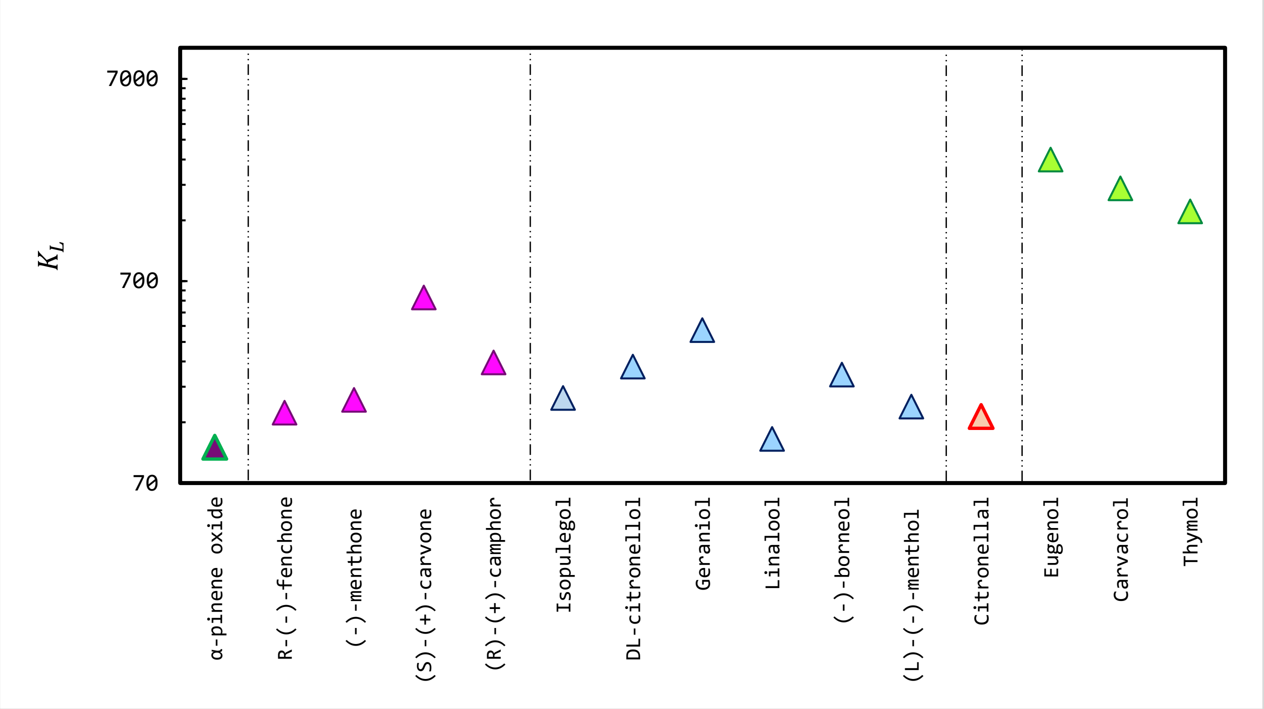


Figure 19: Gas-liquid partition coefficients (K_L) for the less volatile terpenoids at 413.2 K in [C_4mim][PF_6]. The dotted lines separate the different families for the organic compounds.

4.4. Selectivities and Capacities

To assess the IL potentialities as solvents (separation agent) for a given separation problem (homogeneous binary mixture), the fractionation factors need to be determined. The selectivities (S_{ij}^{∞}), capacities (k_j^{∞}) and respective solvent performance indexes (Q_{ij}^{∞}) for all mixtures under study were calculated from the γ_{13}^{∞} values. For a solvent to be considered suitable for fractionation, it should have high values for selectivities and capacities since low S_{ij}^{∞} result in poor separation efficiency, and low k_j^{∞} represent the poor solute-ionic liquid affinity, and consequently, large amounts of solvent might be required, to carry out the separation.[20,72] This work investigated the potentialities of imidazolium-based IL, in terms of S_{ij}^{∞}, k_j^{∞} and Q_{ij}^{∞} as separation agents for important separation problems, namely the desulfurization and denitrification of fuels, removal of aromatic from aliphatic hydrocarbons, and the separation of terpenic mixtures. Each type of problem is discussed in more detail below.

4.4.1. Fuel Processing

Table 3 represents the selectivities, capacities, and solvent performance indexes for four common separation problems (octane/benzene, cyclohexane/benzene, octane/thiophene, and octane/pyridine) obtained in this work (at 333.2 K). The experimental results are also critically compared with data available in the literature for other ionic liquids.[6,69,70,72] The capacities of all solutes are reported, in detail, in **Appendix C**, **Table C2**. Comparing the results for the equimolar IL mixture [C_4mim][PF_6]/[C_4mim][Cl] with the values for the two pure IL ([C_4mim][PF_6] and [C_4mim][Cl]), it is possible to notice that the selectivities attain a maximum for the mixture and the capacities assume intermediate values between both pure IL.

Table 3: Selectivities (S_{ij}^{∞}), capacities (k_{j}^{∞}), and solvent performance indexes (Q_{ij}^{∞}) at infinite dilution for different mixtures, relevant in fuel separation problems, in methylimidazolium-based ionic liquids, at 333.2 K.

Ionic Liquid	S_{ij}^{∞} / k_{j}^{∞} / Q_{ij}^{∞}				**Source**
	octane/ benzene	**cyclohexane/ benzene**	**octane / thiophene**	**octane/pyridine**	
[C$_4$mim][PF$_6$]	103.7/0.53/54.9	24.1/0.53/12.8	143.4/0.73/104.7	241.9/1.24/299.9	This work
	42.6/0.47/20.0	9.38/0.47/4.40	66.4/0.68/45.1	122.5/1.35/165.4	71
[C$_4$mim][PF$_6$] / [C$_4$mim][Cl] *(equimolar mixture)*	164.4/0.33/54.2	49.0/0.33/16.2	296.3/0.60/177.8	416.5/0.84/349.9	This work
[C$_4$mim][Cl]	100.4/0.24/24.1	15.7/0.24/3.8	243.5/0.58/141.2	348.0/0.82/285.3	69[a]
[C$_4$mim][SCN]	96.7/0.52/50.3	16.6/0.52/8.6	156.9/0.98/153.7	-	73[b]
[C$_4$mim][CF$_3$SO$_3$]	36.9/0.62/22.9	10.2/0.63/6.4	52.6/0.86/45.2	-	74[b]
[C$_4$mim][DCA]	63.3/0.50/31.7	12.4/0.50/6.20	81.4/0.72/58.6	112.6/0.99/111.5	84[b]
[C$_4$mim][BETI]	18.5/0.98/18.1	6.40/0.98/6.30	19.2/1.02/19.6	27.5/1.47/40.4	75[b]
[C$_4$mim][OAc]	33.3/0.39/13.0	7.9/0.39/3.10	69.5/0.81/56.3	67.9/0.79/53.6	6
[C$_4$mim][CH$_3$SO$_3$]	55.5/0.32/17.8	5.99/0.32/1.90	99.3/0.58/57.6	15.6/0.09/1.4	69[a]
[C$_4$mim][(CH$_3$)$_2$PO$_4$]	20.6/0.43/8.80	5.27/0.43/2.30	38.6/0.81/31.3	40.6/0.85/34.5	69[a]
[C$_4$mim][TOS]	14.8/0.51/7.50	8.32/0.51/4.20	57.6/0.90/51.8	-	85[b]
[C$_4$mim][TCM]	45.4/0.77/34.9	10.2/0.77/7.80	62.9/1.07/67.2	96.8/1.64/158.8	76[b]
[C$_4$mim][DBP]	6.83/1.07/7.30	3.05/1.07/3.30	-	-	86
[C$_8$mim]Cl	27.9/0.48/13.4	19.8/0.48/9.50	53.6/0.93/49.9	59.5/1.03/61.3	72
[C$_4$mim]Cl / [C$_{12}$mim]Cl *(equimolar mixture)*	13.06/0.50/6.5	10.3/0.50/5.2	23.9/0.92/22.0	23.2/0.89/20.6	
[C$_{12}$mim]Cl	4.91/0.82/4.0	3.27/0.82/2.7	7.28/1.24/9.00	5.77/0.97/5.6	

[a] Extrapolated using the data reported by the authors.
[b] Interpolated using the data reported by the authors.

Desulfurization and denitrification of fuels

Fuels are complex multicomponent mixtures of saturated, unsaturated, and aromatic hydrocarbons. The presence of sulfur- and aromatic nitrogen compounds contribute to environmental pollution and human respiratory diseases. These compounds are difficult to remove because of their high molecular weight and boiling point.

Additionally, they are known for inhibiting the hydrodesulfurization process, which is undesirable in petroleum refining processes,[72,87] and can be responsible for potential equipment corrosion.[72] Thus, the desulfurization and denitrification process are important to reduce the concentration of these compounds in fuels such as gasoline, jet fuel, kerosene, diesel, and heating oil so that the resulting fuels meet environmental protection standards.[88]

The use of IL is promising once they have the ability of extracting aromatic sulfur- and nitrogen-containing compounds at ambient conditions, while presenting low affinity with the aliphatic hydrocarbons present in the fuels.[6,89]

This research focuses on the potential evaluation of two methylimidazolium-based IL for the separation of octane/pyridine and octane/thiophene. As represented in **Table 3**, the results for these mixture pairs seems to be promising. For [C$_4$mim][PF$_6$], the best results were observed for the pair octane/pyridine, with high selectivity and reasonable capacity ($S^{\infty}_{octane/pyridine}$= 241.4 and $k^{\infty}_{pyridine}$ = 1.24). The equimolar IL mixture investigated, showed a higher solvent performance index ($Q^{\infty}_{octane/pyridine} = 349.9$) compared to [C$_4$mim][PF$_6$] ($Q^{\infty}_{octane/pyridine} = 299.9$). Considering this equimolar IL mixture, the best result was also for the separation of octane/pyridine, with high selectivity but relatively poor capacity ($S^{\infty}_{octane/pyridine}$= 416.5 and $k^{\infty}_{pyridine}$ = 0.84).

For the separation of the octane/thiophene mixture, both IL also showed high selectivities, however, poor capacities ($S^{\infty}_{octane/thiophene}$= 143.4 and $k^{\infty}_{thiophene}$ = 0.73 for [C$_4$mim][PF$_6$] and $S^{\infty}_{octane/thiophene}$= 296.3 and $k^{\infty}_{thiophene}$ =0.60 for the equimolar IL mixture). The high solvent performance indexes values for this separation problem, 104.7 for the [C$_4$mim][PF$_6$] and 177.8 for the equimolar IL mixture, result only from the high selectivities.

These results show that both IL investigated have the potential to carry out desulfurization and denitrification processes (removal of contaminants from fuels) as solvents, since high-performance indexes for the mixture pairs octane/pyridine and octane/thiophene were observed. Compared to the other IL in **Table 3**, the solvents studied in this work are among the ones having the best performance indexes.

Separation of aromatic hydrocarbons from C$_4$-C$_{10}$ aliphatic hydrocarbons

In order to perform the separation of aromatic hydrocarbons (benzene, toluene, ethylbenzene, and xylenes) from C$_4$-C$_{10}$ aliphatic hydrocarbons some conventional processes are used, *e.g.*, liquid-liquid extraction, extractive or azeotropic distillation using polar solvents, such as sulfolane, N-formyl morpholine (NFM), and N-methyl pyrrolidone (NMP).[72,90] The removal of these aromatics from aliphatics is one of the most challenging issues in refinery processes since these compounds have boiling points in a close range and several combinations form azeotropes.[90,91]

This work investigated two pairs of common aromatic/aliphatic separation processes in the petrochemical industry: octane/benzene, and cyclohexane/benzene. The equimolar IL mixture resulted in the best selectivities ($S^{\infty}_{octane/benzene}$= 164.4 and $S^{\infty}_{cyclohexane/benzene}$ = 49.0), and the k^{∞}_{j} values for [C$_4$mim][PF$_6$] are slightly higher ($k^{\infty}_{benzene}$=0.53) than for the equimolar IL mixture ($k^{\infty}_{benzene}$=0.33). Besides that, [C$_4$mim][PF$_6$] also presented good selectivities ($S^{\infty}_{octane/benzene}$= 103.8 and $S^{\infty}_{cyclohexane/benzene}$ = 24.1). Once again, the solvents studied in this work are among the ones having the best performance indexes when compared to the other methylimidazolium-based IL.

4.4.2. Fractionation of Terpenes Mixtures

In order to evaluate the studied IL potentials for the separation of terpenic mixtures, the experimental selectivities, capacities, and solvents performance indexes obtained at 403.2 K for some important terpene mixtures (which are abundant in some EO), such as α-pinene/β-pinene, β-pinene/*R-(+)*-limonene, p-cymene/*R-(+)*-limonene, *R-(+)*-limonene/linalool, (-)-menthone/L-(-)-menthol, (-)-borneol/(1R)-(+)-camphor, and *R-(+)*-limonene/*S-(+)*-carvone, are represented in **Table 4**. For some terpenes the activity coefficients were extrapolated or interpolated to 403.2 K using the experimental data obtained for other authors[6,70,72] at 433.2-458.2 K or 398.2-448.2 K.

In addition, to our best knowledge, some mixtures involving phenolic terpenoids (in these IL) were investigated, for the first time, in this work (carvacrol/p-cymene, thymol/p-cymene, eugenol/linalool, eugenol/eucalyptol, and carvacrol/γ-terpinene). The corresponding results for S^{∞}_{ij}, k^{∞}_{j}, and Q^{∞}_{ij} (at 413.2 K) are presented in **Table 5**. In some cases, the experimental γ^{∞}_{13} values were extrapolated to 413.2 K using the experimental data obtained at 353.2-403.2 K, and the literature data were interpolated using the values obtained by other authors[70] at 398.2-448.2 K.

For both IL systems investigated, low S^{∞}_{ij} and k^{∞}_{j} values were observed for the terpene pairs: α-pinene/β-pinene, β-pinene/*R-(+)*-limonene, p-cymene/*R-(+)*-limonene, (-)-menthone/L-(-)-menthol, and (-)-borneol/(1R)-(+)-camphor.

Particularly, the separation of α-pinene/β-pinene is industrially attractive since they are present in most EO from *Pinus* species.[92] Since α/β-pinene are isomers, and consequently have similar physical properties, their fractionating by distillation or solvent extraction is very difficult, which is reflected in the low S_{ij}^{∞} and k_j^{∞} values.

For the equimolar IL mixture [C_4mim][PF_6]/[C_4mim][Cl] the best selectivity found was in the *R-(+)*-limonene/linalool mixture ($S_{R(+)-limonene/linalool}^{\infty}$= 10.3) and the best capacity was observed for (1R)-(+)-camphor (k_{j}^{∞}= 0.36). For this equimolar IL mixture, the highest solvent performance index was found for the mixture pair *R-(+)*-limonene/linalool (Q_{ij}^{∞}=2.68). In spite of the acceptable selectivity, the poor capacity (k_{j}^{∞}= 0.26), and relatively low performance index suggest that this ionic liquid as not feasible for the fractionation of *Citrus* EO.

Table 4: Selectivities (S_{ij}^{∞}), capacities (k_j^{∞}), and performance indexes (Q_{ij}^{∞}) at infinite dilution for different terpenes mixtures in several ionic liquids at 403.2 K.

Ionic Liquid	S_{ij}^{∞} / k_j^{∞} / Q_{ij}^{∞}							**Source**
	α-pinene/ β-pinene	**β-pinene/ *R*-(+)-limonene**	**p-cymene/ *R*-(+)-limonene**	***R*-(+)-limonene / linalool**	**(-)-menthone/ L-(-)-menthol**	**(-)-borneol/(1R)-(+)-camphor**	***R*-(+)-limonene/ *S*-(+)carvone**	
[C_4mim][PF_6]	1.49/0.03/0.04	1.04/0.04/0.42	2.21/0.08/0.18	3.02/0.11/0.33	1.76/0.14/0.25	2.00/0.22/0.44	7.75/0.28/2.17	This work
[C_4mim][PF_6]/ [C_4mim][Cl]	1.69/0.03/0.05	1.02/0.03/0.03	1.93/0.05/0.10	10.3/0.26/2.68	2.83/0.21/0.59	3.02/0.36/1.09	6.63/0.17/1.13	This work
[C_4mim][Cl]	1.41/0.005/0.007	-	-	-	9.08/0.10/0.90	14.8/0.29/4.24	-	[70] [b]
[$P_{6,6,6,14}$][Cl]	1.27/1.10/1.40	1.25/1.10/1.38	1.04/0.88/0.92	10.2/9.01/91.9[a]	10.0/11.5/115.4[a]	9.07/14.2/128.8[a]	1.22/1.08/1.32[a]	[6]
[$P_{6,6,6,14}$][$(C_8H_{17})_2PO_2$]	1.07/1.58/1.69	1.15/1.58/1.82	1.03/1.38/1.42	5.93/8.2/48.6	-	-	1.52/1.38/2.10	[6]
[C_4mim][OAc]	1.33/0.06/0.08	1.35/0.06/0.08	1.62/0.07/0.11	30.3/1.26/38.2	-	-	5.38/0.22/1.18	[6]
[C_8mim][Cl]	1.37/0.08/0.11	1.07/0.09/0.10	1.34/0.12/0.16	15.4/1.34/20.6[a]	11.6/1.76/20.5[a]	19.9/3.21/63.8[a]	3.44/0.30/1.03[a]	72
[C_4mim]Cl/ [C_{12}mim]Cl	1.44/0.11/0.16	1.04/0.11/0.11	1.22/0.13/0.16	14.1/1.54/21.7[a]	11.8/1.97/23.2[a]	18.1/3.28/59.4[a]	3.07/0.34/1.04[a]	
[C_{12}mim]Cl	1.24/0.24/0.30	1.01/0.24/0.24	1.06/0.25/0.27	9.65/2.27/21.9[a]	8.48/2.39/20.3[a]	12.5/4.04/50.7[a]	1.81/0.43/0.78[a]	

[a] Extrapolated using the data reported by the authors.

[b] Interpolated using the data reported by the authors.

From the analyzed terpenic binary mixtures, concerning the ionic liquid [C_4mim][PF_6] the best results were observed for the *R-(+)*-limonene/*S-(+)*-carvone mixture (S_{ij}^{∞}=7.75, k_j^{∞}=0.28, Q_{ij}^{∞}=2.17). Considering the terpenic pairs mixture (-)-menthone/L-(-)-menthol and (-)-borneol/(1R)-(+)-camphor, both IL studied showed poor selectivities, capacities and solvent performance indexes, *i.e*., there are evidences that the IL investigated in this work, are not suitable for the deterpenation of peppermint EO (high concentrations of (-)-menthone/L-(-)-menthol) as well as for the fractionation of EO from flowers of the *Asteraceae* and *Lamiaceae* families (high concentrations of (-)-borneol/(1R)-(+)-camphor).[6,93,94]

When comparing the results between the two IL systems (**Table 4**), for the terpenic mixtures α-pinene/β-pinene, *R-(+)*-limonene/linalool, (-)-menthone/*L-(-)*-menthol and (-)-borneol/(1R)-(+)-camphor the equimolar IL mixture showed higher Q_{ij}^{∞} values but still presents poor separation factors (low S_{ij}^{∞} and k_j^{∞}values). For the pairs β-pinene/*R-(+)*-limonene, p-cymene/*R-(+)*-limonene and *R-(+)*-limonene/*S-(+)*-carvone, the pure [C_4mim][PF_6] presented higher Q_{ij}^{∞} values. By analysing the hydrocarbon terpene mixtures (α-pinene/β-pinene, β-pinene/*R-(+)*-limonene, and p-cymene/*R-(+)*-limonene), it is possible to observe only a slight increase in the selectivities and capacities; this happens because both IL showed weak affinity with hydrocarbon terpenes.

Concerning the pair *R-(+)*-limonene/linalool, the selectivity showed an increase of more than three times in the equimolar IL mixture [C_4mim][PF_6]/[C_4mim][Cl] compared to [C_4mim][PF_6]. This behaviour can be explained by the stronger interaction between the equimolar IL mixture and linalool (due the easer formation of hydrogen bonds) comparing with the [C_4mim][PF_6]-linalool interactions.

A similar behavior was observed for the (-)-menthone/L-(-)-menthol, and (-)-borneol/(1R)-(+)-camphor pairs. However, the change was not as significant as for the *R-(+)*-limonene/linalool mixture, once that, for hydrocarbon terpenes/alcohol terpenoids mixtures the polarity difference is higher than alcohol terpenoids/ketone terpenoids mixtures, for instance.

For a few systems ((α-pinene/β-pinene, (-)-menthone/L-(-)-menthol, and (-)-borneol/(1R)-(+)-camphor), information is also available for [C_4mim][Cl]. When comparing the results for the equimolar IL mixture studied and the respective values for the pure ionic liquids, better solvent performance indexes are obtained using [C_4mim][Cl] (except for the α-pinene/β-pinene). Finally, the experimental data for S_{ij}^{∞}, k_j^{∞} and Q_{ij}^{∞} values for the separation of phenolic terpenoids from hydrocarbon terpenes and/or alcohol terpenoids are presented in **Table 5**. The choice of the binary terpenic mixtures is based on the composition of some essential oils.

The essential oil of oregano is mainly composed of carvacrol and/or thymol (depending on the plant origin)[95,96], for example, plants collected from the northern part of Greece are commonly rich in thymol, whereas those from the southern part of the country are rich in carvacrol. Followed by γ-terpinene, p-cymene, linalool, terpinen-4-ol, and sabinene hydrate.[97,98]

Several studies have shown that carvacrol and thymol are the main compounds responsible for the antioxidant effects provided by oregano essential oil.[98–100] Taking this into account, is important to perform the separation of carvacrol and/or thymol from hydrocarbon terpenes to increase the oregano essential oil value in the industrial market.

Regarding the phenolic terpenoid eugenol, it is commonly found in the EO of *Cinnamomum zeylanicum* Blume (cinnamon) and *Eugenia caryophyllata* (clove) species. Cinnamon is widely cultivated in Sri Lanka and in some parts of India while clove is native from Moluccas Islands, Indonesia but is currently cultivated in other regions of the world, such as the islands of Madagascar and Grenada. Cinnamon barks and leaves are widely used as spice and flavouring agent in foods and for several medicine applications.

The EO of cinnamon are rich in eugenol[101–103] following for caryophyllene, benzyl benzoate, and linalool.[103] Knowing that, the separation problems present in **Table 5** which include eugenol are clearly important to several industries.

Table 5: Selectivities (S_{ij}^{∞}), capacities (k_{j}^{∞}), and performance indexes (Q_{ij}^{∞}) at infinite dilution in the ionic liquids [C_4mim][PF_6] and [C_4mim][CF_3SO_3] for some pairwise separation problems including phenolic terpenoids (at 413.2 K).

Mixture	Ionic liquid	S_{ij}^{∞}	k_{j}^{∞}	Q_{ij}^{∞}	Source
carvacrol/*p*-cymene	[C_4mim][PF_6]	6.90[a]	0.55	3.80[a]	This work
thymol/*p*-cymene		6.74[a]	0.54	3.64[a]	
thymol/linalool	[C_4mim][PF_6]	4.75	0.54	2.57	This work
	[C_4mim][CF_3SO_3]	113.1[b]	1.57[b]	177.6[b]	[70]
eugenol/linalool	[C_4mim][PF_6]	2.73	0.31	0.85	This work
	[C_4mim][CF_3SO_3]	55.4[b]	0.77[b]	42.6[b]	[70]
eugenol/eucalyptol	[C_4mim][PF_6]	4.73[a]	0.31	1.47[a]	This work
	[C_4mim][CF_3SO_3]	9.47[b]	0.77[b]	7.28[b]	[70]
carvacrol/γ-terpinene	[C_4mim][PF_6]	13.0[a]	0.55	7.16[a]	This work

[a] Extrapolated values.
[b] Interpolated using the data reported by the authors.

It is worth noting (**Table 5**), that using [C_4mim][PF_6], the highest performance index was obtained for the carvacrol/γ-terpinene mixture (S_{ij}^{∞} =13.0, $k_{carvacrol}^{\infty}$=0.55, and Q_{ij}^{∞} =7.16) and the worst for the eugenol/linalool pair (S_{ij}^{∞} =2.73, $k_{eugenol}^{\infty}$=0.31, and Q_{ij}^{∞} =0.85). Considering the results studied by Martins et al.[70], the ionic liquid [C_4mim][CF_3SO_3] has the potential to perform these type of separation problems, once that all the Q_{ij}^{∞} values are higher than those reported in this work, being the best results for thymol/linalool (S_{ij}^{∞} =113.1, k_{thymol}^{∞}=1.57, and Q_{ij}^{∞} =177.6) being also promising for the separation of the eugenol/linalool pair (S_{ij}^{∞} =55.4, $k_{eugenol}^{\infty}$=0.77, and Q_{ij}^{∞} =42.6).

This is the first time that it was possible to obtain experimental data considering these IL for the phenolic terpenoids (carvacrol, thymol, and eugenol). Due to the high boiling point of these compounds, in our previous works[6,20,72,104] was not possible to perform the analysis.

For all mixture pairs studied, poor capacities were found, being the lowest for eugenol and the highest for carvacrol. Besides the reasonable selectivities and solvent performance indexes, the very low capacities indicate that this ionic liquid is not a suitable entrainer for these separation problems.

Comparing the experimental results with the available literature data (**Table 5**), it is possible to see that, in order to have good separation factors for terpenic mixtures – involving phenolic terpenoids, an ionic liquid with low polarity seems to be a promisor option. Additionally, its evidently that the anion has a great influence on the ionic liquid-solute interactions.

Chapter 5. Conclusions and Future Work

The activity coefficients at infinite dilution of 52 organic solutes (including terpenes/terpenoids) and water were measured by IGC at different temperature ranges. The majority of the studied solutes showed higher γ_{13}^{∞} values in the equimolar IL mixture [C_4mim][PF_6]/[C_4mim][Cl] than in pure [C_4mim][PF_6]. An opposite behavior was reported for solutes classified as hydrogen donors and acceptors, such as alcohols and water, which showed high interaction with the equimolar IL mixture [C_4mim][PF_6]/[C_4mim][Cl]. On the other hand, poor interaction was reported between both IL studied and the less polar solutes (alkanes and cycloalkanes).

The results of this research suggest that, the pure ionic liquid [C_4mim][PF_6] is a suitable solvent for the desulfurization and denitrification of fuels. Regarding hydrocarbon terpenes, pure [C_4mim][PF_6] has more affinity than the equimolar IL mixture [C_4mim][PF_6]/[C_4mim][Cl]. Similar behavior was observed for ether and ketone terpenoids. On the contrary, for alcohol terpenoids, the equimolar IL mixture [C_4mim][PF_6]/[C_4mim][Cl] showed higher interactions.

Concerning the excess partial molar properties, for [C_4mim][PF_6] systems, in the less polar solutes such as alkanes and cycloalkanes, positive deviations to Raoult's law were found, and the $\overline{H}_m^{E,\infty}$ was always positive, indicating that solute-IL interactions increase with temperature. For aromatic hydrocarbons and acetates, the $\overline{H}_m^{E,\infty}$ values are nearly zero, *i.e*, the entropic factor predominates. Additionally, the $\bar{G}_m^{E,\infty}$ is positive while the $T_{ref}\bar{S}_m^{E,\infty}$ is negative, this indicates poor solvation of these compounds with the IL investigated. For the protic solutes (alcohol and water), no clear trend is found.

By looking at the results for the equimolar IL mixture [C_4mim][PF_6]/[C_4mim][Cl] a different trend was observed. For almost all solutes studied the $\bar{H}_m^{E,\infty}$ and $\bar{G}_m^{E,\infty}$ are negative, except for the *tert*-butanol that showed $\bar{G}_m^{E,\infty}$ close to zero. For the less polar solutes, the enthalpic effect seems to dominate over the entropic; for the polar solutes, such as alcohols, water, and terpenoids, it is more difficult to identify a trend.

With regard to separation factors, the IL studied showed, in general, poor selectivities and capacities for terpenes/terpenoids mixtures being the best result for the carvacrol/γ-terpinene mixture (Q_{ij}^{∞} =7.16). However, very promising results for the removal of nitrogen- and sulphur-compounds from fuels using the ionic liquid [C_4mim][PF_6] ($Q_{\mathrm{octane/pyridine}}^{\infty}$=299.9 and $Q_{\mathrm{octane/thiophene}}^{\infty}$=104.7) or the equimolar IL mixture of IL. The latter showed higher Q_{ij}^{∞} values ($Q_{\mathrm{octane/pyridine}}^{\infty}$=349.9 and $Q_{\mathrm{octane/thiophene}}^{\infty}$=177.8), with lower k_{j}^{∞} values.

The IL studied in this work showed the best solvent performance indexes compared to other IL previously investigated by different authors for common separation processes in fuel industries (octane/benzene, cyclohexane/benzene, octane/thiophene, and octane/pyridine), providing important insights on the use of alternative solvents for the removal of aromatics from aliphatic hydrocarbons and the removal of contaminants from fuels.

As the solutes in this screening studies were infinitely diluted in the ionic liquid, future work should include the study of the phase equilibria at other solute and solvent concentration (closer to practical industrial conditions) to have more insights about the real efficiency of an ionic liquid for a given separation problem.

For future work, it would be interesting to perform more studies using IL with different cations and keeping some of the studied anions (PF_6^- or Cl^-). Besides that, the study of mixtures of ionic liquids with low polarity seems to be promising to carry out the separation of polar terpenoids (as alcohol e/or phenolic terpenoids) from hydrocarbon terpenes, for instance. Furthermore, studies to improve the aqueous solubility of terpenes (*e.g.*, by adding hydrotropes) would perhaps be interesting, since most terpenes have poor aqueous solubility.

Bibliographic References

1. Ali B, Al-Wabel NA, Shams S, Ahamad A, Khan SA, Anwar F. Essential oils used in aromatherapy: A systemic review. *Asian Pac J Trop Biomed*. 2015;5(8):601-611. doi:10.1016/j.apjtb.2015.05.007
2. Paduch R, Kandefer-Szerszeń M, Trytek M, Fiedurek J. Terpenes: Substances useful in human healthcare. *Arch Immunol Ther Exp (Warsz)*. 2007;55(5):315-327. doi:10.1007/s00005-007-0039-1
3. Tetali SD. Terpenes and isoprenoids: a wealth of compounds for global use. *Planta*. 2019;249(1):1-8. doi:10.1007/s00425-018-3056-x
4. Sathasivam R, Ki JS. A review of the biological activities of microalgal carotenoids and their potential use in healthcare and cosmetic industries. *Mar Drugs*. 2018;16(1). doi:10.3390/md16010026
5. Wang G, Tang W, Bidigare RR. Terpenoids As Pharmaceutical Drugs and Pharmaceutical Agents. *Nat Prod Drug Discov Ther Med*. 2005;(2):197-227. doi:10.1007/978-1-59259-976-9_9
6. Vilas-Boas SM, Teixeira G, Rosini S, et al. Ionic liquids as entrainers for terpenes fractionation and other relevant separation problems. *J Mol Liq*. 2021;323. doi:10.1016/j.molliq.2020.114647
7. Su C, Ran X, Hu J, Shao C. Photocatalytic process of simultaneous desulfurization and denitrification of flue gas by TiO2-polyacrylonitrile nanofibers. *Environ Sci Technol*. 2013;47(20):11562-11568. doi:10.1021/es4025595
8. Domańska U, Wlazło M. Effect of the cation and anion of the ionic liquid on desulfurization of model fuels. *Fuel*. 2014;134:114-125. doi:10.1016/j.fuel.2014.05.048
9. Francisco M, Arce A, Soto A. Ionic liquids on desulfurization of fuel oils. *Fluid Phase Equilib*. 2010;294(1-2):39-48. doi:10.1016/j.fluid.2009.12.020
10. Meindersma GW, Hansmeier AR, De Haan AB. Ionic liquids for aromatics extraction. Present status and future outlook. *Ind Eng Chem Res*. 2010;49(16):7530-7540. doi:10.1021/ie100703p
11. Meindersma GW, Simons BTJ, De Haan AB. Physical properties of 3-methyl-N-butylpyridinium tetracyanoborate and 1-butyl-1-methylpyrrolidinium tetracyanoborate and ternary LLE data of [3-mebupy]B(CN)4 with an aromatic and an aliphatic hydrocarbon at T = 303.2 K and 328.2 K and p = 0.1 MPa. *J Chem Thermodyn*. 2011;43(11):1628-1640. doi:10.1016/j.jct.2011.05.022
12. Kêdra-Królik K, Fabrice M, Jaubert JN. Extraction of thiophene or pyridine from n-heptane using ionic liquids. gasoline and diesel desulfurization. *Ind Eng Chem Res*. 2011;50(4):2296-2306. doi:10.1021/ie101834m
13. Cheng G, Zhang C. Desulfurization and denitrification technologies of coal-fired flue gas. *Polish J Environ Stud*. 2018;27(2):481-489. doi:10.15244/pjoes/75959
14. Bassolé IHN, Juliani HR. Essential oils in combination and their antimicrobial properties. *Molecules*. 2012;17(4):3989-4006. doi:10.3390/molecules17043989
15. Burt S. Essential oils: Their antibacterial properties and potential applications in foods - A review. *Int J Food Microbiol*. 2004;94(3):223-253. doi:10.1016/j.ijfoodmicro.2004.03.022
16. Guenther E. *The Essential Oils: History, Origin in Plants, Production*. Vol 1. 3rd ed.; 1948.
17. Preedy VR. *Essential Oils in Food Preservation, Flavor and Safety*. (Preedy VR, ed.).; 2015. doi:10.1016/C2012-0-06581-7
18. Poole CF, Lenca N. Gas chromatography on wall-coated open-tubular columns with ionic liquid stationary phases. *J Chromatogr A*. 2014;1357:87-109. doi:10.1016/j.chroma.2014.03.029
19. Aldred EM. *Pharmacology: A Handbook for Complementary Healthcare Professionals*. (Buck, Charles, Vall K, ed.). Churchill Livingstone Elsevier; 2009.
20. Martins MAR. Studies for the development of new separation processes with terpenes and their environmental distribution. Published online 2017. http://opac.ua.pt/cgi-bin/koha/opac-detail.pl?biblionumber=287331
21. Avalos J, Limón MC. Fungal Secondary Metabolism. *Encyclopedia*. 2021;2(1):1-13. doi:10.3390/encyclopedia2010001
22. Caputi L, Aprea E. Use of Terpenoids as Natural Flavouring Compounds in Food Industry. *Recent Patents Food, Nutr Agric*. 2012;3(1):9-16. doi:10.2174/2212798411103010009
23. Ozturk B. Green Processes for Deterpenation of Essential Oils and Extraction of Bioactive Compounds from Orange Peel Waste. *Univ Manchester*. Published online 2019. http://www.manchester.ac.uk/escholar/uk-ac-man-

scw:323151

24. Zwenger S, Basu C. Plant terpenoids: applications and future potentials. *Sch Biol Sci Fac Publ*. 2008;3:1-7. https://digscholarship.unco.edu/biofacpub/4

25. Khayyat SA, Roselin LS. Recent progress in photochemical reaction on main components of some essential oils. *J Saudi Chem Soc*. 2018;22(7):855-875. doi:10.1016/j.jscs.2018.01.008

26. Silva CB, Guterres SS, Weisheimer V, Schapoval EES. Antifungal activity of the lemongrass oil and citral against Candida spp. *Brazilian J Infect Dis*. 2008;12(1):63-66. doi:10.1590/s1413-86702008000100014

27. Cox-Georgian D, Ramadoss N, Dona C, Basu C. Therapeutic and medicinal uses of terpenes. In: Joshee N, Dhekney SA, Parajuli P, eds. *Medicinal Plants: From Farm to Pharmacy*. Springer; 2019:333-359. doi:10.1007/978-3-030-31269-5_15

28. Lanny I, Franklin U, Cunnington GD, Young DE. Terpene based Pesticide Treatments for Killing Terrestrial Arthropods including, among others, lice, lice eggs, mites and ants. 2000;(19):3.

29. Chen W, Viljoen AM. Geraniol - A review of a commercially important fragrance material. *South African J Bot*. 2010;76(4):643-651. doi:10.1016/j.sajb.2010.05.008

30. Yang W, Chen X, Li Y, Guo S, Wang Z, Yu X. Advances in Pharmacological Activities of Terpenoids. *Nat Prod Commun*. 2020;15(3). doi:10.1177/1934578X20903555

31. Wang S, Meng X, Dong Y. Ursolic acid nanoparticles inhibit cervical cancer growth in vitro and in vivo via apoptosis induction. *Int J Oncol*. 2017;50(4):1330-1340. doi:10.3892/ijo.2017.3890

32. De Assis Oliveira F, Andrade LN, De Sousa ÉBV, De Sousa DP. Anti-ulcer activity of essential oil constituents. *Molecules*. 2014;19(5):5717-5747. doi:10.3390/molecules19055717

33. Kamatou GPP, Vermaak I, Viljoen AM, Lawrence BM. Menthol: A simple monoterpene with remarkable biological properties. *Phytochemistry*. 2013;96:15-25. doi:10.1016/j.phytochem.2013.08.005

34. Crowell PL. Monoterpenes in breast cancer chemoprevention. Breast cancer research and treatment. Published online 1997:191-197. doi:https://doi.org/10.1023/A:1005939806591

35. Alasbahi RH, Melzig MF. Forskolin and derivatives as tools for studying the role of cAMP. *Pharmazie*. 2012;67(1):5-13. doi:10.1691/ph.2012.1642

36. Jaeger R, Cuny E. Terpenoids with special pharmacological significance: A review. *Nat Prod Commun*. 2016;11(9):1373-1390. doi:10.1177/1934578x1601100946

37. Chen J, Gao P, Yu F, Yang Y, Zhu S, Zhai H. Total synthesis of (±)-merrilactone A. *Angew Chemie - Int Ed*. 2012;51(24):5897-5899. doi:10.1002/anie.201200378

38. Ramadan M, Goeters S, Watzer B, et al. Chamazulene carboxylic acid and matricin: A natural profen and its natural prodrug, identified through similarity to synthetic drug substances. *J Nat Prod*. 2006;69(7):1041-1045. doi:10.1021/np0601556

39. Tsuneki H, Ma EL, Kobayashi S, et al. Antiangiogenic activity of β-eudesmol in vitro and in vivo. *Eur J Pharmacol*. 2005;512(2-3):105-115. doi:10.1016/j.ejphar.2005.02.035

40. Koshima CC, Capellini MC, Geremias IM, Aracava KK, Gonçalves CB, Rodrigues CEC. Fractionation of lemon essential oil by solvent extraction: Phase equilibrium for model systems at T = 298.2 K. *J Chem Thermodyn*. 2012;54:316-321. doi:10.1016/j.jct.2012.05.011

41. Ganem F, Mattedi S, Rodríguez O, Rodil E, Soto A. Deterpenation of citrus essential oil with 1-ethyl-3-methylimidazolium acetate: A comparison of unit operations. *Sep Purif Technol*. 2020;250:117208. doi:10.1016/j.seppur.2020.117208

42. Diaz S, Espinosa S, Brignole EA. Citrus peel oil deterpenation with supercritical fluids: Optimal process and solvent cycle design. *J Supercrit Fluids*. 2005;35(1):49-61. doi:10.1016/j.supflu.2004.12.002

43. Akamoto KS, Ujii KF, Noue AI, Ozuka HK, Hta HO. Differential Recovery of Terpene Hydrocarbons and Oxygenated Compounds from Condensates Containing Essential Oil Discharged during Concentration of Citrus Juices Using a Ceramic Membrane. *Food Sci Technol Res*. 2003;9(1):11-16. doi:https://doi.org/10.3136/fstr.9.11

44. Sevgili LM, Şahin S, Kirbaşlar SI. Liquid-liquid equilibria of (limonene + linalool + ethylene glycol or diethylene glycol or triethylene glycol or 1,2-propylene glycol) ternary systems. *J Chem Eng Data*. 2008;53(3):737-741. doi:10.1021/je700577t

45. Oliveira CM, Koshima CC, Capellini MC, et al. Liquid-liquid equilibrium data for the system

limonene+carvone+ethanol+water at 298.2K. *Fluid Phase Equilib*. 2013;360:233-238. doi:10.1016/j.fluid.2013.09.057

46. Garcia-Chavez LY, Schuur B, De Haan AB. Liquid-liquid equilibrium data for mono ethylene glycol extraction from water with the new ionic liquid tetraoctyl ammonium 2-methyl-1-naphtoate as solvent. *J Chem Thermodyn*. 2012;51:165-171. doi:10.1016/j.jct.2012.03.009
47. Gonçalves D, Teschke MEE, Koshima CC, Gonçalves CB, Oliveira AL, Rodrigues CEC. Fractionation of orange essential oil using liquid-liquid extraction: Equilibrium data for model and real systems at 298.2 K. *Fluid Phase Equilib*. 2015;399:87-97. doi:10.1016/j.fluid.2015.04.022
48. Armstrong DW. Gas Chromatography Columns Using Ionic Liquids as Stationary Phase. In: Shiflett MB, ed. *Green Chemistry and Sustainable Technology*. Springer; 2020:131-165. doi:10.1201/9780367808310
49. Ben Salha G, Abderrabba M, Labidi J. A status review of terpenes and their separation methods. *Rev Chem Eng*. 2021;37(3):433-447. doi:10.1515/revce-2018-0066
50. Beneti SC, Rosset E, Corazza ML, Frizzo CD, Di M, Oliveira JV. Fractionation of citronella (Cymbopogon winterianus) essential oil and concentrated orange oil phase by batch vacuum distillation. *J Food Eng*. 2011;102(4):348-354. doi:10.1016/j.jfoodeng.2010.09.011
51. Silvestre WP, Agostini F, Muniz LAR, Pauletti GF. Fractionating of green mandarin (Citrus deliciosa Tenore) essential oil by vacuum fractional distillation. *J Food Eng*. 2016;178:90-94. doi:10.1016/j.jfoodeng.2016.01.011
52. Huie CW. A review of modern sample-preparation techniques for the extraction and analysis of medicinal plants. *Anal Bioanal Chem*. Published online 2002:23-30. doi:10.1007/s00216-002-1265-3
53. Sharif KM, Rahman MM, Azmir J, et al. Experimental design of supercritical fluid extraction - A review. *J Food Eng*. 2014;124:105-116. doi:10.1016/j.jfoodeng.2013.10.003
54. Dai W, Keokurngsamay S, Chen Y, et al. Influence of Modifier in Supercritical CO2 on Qualitative and Quantitative Extraction Results of Eucalyptus Ecential Oil. *Am J Plant Sci*. 2018;9:163-171. doi:10.4236/ajps.2018.92014
55. da Silva RPFF, Rocha-Santos TAP, Duarte AC. Supercritical fluid extraction of bioactive compounds. *TrAC - Trends Anal Chem*. 2016;76:40-51. doi:10.1016/j.trac.2015.11.013
56. Dupuy A, Athes V, Schenk J, Jenelten U, Souchon I. Experimental and theoretical considerations on breakthrough pressure in membrane-based solvent extraction: Focus on citrus essential oil/hydro-alcoholic solvent systems with low interfacial tension. *J Memb Sci*. 2011;378(1-2):203-213. doi:10.1016/j.memsci.2011.05.005
57. Armstrong DW, He L, Liu YS. Examination of ionic liquids and their interaction with molecules, when used as stationary phases in gas chromatography. *Anal Chem*. 1999;71(17):3873-3876. doi:10.1021/ac990443p
58. Younas M, Druon Bocquet S, Sanchez J. Extraction of aroma compounds in a HFMC: Dynamic modelling and simulation. *J Memb Sci*. 2008;323(2):386-394. doi:10.1016/j.memsci.2008.06.045
59. Smith EL, Abbott AP, Ryder KS. Deep Eutectic Solvents (DESs) and Their Applications. *Chem Rev*. 2014;114(21):11060-11082. doi:10.1021/cr300162p
60. Hansen BB, Spittle S, Chen B, et al. Deep Eutectic Solvents: A Review of Fundamentals and Applications. *Chem Rev*. 2021;121(3):1232-1285. doi:10.1021/acs.chemrev.0c00385
61. Martins MAR, Pinho SP, Coutinho JAP. Insights into the Nature of Eutectic and Deep Eutectic Mixtures. *J Solution Chem*. 2019;48(7):962-982. doi:10.1007/s10953-018-0793-1
62. Abbott AP, Boothby D, Capper G, Davies DL, Rasheed RK. Deep Eutectic Solvents formed between choline chloride and carboxylic acids: Versatile alternatives to ionic liquids. *J Am Chem Soc*. 2004;126(29):9142-9147. doi:10.1021/ja048266j
63. Abranches DO, Martins MAR, Silva LP, Schaeffer N, Pinho SP, Coutinho JAP. Phenolic hydrogen bond donors in the formation of non-ionic deep eutectic solvents: The quest for type V DES. *Chem Commun*. 2019;55(69):10253-10256. doi:10.1039/c9cc04846d
64. Martins MAR, Crespo EA, Pontes PVA, et al. Tunable Hydrophobic Eutectic Solvents Based on Terpenes and Monocarboxylic Acids. *ACS Sustain Chem Eng*. 2018;6(7):8836-8846. doi:10.1021/acssuschemeng.8b01203
65. Poole CF, Atapattu SN. Determination of physicochemical properties of ionic liquids by gas chromatography. *J Chromatogr A*. 2021;1644:461964. doi:10.1016/j.chroma.2021.461964

66. Poole CF. Chromatographic and spectroscopic methods for the determination of solvent properties of room temperature ionic liquids. *J Chromatogr A*. 2004;1037(1-2):49-82. doi:10.1016/j.chroma.2003.10.127

67. Plechkova N V., Seddon KR. Applications of ionic liquids in the chemical industry. *Chem Soc Rev*. 2008;37(1):123-150. doi:10.1039/b006677j

68. Niedermeyer H, Hallett JP, Villar-Garcia IJ, Hunt PA, Welton T. Mixtures of ionic liquids. *Chem Soc Rev*. 2012;41(23):7780-7802. doi:10.1039/c2cs35177c

69. Martins MAR, Coutinho JAP, Pinho SP, Domańska U. Measurements of activity coefficients at infinite dilution of organic solutes and water on polar imidazolium-based ionic liquids. *J Chem Thermodyn*. 2015;91:194-203. doi:10.1016/j.jct.2015.07.042

70. Martins MAR, Domańska U, Schröder B, Coutinho JAP, Pinho SP. Selection of Ionic Liquids to be Used as Separation Agents for Terpenes and Terpenoids. *ACS Sustain Chem Eng*. 2016;4(2):548-556. doi:10.1021/acssuschemeng.5b01357

71. Mutelet F, Butet V, Jaubert JN. Application of inverse gas chromatography and regular solution theory for characterization of ionic liquids. *Ind Eng Chem Res*. 2005;44(11):4120-4127. doi:10.1021/ie048806L

72. Vilas-Boas SM, Tentor FR, Teixeira G, Mónia AR. Effect of alkyl chain length in imidazolium chloride ionic liquids on the separation factors of organic and aqueous mixtures. *Submitt Work*. Published online 2022.

73. Domańska U, Królikowska M. Measurements of activity coefficients at infinite dilution in solvent mixtures with thiocyanate-based ionic liquids using glc technique. *J Phys Chem B*. 2010;114(25):8460-8466. doi:10.1021/jp103496d

74. Domanska U, Andrzej M. Activity Coefficients at Infinite Dilution Measurements for Organic Solutes and Water in the Ionic Liquid 1-Butyl-3-methylimidazolium Trifluoromethanesulfonate. *J Phys Chem B*. 2008;112:11100-11105. doi:10.1021/jp804107y

75. Moïse JC, Mutelet F, Jaubert JN, Grubbs LM, Acree WE, Baker GA. Activity coefficients at infinite dilution of organic compounds in four new imidazolium-based ionic liquids. *J Chem Eng Data*. 2011;56(7):3106-3114. doi:10.1021/je200195q

76. Lukoshko E, Mutelet F, Domanska U. Experimental and theoretically study of interaction between organic compounds and tricyanomethanide based ionic liquids. *J Chem Thermodyn*. 2015;85:49-56. doi:10.1016/j.jct.2014.12.027

77. Chandra Srivastava V. An evaluation of desulfurization technologies for sulfur removal from liquid fuels. *RSC Adv*. 2012;2(3):759-783. doi:10.1039/c1ra00309g

78. Mladenović M, Paprika M, Marinković A. Denitrification techniques for biomass combustion. *Renew Sustain Energy Rev*. 2018;82(November 2017):3350-3364. doi:10.1016/j.rser.2017.10.054

79. Everett DH. Effect of Gas Imperfection on G.L.C. Measurements: A Refined Method for Determining Activity Coefficients and Second Virial Coefficients. *Trans Faraday Soc*. 1965;61(4):1637-1645. doi:10.1039/TF9656101637

80. Cruickshank AJB, Gainey BW, Hicks C. P., Letcher TM, Moody RW, Young CL. Gas-Liquid Chromatographic Determination of Cross-Term. *Trans Faraday Soc*. Published online 1967:1014-1031. doi:10.1039/tf9696501014

81. Fragoso JP. *Properties of Gases and Liquids*. Fifth. (Poling B, Prausnitz J, O'Connell J, eds.). McGraw-Hill; 2001. doi:10.1036/0070116822

82. Castells RC. Determination of gas-liquid partition coefficients by gas chromatography. *J Chromatogr A*. 2004;1037(1-2):223-231. doi:10.1016/j.chroma.2003.12.019

83. Boussaha M, Khimeche K, Dahmani A. Activity coefficients at infinite dilution for hydrocarbons in fatty alcohols determined by gas-liquid chromatography. *J Chem Eng Data*. 2013;58(5):1420-1424. doi:10.1021/je400129d

84. Domańska U, Wlazło M, Karpińska M. 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. *Fluid Phase Equilib*. 2016;417:50-61. doi:10.1016/j.fluid.2016.02.004

85. Domańska U, Królikowski M. Determination of activity coefficients at infinite dilution of 35 solutes in the ionic liquid, 1-butyl-3-methylimidazolium tosylate, using gas-liquid chromatography. *J Chem Eng Data*. 2010;55(11):4817-4822. doi:10.1021/je100410k

86. Ge ML, Song XJ, Li GM, Li YH, Liu FZ, Ma HL. Activity coefficients at infinite dilution of alkanes, alkenes, and alkyl benzenes in 1-butyl-3-methylimidazolium dibutylphosphate using gas-liquid chromatography. *J Chem Eng Data*. 2012;57(8):2109-2113. doi:10.1021/je201310d

87. Turaga UT, Ma X, Song C. Influence of nitrogen compounds on deep hydrodesulfurization of 4,6-dimethyldibenzothiophene over Al2O3- and MCM-41-supported Co-Mo sulfide catalysts. *Catal Today*. 2003;86(1-4):265-275. doi:10.1016/S0920-5861(03)00464-4

88. El-Gendy NS, Speight JG. Desulfurization. *Encycl Chem Process*. Published online 2015:18-47. doi:10.1081/E-ECHP-120007732

89. Domańska U, Wlazło M, Karpińska M. [DCA]-based ionic liquids for the extraction of sulfur and nitrogen compounds from fuels: Activity coefficients at infinite dilution. *Fluid Phase Equilib*. 2020;507. doi:10.1016/j.fluid.2019.112424

90. Meindersma GW, Podt A, Klaren MB, de Haan AB. Separation of aromatic and aliphatic hydrocarbons with ionic liquids. *Chem Eng Commun*. 2006;193(11):1384-1396. doi:10.1080/00986440500511403

91. Addouni M, Benyounes H, Jin S, Haddou B, Shen W. Extraction process design for the separation of aromatic and aliphatic hydrocarbons using organic solvent, ionic liquid or their mixture: a comparative study. *Brazilian J Chem Eng*. 2020;37(1):307-322. doi:10.1007/s43153-019-00006-9

92. Kurose K, Okamura D, Yatagai M. Composition of the leaf, flower and fruit volatile oils of Pittosporum tobira (Thunb.) WT Aiton grown in three locations in Portugal. *Flavour Fragr J*. 2007;22:10-20. doi:10.1002/ffj.1609

93. Avato P, Raffo F, Aldouri NA, Vartanian ST. Essential oils of Varthemia iphionoides from Jordan. *Flavour Fragr J*. 2004;19(6):559-561. doi:10.1002/ffj.1351

94. Moghaddam M, Pourbaige M, Tabar HK, Farhadi N, Hosseini SMA. Composition and Antifungal Activity of Peppermint (Mentha piperita) Essential Oil from Iran. *J Essent Oil-Bearing Plants*. 2013;16(4):506-512. doi:10.1080/0972060X.2013.813265

95. Napoli EM, Curcuruto G, Ruberto G. Screening the essential oil composition of wild Sicilian oregano. *Biochem Syst Ecol*. 2009;37(4):484-493. doi:10.1016/j.bse.2009.07.008

96. Milos M, Radonic A, Bezic N, Dunkic V. Localities and seasonal variations in the chemical composition of essential oils of Satureja montana L. and S. cuneifolia Ten. *Flavour Fragr J*. 2001;16(3):157-160. doi:10.1002/ffj.965

97. Kokkini S, Karousou R, Dardioti A, Krigas N, Lanaras T. Autumn essential oils of Greek oregano. *Phytochemistry*. 1997;44(5):883-886. doi:10.1016/S0031-9422(96)00576-6

98. Azizi A, Yan F, Honermeier B. Herbage yield, essential oil content and composition of three oregano (Origanum vulgare L.) populations as affected by soil moisture regimes and nitrogen supply. *Ind Crops Prod*. 2009;29(2-3):554-561. doi:10.1016/j.indcrop.2008.11.001

99. Yanishlieva N V., Marinova EM, Gordon MH, Raneva VG. Antioxidant activity and mechanism of action of thymol and carvacrol in two lipid systems. *Food Chem*. 1999;64(1):59-66. doi:10.1016/S0308-8146(98)00086-7

100. Kordali S, Cakir A, Ozer H, Cakmakci R, Kesdek M, Mete E. Antifungal, phytotoxic and insecticidal properties of essential oil isolated from Turkish Origanum acutidens and its three components, carvacrol, thymol and p-cymene. *Bioresour Technol*. 2008;99(18):8788-8795. doi:10.1016/j.biortech.2008.04.048

101. De Medici D, Pieretti S, Salvatore G, Nicoletti M, Rasoanaivo P. Chemical analysis of essential oils of malagasy medicinal plants by gas chromatography and NMR spectroscopy. *Flavour Fragr J*. 1992;7(5):275-281. doi:10.1002/ffj.2730070509

102. Mallavarapu GR, Ramesh S, Chandrasekhara RS, Rajeswara Rao BR, Kaul PN, Bhattacharya AK. Investigation of the essential oil of cinnamon leaf grown at Bangalore and Hyderabad. *Flavour Fragr J*. 1995;10(4):239-242. doi:10.1002/ffj.2730100403

103. Senanayake UM, Lee TH, Wills RBH. Volatile Constituents of Cinnamon (Cinnamomum zeylanicum) Oils. *J Agric Food Chem*. 1978;26(4):822-824. doi:10.1021/jf60218a031

104. Santos GT, Amorim MO, Ferreira S, Pedro De Almeida S, Priscilla P, Leite Bragança G. Ionic liquids in the fractionation of terpenes and other relevant separation problems. Published online 2020. https://bibliotecadigital.ipb.pt/bitstream/10198/22987/1/Santos_Gabriel.pdf

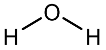
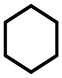
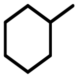
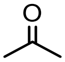
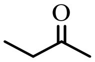
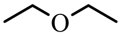
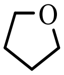
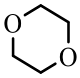
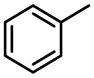
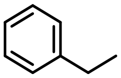
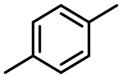
Appendix A. Calculation of the Pressure Drop at Outlet Column Conditions

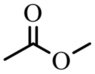
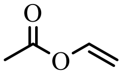
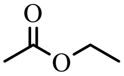
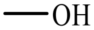
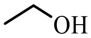
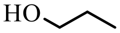
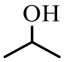
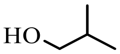
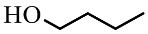
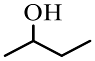
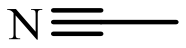
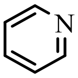
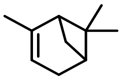
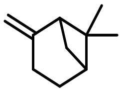
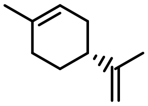
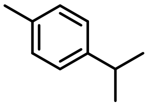
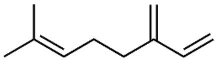
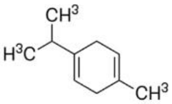
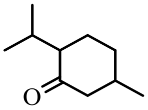
Table A1: Coefficients of Eq. (5) at different temperatures.

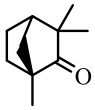
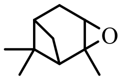
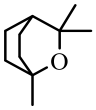
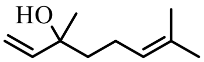
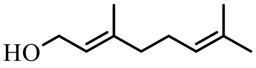
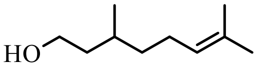
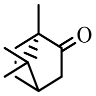
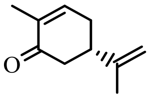
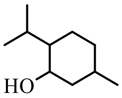
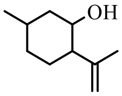
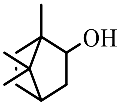
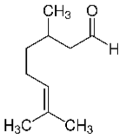
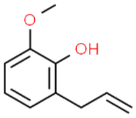
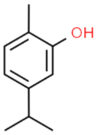
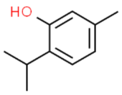
Temperature (K)	333.2	343.2	353.2	363.2	373.2	383.2	393.2
A	0.1384	0.1192	-0.0331	-0.0719	-0.1391	-0.2844	0.0961
B	0.0273	0.0275	0.0310	0.0283	0.0283	0.0288	0.0283
R^2	0.9984	0.9978	0.9956	0.9997	0.9996	0.9993	0.9992
Temperature (K)	403.2	413.2	423.2	433.2	443.2	453.2	-
A	-0.0729	-0.4682	-0.4876	-0.5689	-0.5689	-0.5689	-
B	0.0260	0.0285	0.0295	0.0289	0.0289	0.0289	-
R^2	0.9995	0.9999	0.9996	0.9988	0.9988	0.9988	-

Appendix B. List of Solutes

Table B1: Name, source and mass fraction purities of the organic solutes used. Names in parentheses correspond to common names used in the text.

Family	Compounds	Chemical structure	Supplier	Boiling temperature (K)[b]	Purity (mass fraction)[b]
	water		-[a]	373.15	-[a]
Alkanes	heptane		Aldrich	371.15	≥ 0.990
	octane		Aldrich	398.77	≥ 0.990
	nonane		Aldrich	423.91	≥ 0.990
	decane		Aldrich	447.20	≥ 0.990
Cycloalkanes	cyclohexane		Aldrich	353.90	≥ 0.990
	methylcyclohexane		Aldrich	374.00	≥ 0.990
Ketones	propanone (acetone)		Aldrich	329.30	≥ 0.999
	2-butanone		Aldrich	353.00	≥ 0.990
Ethers	ethoxyethane (diethyl ether)		Aldrich	307.70	≥ 0.999
Cyclic Ethers	oxolane (THF)		Aldrich	339.00	≥ 0.999
	1,4-dioxane		Aldrich	374.30	≥ 0.998
Aromatic Hydrocarbons	benzene		Aldrich	353.22	≥ 0.998
	toluene		Aldrich	383.75	≥ 0.998
	ethylbenzene		Aldrich	409.35	≥ 0.998
	p-xylene		Aldrich	411.51	≥ 0.990

Esters	methyl acetate		Aldrich	330.00	≥ 0.998
	vinyl acetate		Riedel-de-Häen	345.70	≥ 0.990
	ethyl acetate		Aldrich	349.65-350.65	≥ 0.998
Alcohols	methanol		Aldrich	337.80	≥ 0.998
	ethanol		Aldrich	351.50	≥ 0.999
	1-propanol		Aldrich	370.30	≥ 0.999
	2-propanol		Fluka	355.50	≥ 0.995
	2-methyl-1-propanol (isobutanol)		Aldrich	380.80	≥ 0.998
	1-butanol		Aldrich	390.60	≥ 0.995
	2-butanol		Aldrich	372.00	≥ 0.997
	2-methyl-2-propanol (*tert*-butanol)		Aldrich	355.50	≥ 0.999
	acetonitrile		Fluka	355.15	≥ 0.998
	pyridine		Aldrich	388.15	≥ 0.990
	thiophene		Aldrich	357.15	≥ 0.980
Terpenes	α-pinene		Aldrich	430.00	≥ 0.990
	β-pinene		Aldrich	439.20	≥ 0.970
	R-(+)-limonene		Aldrich	449.65	≥ 0.990
	p-cymene		Aldrich	450.28	≥ 0.990
	myrcene		Aldrich	440.20	≥ 0.990
	γ-terpinene		Aldrich	455.15	≥ 0.970
Terpenoids	(−)-menthone		Fluka	490.79	≥ 0.980

Terpenoids	(1R)-(−)-fenchone		Aldrich	466.65	≥ 0.970
	α-pinene oxide		Aldrich	447.15	≥ 0.990
	eucalyptol		Aldrich	449.55	≥ 0.970
	linalool		Aldrich	471.65	≥ 0.980
	geraniol		Aldrich	502.15	≈ 0.950
	DL-citronellol		Aldrich	497.65	≥ 0.980
	(1R)-(+)-camphor		Aldrich	480.55	≥ 0.980
	(S)-(+)-carvone		Merck	503.65	≥ 0.997
	L(-)-menthol		Acros	488.55	≥ 0.980
	(-)-isopulegol		SAFC	470.15	≥ 0.990
	(−)-borneol		Fluka	485.15	≥ 0.990
	citronellal		Aldrich	480.15	≥ 0.950
	eugenol		Aldrich	526.35	0.990
	carvacrol		SAFC	510.15	0.990
	thymol		Sigma	505.65	≥ 0.995

[a] Ultrapure water (resistivity of18.2MΩ·cm, free particles ≥ 0.22 µm and total organic carbon < 5 µg·dm^{-3}) was used.

[b] Declared by the suppliers.

Appendix C. Thermodynamics Properties

Table C1: Activity coefficients at infinite dilution for all solutes in the ionic liquid [C_4mim][PF_6] and in the equimolar mixture of [C_4mim][PF_6]/[C_4mim][Cl].

Organic solutes	**[C_4mim][PF_6]**								**[C_4mim][PF_6]/[C_4mim][Cl]**						
	T/K	333.2	343.2	353.2	363.2	373.2	383.2	-	333.2	343.2	353.2	363.2	373.2	383.2	-
heptane		154.49	146.39	123.63	117.02	101.65	88.29	-	-	-	-	-	-	-	-
octane		195.69	178.52	167.14	151.10	133.73	124.93	-	495.22	441.00	406.98	328.86	-	-	-
nonane		254.49	229.86	206.11	192.74	171.79	162.79	-	573.68	527.96	482.31	416.77	380.42	341.55	-
decane		338.66	310.83	276.48	248.86	230.93	211.51	-	704.16	649.54	584.53	508.28	475.13	437.91	-
cyclohexane		45.46	41.02	38.27	35.43	32.15	29.88	-	147.66	117.22	95.78	78.23	-	-	-
methylcyclohexane		62.95	56.98	53.95	49.19	45.47	42.32	-	183.48	157.91	138.15	114.31	-	-	-
benzene		1.886	1.913	1.929	1.956	1.980	2.013	-	3.013	2.993	2.956	2.919	2.914	2.878	-
toluene		2.920	2.945	2.972	2.993	3.022	3.042	-	4.827	4.821	4.799	4.649	4.558	4.552	-
ethylbenzene		5.225	5.260	5.291	5.310	5.322	5.348	-	8.577	8.547	8.394	8.158	8.186	8.230	-
p-xylene		4.396	4.479	4.472	4.497	4.478	4.527	-	7.451	7.415	7.496	7.406	7.271	7.264	-
methyl acetate		1.240	1.260	1.298	1.319	1.359	1.382	-	2.471	2.424	2.418	2.395	2.390	2.372	-
ethyl acetate		1.945	1.966	1.998	2.031	2.073	-	-	4.196	4.129	4.051	3.987	3.903	3.854	-
vinyl acetate		1.712	1.738	1.763	1.791	1.820	1.850	-	3.221	3.170	3.124	3.085	3.063	3.016	-
THF		1.521	1.540	1.570	1.594	1.619	1.652	-	2.996	2.957	2.931	2.858	2.857	2.767	-
1,4-dioxane		-	0.931	0.999	1.031	1.070	1.105	-	1.627	1.662	1.704	1.729	1.751	1.769	-
diethyl ether		-	7.928	7.925	7.895	7.755	7.615	-	25.820	24.299	22.399	-	-	-	-
acetonitrile		0.515	0.525	0.529	0.536	0.543	0.551	-	0.754	0.759	0.766	0.774	0.778	0.781	-
pyridine		0.809	0.860	0.886	0.936	0.974	1.029	-	1.189	1.235	1.287	1.324	1.379	1.431	-
thiophene		1.365	1.391	1.411	1.433	1.455	1.475	-	1.672	1.685	1.714	1.736	1.750	1.774	-
acetone		0.709	0.737	0.749	0.768	0.788	0.822	-	1.420	1.428	1.438	1.455	1.451	1.465	-
2-butanone		1.070	1.098	1.118	1.147	1.179	1.216	-	2.136	2.143	2.418	2.395	2.151	2.150	-
methanol		1.930	1.828	1.765	1.665	1.571	1.533	-	0.204	0.214	0.226	0.238	0.248	0.269	-
ethanol		2.577	2.351	2.204	1.986	1.799	1.708	-	0.361	0.369	0.373	0.377	0.377	0.388	-
1-propanol		-	3.135	2.917	2.638	2.407	2.284	-	0.477	0.481	0.488	0.490	0.495	0.509	-
2-propanol		3.178	2.881	2.646	-	2.239	2.131	-	0.600	0.601	0.611	0.616	0.617	0.622	-
1-butanol		4.742	4.244	3.818	3.447	3.155	2.945	-	-	0.658	0.663	0.668	0.670	0.683	-

2-butanol		3.962	3.620	3.314	3.048	2.884	2.729	-	-	0.786	0.798	0.815	0.822	0.840	-
isobutanol		-	4.052	3.656	3.328	3.071	2.871	-	-	0.631	0.634	0.636	0.638	0.641	-
tert-butanol		3.727	3.446	3.243	3.081	2.940	2.819	-	1.019	1.033	1.051	1.076	1.095	1.123	-
water		2.831	2.521	2.213	2.002	1.823	1.625	-	0.131	-	0.150	0.155	0.160	0.168	-
Terpenes/terpenoids	*T*/K	**353.2**	**363.2**	**373.2**	**383.2**	**393.2**	**403.2**	**-**	**353.2**	**363.2**	**373.2**	**383.2**	**393.2**	**403.2**	**-**
α-pinene		56.78	53.33	50.60	47.82	45.27	43.07	-	101.58	78.65	75.24	74.80	73.37	64.28	-
β-pinene		35.80	33.03	32.34	30.50	29.34	28.87	-	59.82	51.00	49.25	44.38	41.78	37.97	-
R-(+)-limonene		34.50	32.93	31.16	29.92	28.70	27.67	-	53.69	48.77	45.39	43.66	39.20	38.82	-
myrcene		31.30	30.87	30.43	30.07	29.82	29.52	-	51.16	51.19	46.09	46.37	44.03	42.76	-
p-cymene		13.12	12.98	12.88	12.75	12.62	12.53	-	22.73	21.51	20.49	21.23	20.26	20.19	-
g-terpinene		24.77	24.45	24.21	23.99	23.81	23.67	-	38.03	37.15	35.64	34.89	35.01	34.62	-
eucalyptol		18.67	17.45	17.28	16.64	16.03	15.70	-	35.82	32.67	29.57	30.45	28.02	26.30	-
Low volatile terpenoids	*T*/K	**373.2**	**383.2**	**393.2**	**403.2**	**413.2**	**423.2**	**433.2**	**373.2**	**383.2**	**393.2**	**403.2**	**413.2**	**423.2**	**433.2**
α-pinene oxide		6.140	6.251	6.510	6.672	6.829	7.067	7.205	-	11.550	11.693	11.941	11.988	12.122	-
(1R)-(−)-fenchone		5.581	5.618	5.662	5.720	5.733	5.726	5.764	-	10.875	10.910	11.309	10.726	10.782	11.083
(-)-menthone		6.773	6.797	6.843	6.923	6.998	7.037	7.050	-	13.212	13.257	13.263	13.084	12.877	12.643
S-(+)-carvone		-	3.413	3.490	3.575	3.677	3.749	3.849	-	5.638	5.650	5.860	5.895	6.129	6.398
geraniol		-	8.772	8.150	7.796	7.446	6.997	6.726	-	-	2.161	2.203	2.301	2.393	2.496
DL-citronellol		-	11.105	10.639	-	9.309	8.760	8.349	-	2.826	2.899	3.008	3.029	3.053	3.099
(1R)-(+)-camphor		-	4.378	4.433	4.539	4.640	4.726	4.852	-	-	8.446	8.471	8.386	8.742	8.912
L-(-)-menthol		-	13.249	12.610	12.173	11.400	10.709	10.111	-	4.380	4.573	4.692	4.660	4.818	4.897
(-)-isopulegol		-	7.017	6.919	6.814	6.728	6.539	6.479	-	3.024	3.247	3.338	3.481	3.746	3.942
(−)-borneol		-	10.969	10.020	9.091	8.149	7.514	6.996	-	2.906	2.900	2.801	2.724	2.730	-
linalool		-	10.047	9.493	9.168	8.759	8.397	8.183	-	3.491	3.630	3.811	3.875	3.914	4.243
citronellal		-	8.498	8.282	8.145	8.044	7.870	7.670	-	15.250	14.422	13.830	12.331	12.240	-
Phenolic terpenoids	*T*/K	**413.2**	**423.2**	**433.2**	**443.2**	**453.2**	**-**	**-**	**413.2**	**423.2**	**433.2**	**443.2**	**453.2**	**-**	**-**
eugenol		3.213	3.464	3.621	3.899	26.385	-	-	-	-	-	-	-	-	-
carvacrol		1.803	1.917	2.047	2.167	2.305	-	-	-	-	-	-	-	-	-
thymol		1.845	1.922	2.012	2.087	2.133	-	-	-	-	-	-	-	-	-

Table C2: Capacities of all solutes in the ionic liquid [C$_4$mim][PF$_6$] and in the equimolar mixture of [C$_4$mim][PF$_6$]/[C$_4$mim][Cl].

Organic solutes	**[C$_4$mim][PF$_6$]**								**[C$_4$mim][PF$_6$]/[C$_4$mim][Cl]**						
	***T*/K**	**333.2**	**343.2**	**353.2**	**363.2**	**373.2**	**383.2**	**-**	**333.2**	**343.2**	**353.2**	**363.2**	**373.2**	**383.2**	**-**
heptane		0.006	0.007	0.008	0.009	0.010	0.011	-	-	-	-	-	-	-	-
octane		0.005	0.006	0.006	0.007	0.007	0.008	-	0.002	0.002	0.002	0.003	-	-	-
nonane		0.004	0.004	0.005	0.005	0.006	0.006	-	0.002	0.002	0.002	0.002	0.003	0.003	-
decane		0.003	0.003	0.004	0.004	0.004	0.005	-	0.001	0.002	0.002	0.002	0.002	0.002	-
cyclohexane		0.022	0.024	0.026	0.028	0.031	0.033	-	0.007	0.009	0.010	0.013	-	-	-
methylcyclohexane		0.016	0.018	0.019	0.020	0.022	0.024	-	0.005	0.006	0.007	0.009	-	-	-
benzene		0.530	0.523	0.518	0.511	0.505	0.497	-	0.332	0.334	0.338	0.343	0.343	0.347	-
toluene		0.342	0.340	0.337	0.334	0.331	0.329	-	0.207	0.207	0.208	0.215	0.219	0.220	-
ethylbenzene		0.191	0.190	0.189	0.188	0.188	0.187	-	0.117	0.117	0.119	0.123	0.122	0.122	-
p-xylene		0.227	0.223	0.224	0.222	0.223	0.221	-	0.134	0.135	0.133	0.135	0.138	0.138	-
methyl acetate		0.806	0.794	0.770	0.758	0.736	0.724	-	0.405	0.413	0.413	0.418	0.418	0.422	-
ethyl acetate		0.514	0.509	0.500	0.492	0.482	-	-	0.238	0.242	0.247	0.251	0.256	0.259	-
vinyl acetate		0.584	0.575	0.567	0.558	0.550	0.540	-	0.310	0.316	0.320	0.324	0.326	0.332	-
THF		0.657	0.650	0.637	0.627	0.618	0.605	-	0.334	0.338	0.341	0.350	0.350	0.361	-
1,4-dioxane		-	1.074	1.001	0.970	0.935	0.905	-	0.615	0.602	0.587	0.578	0.571	0.565	-
diethyl ether		-	0.126	0.126	0.127	0.129	0.131	-	0.039	0.041	0.045	-	-	-	-
acetonitrile		1.942	1.904	1.891	1.866	1.840	1.816	-	1.326	1.318	1.305	1.292	1.286	1.281	-
pyridine		1.236	1.162	1.128	1.068	1.027	0.971	-	0.841	0.810	0.777	0.756	0.725	0.699	-
thiophene		0.733	0.719	0.709	0.698	0.687	0.678	-	0.598	0.594	0.583	0.576	0.571	0.564	-
acetone		1.411	1.357	1.335	1.302	1.268	1.217	-	0.704	0.700	0.695	0.687	0.689	0.682	-
2-butanone		0.935	0.911	0.895	0.871	0.848	0.823	-	0.468	0.467	0.413	0.418	0.465	0.465	-
methanol		0.518	0.547	0.566	0.600	0.637	0.652	-	4.898	4.674	4.422	4.208	4.040	3.721	-
ethanol		0.388	0.425	0.454	0.503	0.556	0.586	-	2.769	2.713	2.678	2.651	2.655	2.579	-
1-propanol		-	0.319	0.343	0.379	0.415	0.438	-	2.099	2.077	2.048	2.040	2.018	1.966	-
2-propanol		0.315	0.347	0.378	-	0.447	0.469	-	1.666	1.663	1.637	1.623	1.619	1.609	-

1-butanol		0.211	0.236	0.262	0.290	0.317	0.340	-	-	1.519	1.507	1.496	1.493	1.465	-
2-butanol		0.252	0.276	0.302	0.328	0.347	0.366	-	-	1.272	1.253	1.227	1.216	1.191	-
isobutanol		-	0.247	0.274	0.300	0.326	0.348	-	-	1.586	1.576	1.571	1.566	1.560	-
tert-butanol		0.268	0.290	0.308	0.325	0.340	0.355	-	0.981	0.968	0.951	0.930	0.913	0.890	-
water		0.353	0.397	0.452	0.499	0.549	0.615	-	7.609	-	6.684	6.452	6.258	5.967	-
Terpenes/terpenoids	***T*/K**	**353.2**	**363.2**	**373.2**	**383.2**	**393.2**	**403.2**	**-**	**353.2**	**363.2**	**373.2**	**383.2**	**393.2**	**403.2**	**-**
α-pinene		0.018	0.019	0.020	0.021	0.022	0.023	-	0.010	0.013	0.013	0.013	0.014	0.016	-
β-pinene		0.028	0.030	0.031	0.033	0.034	0.035	-	0.017	0.020	0.020	0.023	0.024	0.026	-
R-(+)-limonene		0.029	0.030	0.032	0.033	0.035	0.036	-	0.019	0.021	0.022	0.023	0.026	0.026	-
myrcene		0.032	0.032	0.033	0.033	0.034	0.034	-	0.020	0.020	0.022	0.022	0.023	0.023	-
p-cymene		0.076	0.077	0.078	0.078	0.079	0.080	-	0.044	0.046	0.049	0.047	0.049	0.050	-
g-terpinene		0.040	0.041	0.041	0.042	0.042	0.042	-	0.026	0.027	0.028	0.029	0.029	0.029	-
eucalyptol		0.054	0.057	0.058	0.060	0.062	0.064	-	0.028	0.031	0.034	0.033	0.036	0.038	-
Low volatile terpenoids	***T*/K**	**373.2**	**383.2**	**393.2**	**403.2**	**413.2**	**423.2**	**433.2**	**373.2**	**383.2**	**393.2**	**403.2**	**413.2**	**423.2**	**433.2**
α-pinene oxide		0.163	0.160	0.154	0.150	0.146	0.141	0.139	-	0.087	0.086	0.084	0.083	0.082	-
(1R)-(−)-fenchone		0.179	0.178	0.177	0.175	0.174	0.175	0.173	-	0.092	0.092	0.088	0.093	0.093	0.090
(-)-menthone		0.148	0.147	0.146	0.144	0.143	0.142	0.142	-	0.076	0.075	0.075	0.076	0.078	0.079
S-(+)-carvone		-	0.293	0.287	0.280	0.272	0.267	0.260	-	0.177	0.177	0.171	0.170	0.163	0.156
geraniol		-	0.114	0.123	0.128	0.134	0.143	0.149	-	-	0.463	0.454	0.435	0.418	0.401
DL-citronellol		-	0.090	0.094	-	0.107	0.114	0.120	-	0.354	0.345	0.332	0.330	0.328	0.323
(1R)-(+)-camphor		-	0.228	0.226	0.220	0.216	0.212	0.206	-	-	0.118	0.118	0.119	0.114	0.112
L-(-)-menthol		-	0.075	0.079	0.082	0.088	0.093	0.099	-	0.228	0.219	0.213	0.215	0.208	0.204
(-)-isopulegol		-	0.143	0.145	0.147	0.149	0.153	0.154	-	0.331	0.308	0.300	0.287	0.267	0.254
(−)-borneol		-	0.091	0.100	0.110	0.123	0.133	0.143	-	0.344	0.345	0.357	0.367	0.366	-
linalool		-	0.100	0.105	0.109	0.114	0.119	0.122	-	0.286	0.275	0.262	0.258	0.255	0.236
citronellal		-	0.118	0.121	0.123	0.124	0.127	0.130	-	0.066	0.069	0.072	0.081	0.082	-
Phenolic terpenoids	***T*/K**	**413.2**	**423.2**	**433.2**	**443.2**	**453.2**	**-**	**-**	**413.2**	**423.2**	**433.2**	**443.2**	**453.2**	**-**	**-**

eugenol	0.311	0.289	0.276	0.256	0.038	-	-	-	-	-	-	-	-	-
carvacrol	0.555	0.522	0.489	0.462	0.434	-	-	-	-	-	-	-	-	-
thymol	0.542	0.520	0.497	0.479	0.469	-	-	-	-	-	-	-	-	-

Table C3: Activity coefficients at infinite dilution in the ionic liquid [C_4mim][PF_6] (second column).

Solutes	**Temperature (K)**				
	343.2	**363.2**	**383.2**	**403.2**	**423.2**
octane	185.6954	154.9271	129.7576	-	-
cyclohexane	42.6566	36.1066	30.9638	-	-
toluene	3.0638	3.1013	3.1592	-	-
THF	1.5866	1.6448	1.6939	-	-
acetone	0.7520	0.7904	0.8341	-	-
ethyl acetate	2.0244	2.0715	2.1638	-	-
acetonitrile	0.5416	0.5567	0.5738	-	-
ethanol	2.3865	2.0024	1.7474	-	-
2-propanol	2.9129	2.4493	2.0901	-	-
water	2.5189	2.0321	1.6360	-	-
β-pinene	-	33.6810	30.8698	28.2093	-
eucalyptol	-	18.4508	16.8142	15.7331	-
linalool	-	-	10.3066	9.2379	8.3402
fenchone	-	-	5.7205	5.7638	5.8124

Table C4: Capacities of all solutes in the ionic liquid [C_4mim][PF_6] (second column).

Solutes	**Temperature (K)**				
	343.2	**363.2**	**383.2**	**403.2**	**423.2**
octane	0.0054	0.0065	0.0077	-	-
cyclohexane	0.0234	0.0277	0.0323	-	-
toluene	0.3264	0.3224	0.3165	-	-
THF	0.6303	0.6080	0.5904	-	-
acetone	1.3298	1.2652	1.1989	-	-
ethyl acetate	0.4940	0.4827	0.4621	-	-
acetonitrile	1.8462	1.7962	1.7428	-	-
ethanol	0.4190	0.4994	0.5723	-	-
2-propanol	0.3433	0.4083	0.4785	-	-
water	0.3970	0.4921	0.6112	-	-
β-pinene	-	0.0297	0.0324	0.0354	-
eucalyptol	-	0.0542	0.0595	0.0636	-
linalool	-	-	0.0970	0.1082	0.1199
fenchone	-	-	0.1748	0.1735	0.1720

Table C5: Thermodynamic functions at infinite dilution: partial molar excess Gibbs free energies ($\bar{G}_m^{E,\infty}$ /kJ·mol^{-1}), partial molar excess enthalpies ($\bar{H}_m^{E,\infty}$/kJ·mol^{-1}) and partial molar excess entropies ($\bar{S}_m^{E,\infty}$/kJ·mol^{-1}) of water, and organic solutes in the ionic liquid [C_4mim][PF_6] and in the equimolar mixture of [C_4mim][PF_6]/[C_4mim][Cl].

Different Organic Solutes	**[C_4mim][PF_6]/[C_4mim][Cl]**			**[C_4mim][PF_6]**		
	$\overline{G}_m^{E,\infty}$	$\overline{H}_m^{E,\infty}$	$T_{ref}\,\overline{S}_m^{E,\infty}$	$\overline{G}_m^{E,\infty}$	$\overline{H}_m^{E,\infty}$	$T_{ref}\,\overline{S}_m^{E,\infty}$
			T_{Ref} = 353.2 K			
heptane	-	-	-	14.144	11.921	-2.223
octane	17.642	13.098	-4.544	15.029	9.717	-5.312
nonane	18.141	11.262	-6.879	15.645	9.643	-6.001
decane	18.705	10.477	-8.228	16.507	10.169	-6.338
cyclohexane	13.395	21.206	7.811	10.701	8.811	-1.890
methylcyclohexane	14.470	15.594	1.124	11.710	8.350	-3.360
benzene	3.183	0.981	-2.202	1.929	-1.341	-3.270
toluene	4.605	1.488	-3.118	3.198	-0.875	-4.073
ethylbenzene	6.247	1.118	-5.129	4.891	-0.470	-5.361
p-xylene	5.915	0.589	-5.325	4.398	-0.467	-4.865
methyl acetate	2.593	0.788	-1.805	0.766	-2.379	-3.145
ethyl acetate	4.107	1.849	-2.258	2.032	-1.642	-3.674
vinyl acetate	3.344	1.350	-1.994	1.665	-1.637	-3.303
THF	3.157	1.587	-1.570	1.324	-1.753	-3.077
1,4-dioxane	1.565	-1.802	-3.367	-0.004	-4.514	-4.510
diethyl ether	9.128	6.939	-2.189	6.078	1.099	-4.978
acetonitrile	-0.781	-0.783	-0.002	-1.871	-1.372	0.499
pyridine	0.741	-3.898	-4.639	-0.354	-4.941	-4.587
thiophene	1.583	-1.288	-2.870	1.011	-1.642	-2.652
acetone	1.066	-0.651	-1.718	-0.848	-2.930	-2.082
2-butanone	2.241	-0.137	-2.378	0.326	-2.658	-2.985
methanol	-4.365	-5.625	-1.260	1.669	5.048	3.379
ethanol	-2.893	-1.301	1.591	2.321	8.983	6.662
1-propanol	-2.104	-1.254	0.851	3.143	9.036	5.893
2-propanol	-1.447	-0.799	0.648	2.857	8.611	5.754
1-butanol	-1.205	-0.885	0.319	3.806	9.454	5.648
2-butanol	-0.661	-1.765	-1.104	3.934	10.253	6.320
isobutanol	-1.336	-0.426	0.910	3.518	8.001	4.483
tert-butanol	0.147	-2.069	-2.215	3.455	5.857	2.402
water	-5.578	-5.021	0.557	2.333	11.672	9.340
Terpenes/terpenoids			**T_{Ref} = 353.2 K**			
α-pinene	13.567	8.547	-5.020	11.860	6.530	-5.330
β-pinene	12.013	10.083	-1.929	10.505	5.063	-5.442
R-(+)-limonene	11.696	7.861	-3.835	10.397	5.273	-5.124
myrcene	11.553	4.542	-7.011	10.111	1.384	-8.726
p-cymene	9.172	2.519	-6.653	7.559	1.098	-6.462
γ-terpinene	10.683	2.293	-8.391	9.424	1.071	-8.353

eucalyptol	10.508	6.707	-3.800	8.595	3.930	-4.664
Low volatile terpenoids			**T_{Ref} = 393.2 K**			
α-pinene oxide	8.038	-1.644	-9.681	6.123	-3.723	-9.846
(1R)-(−)-fenchone	7.811	-0.026	-7.837	5.667	-0.756	-6.423
(-)-menthone	8.448	1.243	-7.205	6.286	-1.084	-7.371
S-(+)-carvone	5.660	-3.451	-9.111	4.085	-3.234	-7.320
geraniol	2.519	-5.236	-7.755	6.858	7.318	0.460
DL-citronellol	3.479	-2.473	-5.952	7.729	8.185	0.456
(1R)-(+)-camphor	6.974	-1.939	-8.913	4.867	-2.674	-7.541
L-(-)-menthol	4.969	-2.805	-7.774	8.284	7.075	-1.209
(-)-isopulegol	3.850	-7.066	-10.916	6.322	2.272	-4.051
(−)-borneol	3.480	2.533	-0.947	7.533	12.978	5.445
linalool	4.214	-4.795	-9.009	7.356	5.924	-1.432
citronellal	8.723	8.042	-0.681	6.910	2.468	-4.442
Phenolic terpenoids			**T_{Ref} = 413.2 K**			
eugenol	-	-	-	4.009	-9.587	-13.596
carvacrol	-	-	-	2.024	-9.548	-11.572
thymol	-	-	-	2.103	-5.812	-7.916

Table C6: Gas-liquid partition coefficients of all solutes in the ionic liquid [C_4mim][PF_6].

Organic solutes	**[C_4mim][PF6]**						
	T/K	333.2	343.2	353.2	363.2	373.2	383.2	-
heptane		3.099	2.492	2.019	1.595	1.403	1.257	-
octane		6.447	4.801	3.585	2.843	2.358	1.894	-
nonane		12.955	9.276	6.907	5.075	4.019	3.066	-
decane		25.550	17.152	12.322	8.938	9.009	6.587	-
cyclohexane		5.684	4.645	3.753	3.118	2.691	2.307	-
methylcyclohexane		7.749	6.155	4.789	3.957	3.289	2.766	-
benzene		135.684	97.889	72.681	54.790	42.189	32.905	-
toluene		244.944	170.274	121.342	88.637	65.968	50.192	-
ethylbenzene		340.113	227.060	155.793	110.115	79.793	58.919	-
p-xylene		437.288	287.667	198.667	139.795	101.719	74.469	-
methyl acetate		98.503	72.234	53.421	40.915	31.524	24.627	-
ethyl acetate		124.882	89.054	64.727	48.136	36.428	27.462	-
vinyl acetate		121.328	86.773	63.595	47.596	36.344	28.246	-
THF		106.043	77.888	58.048	44.318	34.453	27.107	-
1,4-dioxane		590.750	400.445	279.130	199.169	144.379	107.113	-
diethyl ether		7.744	6.034	4.817	3.925	3.295	2.806	-
acetonitrile		544.687	391.318	290.878	219.009	167.823	130.770	-
pyridine		1100.380	709.147	484.550	331.025	234.762	167.193	-
thiophene		215.503	153.336	112.256	83.916	63.980	49.781	-

acetone		168.647	121.651	91.728	69.867	54.111	41.920	-
2-butanone		240.016	169.775	124.066	91.800	69.218	52.987	-
methanol		82.523	60.669	44.871	34.779	27.532	21.489	-
ethanol		110.361	80.953	59.451	46.650	37.313	29.114	-
1-propanol		188.710	134.045	95.538	72.280	55.737	42.445	-
2-propanol		108.166	78.189	57.673	-	34.231	26.526	-
1-butanol		346.040	236.061	166.450	121.140	89.749	67.143	-
2-butanol		183.224	127.223	91.561	67.901	50.501	38.645	-
isobutanol		235.688	163.989	116.511	85.070	63.329	47.940	-
tert-butanol		92.642	65.778	47.599	35.290	26.858	20.912	-
water		232.149	170.921	131.356	100.527	78.256	63.573	-
Terpenes/terpenoids	*T*/K	353.2	363.2	373.2	383.2	393.2	403.2	-
α-pinene		26.973	20.231	15.401	12.042	9.594	7.748	-
β-pinene		59.835	44.565	32.083	24.530	18.248	14.323	-
R-(+)-limonene		102.030	71.164	51.411	37.520	28.024	21.259	-
myrcene		91.270	61.755	43.340	31.297	23.163	17.604	-
p-cymene		314.045	210.556	145.126	103.098	75.055	55.728	-
g-terpinene		140.620	96.377	67.663	48.625	35.685	26.666	-
eucalyptol		186.302	132.139	90.562	65.226	47.844	35.204	-
Low volatile terpenoids	*T*/K	373.2	383.2	393.2	403.2	413.2	423.2	433.2
α-pinene oxide		384.911	270.430	190.738	139.976	105.074	79.503	62.119
(1R)-(−)-fenchone		590.037	410.115	291.033	210.223	155.912	118.060	90.092
(-)-menthone		747.881	507.242	352.239	249.377	180.613	134.156	101.873
S-(+)-carvone		-	1854.645	1230.151	836.008	579.417	413.902	299.536
geraniol		-	1379.304	900.399	590.071	399.067	281.989	199.722
DL-citronellol		-	890.400	565.372	-	263.389	186.510	133.776
(1R)-(+)-camphor		-	768.101	537.125	380.464	275.888	204.770	153.555
L-(-)-menthol		-	514.574	345.536	234.074	166.986	121.169	89.131
(-)-isopulegol		-	541.769	368.764	257.825	184.104	136.446	101.190
(−)-borneol		-	712.006	476.423	331.395	240.373	174.093	128.031
linalool		-	348.888	238.711	163.466	115.573	83.092	59.893
citronellal		-	439.899	300.529	209.286	148.948	109.577	82.703
Phenolic terpenoids	*T*/K	413.2	423.2	433.2	443.2	453.2	-	-
eugenol		2793.293	1839.157	1276.316	876.732	624.550	-	-
carvacrol		2007.138	1327.991	896.860	624.453	441.412	-	-
thymol		1548.369	1034.418	700.962	488.020	350.614	-	-